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Destabilization of Emulsions in Porous Media

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Preface

The motivation of this project was to study the stability of different oil-in-water, water-in-oil, and oil-in-water-in-oil emulsion systems during filtration through porous media.

This thesis concludes my Master of Science degree at the Department of Chemical Engineering, with specialization in Colloid and Polymer Chemistry, at the Norwegian University of Science and Technology, NTNU. This project is based on a specialization project from the fall of 2015. The experimental work has been performed at the Ugelstad Laboratory during the spring of 2016 under supervision of Professor Johan Sjöblom (main supervisor), and Dr. Sebastien Simon and Camilla I. Dagsgård (co-supervisors).

I would like to express my gratitude to my supervisor Johan Sjöblom for his appreciated suggestions and guidance of the project. Furthermore I would like to thank my co-supervisors Sebastien Simon and Camilla I. Dagsgård for their great supervision regarding my work and insightful discussions. Many thanks to May Grete Sætran for her help regarding the laboratory set-up and her great spirit in the lab. In addition, I would like to thank Geir Sørland for his help and guidance regarding the low-field NMR instrument.

I would also like to thank my loved ones: My parents Anne and Jon Erik, for their morally and economically support, and my boyfriend Olav, for his patience and support throughout these five years in Trondheim. I will forever be grateful for their love.

I declare this as an independent work according to the exam regulations of the Norwegian University of Science and Technology (NTNU).

Trondheim, June 9th, 2016

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Abstract

Oil and water can form emulsions with different stability conditions while flowing through the porous systems in an oil reservoir. The stability of different oil-in-water (o/w), water-in-oil (w/o), and oil-in-water-in-oil (o/w/o) emulsion systems during filtration through porous media were studied in this project. Emulsions were stabilized using different surface active components, such as surfactants, particles, and natural indigenous crude oil components.

The influence of surface active components and the dispersed phase on the stability of o/w and w/o emulsions during filtration were investigated by analyzing the droplet size distribution and the content of the dispersed phase in the emulsions by low-field NMR, microscopy and bottle testing. The NMR program required extensive optimization and improvement for several of the emulsion systems.

Surfactant-stabilized emulsion systems (o/w and w/o) were not destabilized within one day after filtration, therefore could it be assumed that flexible droplets which were able to pass the filter pores were formed. Particle-stabilized emulsion systems (o/w and w/o) were destabilized during filtration due to coalescence and breaking of rigid droplets. Particle-stabilized o/w emulsions initially formed larger droplets in the continuous phase than w/o emulsions, which led to increased coalescence, destabilization, and filter clogging during filtration. W/O crude oil emulsions were also destabilized during filtration, but to a lower extent than particle-stabilized emulsions. Free water was formed after filtration of the different crude oil emulsions. Since the crude oil emulsions showed a similar trend as the different particle-stabilized emulsions, it could be concluded that the behavior of crude oil emulsions were closer to particle-stabilized emulsions than surfactant-stabilized emulsions.

Little is known about the flow of multiple emulsions through porous media, therefore analyzing the stability of multiple emulsions during filtration by microscopy was conducted. The multiple (double) o/w/o emulsions were destabilized during filtration: Double emulsions were not observed after filtration, but two different zones were formed, containing clusters or single droplets which indicated coalescence of some droplets in the double emulsions.

Sammendrag

Olje og vann kan danne emulsjoner med forskjellig stabilitet når de strømmer gjennom den porøse formasjonen i et oljereservoar. I dette prosjektet ble stabiliteten til forskjellige olje-i-vann- (o/w), vann-i-olje- (w/o) og olje-i-vann-i-olje- (o/w/o) emulsjoner ved filtrering gjennom porøse medier studert. Emulsjonene ble stabilisert av forskjellige overflateaktive stoffer, som for eksempel surfaktanter, partikler og naturlige stabiliserende komponenter i råolje. Effekten de overflateaktive stoffene og den dispergerte fasen hadde på stabiliteten av o/w- og w/o-emulsjonene ved filtrering ble undersøkt ved å analysere dråpestørrelses-fordelingen og innholdet/mengden av den dispergerte fasen i emulsjonen ved NMR, mikroskopering og «*bottle test*». Omfattende optimalisering og modifisering av NMR-programmet var nødvendig for flere av de de ulike emulsjonene.

De surfaktantstabiliserte emulsjonene (både o/w og w/o) var stabile i minst ett døgn etter filtrering, og derfor kunne det antas at fleksibiliteten til dråpene gjorde det mulig for dråpene å passere filterporene. De partikkelstabiliserte emulsjonene (både o/w og w/o) ble destabilisert ved filtrering, rigide dråper ble trolig ødelagt ved passering av filterporene. De partikkelstabiliserte o/w-emulsjonene lagde innledningsvis større dråper i den kontinuerlige fasen enn w/o-emulsjonene. Dette førte til mer koalesens og destabilisering, i tillegg til at filteret ble tettet ved filtrering. W/O-råoljeemulsjoner ble også destabilisert ved filtrering, men i en lavere grad enn de partikkelstabiliserte emulsjonene. Fritt vann ble dannet etter filtrering av de forskjellige råoljeemulsjonene. Siden råoljeemulsjonene viste den samme trenden som de partikkelstabiliserte emulsjonene, kunne det bli konkludert med at oppførselen til råolje-emulsjonene var nærmere partikkelstabiliserte emulsjoner enn surfaktantstabiliserte emulsjoner.

Siden det er lite som er publisert om hvordan doble emulsjoner oppfører seg når de passerer gjennom porøse medier, ble stabiliteten av doble emulsjoner ved filtrering analysert ved mikroskopering. De doble emulsjonene ble destabilisert ved filtrering, og ingen doble emulsjoner kunne detekteres i mikroskopet etter filtrering. To forskjellige soner av enslige dråper og dråper i klynger ble observert.

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1. Introduction

With the world's increasing energy demand due to growth in the world's population and increased living standards, it is becoming more and more important to optimize and improve the energy sources we already have, as well as discovering new. [1] As oil is one of the most important energy sources there is today, it is important to improve the oil recovery. To maximize the recovery from the existing reservoirs, the whole process needs to be considered, including both enhanced oil recovery (EOR) methods, new technologies, and new management and control techniques of the reservoirs. [2, 3]

In the porous systems in an oil reservoir, oil and water can form emulsions with different stability conditions. Different crude oil component, e.g. asphaltenes, can contribute to stabilize the emulsions. Some of the emulsions can be very stable, therefore it can be hard to separate the crude oil from the water. The pores in the reservoirs works as filters, and consequently, emulsions can be formed or destabilized while passing through porous reservoirs during oil production. [4]

In this study, different emulsion systems were prepared to examine the stability of emulsions during filtration, thereby considering flexibility and rigidity of the droplets in the different oil-in-water (o/w) and water-in-oil (w/o) emulsion systems, and also in oil-in-water-in-oil (o/w/o) multiple emulsions. This project was a continuation of the specialization project "*Stability of Water-in-Oil Emulsions in Porous Media*" performed in the fall of 2015 at the Ugelstad Laboratory at NTNU. This spring, three main systems were tested. Initially, crude oil w/o emulsions, secondly, o/w emulsions of model oil with different surface stabilizing components, and finally, multiple o/w/o emulsions of model oil stabilized by surfactants. By using glass filters with porosities similar to oil reservoir rocks (sandstone ~30 μm [5]), the transport ability of droplets through porous solid material was examined. The multiple emulsions were interesting to analyze because little is known about their flow through porous media. Low-field NMR was used to characterize the droplet size distribution (DSD) and to determine the content of dispersed phase during filtration. Microscopy was used to observe the droplet sizes during filtration, and the stability of emulsions were also observed in bottle test tubes after filtration.

2. Theory

2.1 Chemicals

2.1.1 Crude Oil and Crude Oil Composition

Crude oil is a complex mixture of hydrocarbons, but are also containing heteroatoms such as sulfur, nitrogen and oxygen, and metals. Physical properties of crude oil varies due to different compositions and different locations, but crude oils are usually highly viscous liquids. Crude oil is formed in porous rocks in oil reservoirs as a result of decomposition of organic matter under high pressure and temperature conditions for millions of years. [6]

Crude oils, hydrocarbons, and other petroleum liquids can be divided into four groups depending on how heavy e.g. the crude oil is (light, medium, heavy or extra heavy crude oil). The scale is based on the degree of API (American Petroleum Institute) gravity, as in Table 1.

Table 1: API gravity classifying how heavy the crude oils are. [7]

Crude oil	**°API**
Light oil	> 31.1
Medium oil	22.3 – 31.1
Heavy oil	< 22.3
Extra heavy oil	< 10.0

The degrees API are universally used to express and compare the relative densities of crude oils. [8] It is an inverse measure of the crude oil: The denser the crude oil is, the lower the API gravity is. [7] In equation (1) is the API gravity given, where SG is the specific gravity (relative density) of the liquid at 15 °C in relation to water at 15 °C. Specific gravity of an oil is defined as the density of the oil divided by the density of water. [7, 9]

$$°API = \frac{141.5}{SG} - 131.5 \qquad (1)\ [7]$$

The specific gravity of water is 1.000 g/mL, and then the calculated API gravity would be 10.0 °API. If the API gravity of a petroleum oil is higher than 10, the liquid is lighter than water and floats on it, and if the API gravity is lower than 10 the liquid is heavier than water and will sink. [7, 9]

It is difficult to separate the different crude oil compositions, and therefore crude oil can be divided into different fractions based on aromaticity, polarity, size and solubility in hydrocarbon media. Crude oil is divided into saturates, aromatics, resins and asphaltenes, called the SARA fractions: [10-13]

- The saturates are aliphatic non-polar hydrocarbons, and the lightest fraction in crude oil. This fraction group includes alkanes, naphtenes (cycloalkanes) and waxes.
- The aromatics are polar molecules of benzene and its derivatives. As the name says, the aromatics contain aromatic rings, but also alkyl chains and cycloalkanes.
- The resin fraction has a higher molecular weight and polarity than saturates or aromatics, and are soluble in light alkanes. Naphthenic acids are a part of this crude oil fraction. The resins does also differ from saturates and aromatics since they are containing heteroatoms, e.g. nitrogen, oxygen or sulfur.
- The asphaltenes has a larger molecular weight than the resins, and does like the resins contain heteroatoms. The asphaltenes are the heaviest fraction of the crude oil components, and both the polarity and acidity is high. They are soluble in aromatic solvents. Asphaltenes have a polyaromatic core, because of this and the heteroatom content, the asphaltenes can aggregate and are able to migrate and adsorb at interfaces.

In oil reservoirs, crude oil and water can form very stable emulsions. Stabilizing components in crude oil are asphaltenes, naphthenic acids, resins and solid particles (sand, clay and scale products with adsorbed asphaltenes).

2.1.2 Particles

Solid particles can adsorb strongly to the oil-water interface in an emulsion and form rigid interfaces. Stabilization by particles is interesting since, as mentioned in the previous chapter 2.1.1 – Crude Oil and Crude Oil Compositions, particles can stabilize crude oil emulsions. Hydrophobic particles stabilize w/o emulsions and hydrophilic particles stabilize o/w emulsions. [14] The particle size, shape, concentration, wettability and interaction between particles are linked directly to how effective the solids are to stabilize emulsions. [15]

Particles can cluster together, forming loose aggregates in a reversible process called flocculation. The tendency to flocculate is dependent on the particle properties. The particle distances are large in flocs, causing the forces between particles to be small. As the distance between particles becomes smaller, increased amounts of continuous structures can be formed, usually called gels. [16, 17]

Compared to the size of the droplets in the emulsion, the particles stabilizing an emulsion should be small and relatively hydrophobic in w/o emulsions. [16] The particles form a dense film around the dispersed droplets in the emulsion when they adsorb to the oil-water interface, which is preventing coalescence. The contact angle, θ, of particles at the oil-water interface is an important parameter for the stability, wettability and for which emulsions are formed, illustrated in Figure 1. In w/o emulsions, the hydrophobic particles resides mostly in the oil phase (θ>90°), which provides a larger particle area on the external side of the droplet. In o/w emulsions, the hydrophilic particles resides mostly in the water phase (θ<90°), which then provides a larger particle area on the external side of the droplet. [15]

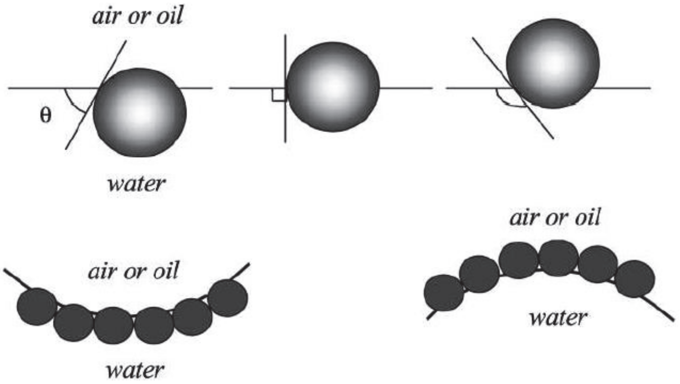


Figure 1: Contact angles formed by particles adsorbed to different air/oil-water interfaces. [15]

Modified silica particles are normally used to mimic the adsorption of asphaltenes to particles in crude oil. Silica particles are normally hydrophilic, containing siloxane and silanol groups. Aerosil ® particles are fumed silica particles which have been modified by structure modifications or after-treatment. The hydrophilic and hydrophobic modified silica particles used in this project are shown in Table 2. Hydrophobic silica particles can stabilize w/o emulsions, while hydrophilic silica particles can stabilize o/w emulsions.

Table 2: Specification of fumed silica particles. [18]

	Product	**Structure modified/ after-treated**	**Specific surface area (BET) [m²/g]**	**Tapped density [g/L]**
Hydrophilic	Aerosil R7200	3-Methacryl-oxypropyl-trimethoxysilane	150 ± 25	230
Hydrophobic	Aerosil R972	Dimethyl-dichlorosilane	110 ± 20	50

2.1.3 Surfactants

Surfactants are amphiphilic chemical molecules. They have both a hydrophilic and a hydrophobic (lipophilic) part, as illustrated in Figure 2. Due to this, there is a strong adsorption to interfaces, which reduces the interfacial tension and increases the stability of emulsions.

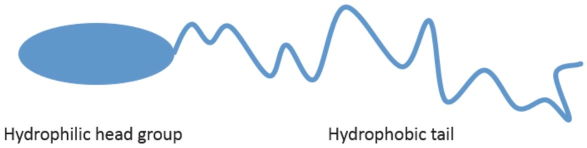


Figure 2: Schematic illustration of a surfactant, containing both a hydrophilic head group and a hydrophobic tale.

The surfactants may be anionic, cationic, non-ionic or zwitterionic (both an anionic and cationic part), and some are more hydrophilic or hydrophobic. Example of the stabilization mechanisms by an anionic and non-ionic surfactants are shown in Figure 3. Ionic surfactants contributes to an electrostatic stabilization of the emulsion by formation of a charged interphase when they adsorb, electrostatic repulsion is induced in o/w emulsion systems. Non-ionic surfactants prevents steric stabilization of emulsions. [16, 17]

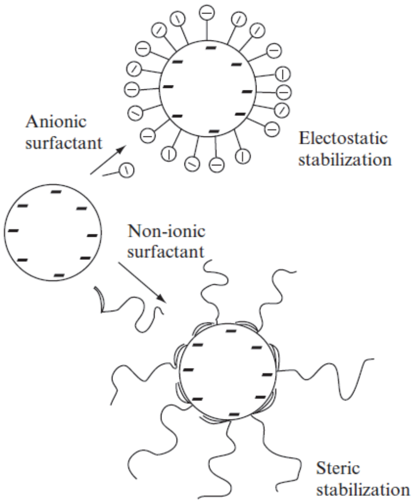


Figure 3: Electrostatic and steric stabilization of emulsions by anionic and non-ionic surfactants respectively. [16]

As mentioned above, surfactants adsorb to interfaces, where the hydrophilic head group is oriented into the water phase and the hydrophobic tail is oriented into the oil phase. The surfactants solubility in the different phases and the stabilizing properties are determined by the amount and type of hydrophilic and hydrophobic groups in the surfactant molecule. This is called the HLB (hydrophilic-lipophilic balance). The lower the HLB values is, the more hydrophobic the surfactant molecule is. Table 3 shows HLB numbers and the corresponding applications. [17, 19]

Table 3: HLB number and applications for surfactants. [17]

HLB number	**Application**
3-6	W/O emulsifier
7-9	Wetting agent
8-18	O/W emulsifier
13-15	Detergent
15-18	Solubilizer

Commonly used surfactants are the different non-ionic Spans and Tweens. In this project, the hydrophobic Span80 (HLB = 4.3) and hydrophilic Tween80 (HLB = 15.6) are used. [17] The hydrophilic anionic surfactant AOT, Sodium dioctyl sulfosuccinate, (HLB > 10) is also used. [20, 21]

2.2 Emulsions

2.2.1 Definition

An emulsion is defined as a mixture of two immiscible liquids. One liquid is dispersed as droplets into another continuous liquid phase. Normally, one of the phases is water, and the other is oil. This can be either oil-in-water (o/w) or water-in-oil (w/o) emulsions. There are also multiple emulsions that can be oil-in-water-in-oil (o/w/o) or water-in-oil-in-water (w/o/w) emulsions, which are described in the next subchapter, chapter 2.2.2 – Multiple Emulsions. In this context, an "oil" is a liquid which is either immiscible or slightly soluble in water. [17, 22]

In terms of the droplet size, emulsions can be classified in three main groups: macro emulsions (diameter, $d > 1$ μm), mini emulsions (50 nm $< d <$ 1 μm) and micro emulsions ($d < 50$ nm). Unlike micro emulsions, which are thermodynamically stable, the macro and mini emulsions are thermodynamically unstable, but can be kinetically stable, and will then phase separate over time. [17] The total free energy of formation, ΔG_f, of an emulsion is expressed as:

$$\Delta G_f = \gamma A - T\Delta S_f \qquad (2)\ [19]$$

γ is the interfacial tension between two phases, A is the total surface area, T is temperature and ΔS is the entropy of the formation of droplets. Because of the increase in surface area when droplets are formed and the fact γ is positive, the interfacial free energy will increase too, and the liquids need energy to form interfaces. [19]

The ability of emulsions to resist changes in properties over time is referred to as stability. Without presence of stabilizing components, the emulsion will break quickly by coalescence or flocculation, and over time separate into two phases. [17] Several surface active components, like particles and surfactants, can be used to stabilize an emulsion. The type of emulsion (o/w, w/o, o/w/o or w/o/w) is controlled by properties of the surface active components and volume fraction of the phases.

In this project, the "oil phase" refers to model oils and crude oils. Model oils can be easier to handle and analyze than crude oils. Unlike crude oils, the model oils are transparent, and does not contain crude oil emulsion stabilizing components like asphaltenes, naphthenic acids, resins and solid particles. The stabilizing components in crude oil are not controllable, and therefore are model oils often preferred.

2.2.2 Multiple Emulsions

Multiple emulsions, or double emulsions, are macro emulsions where droplets contain emulsions inside themselves. They are “emulsions of emulsions”. The dispersed droplets contain dispersed droplets which normally are of the same liquid as the continuous phase. [17] The multiple emulsions contain both o/w and w/o emulsions, and are classified as two types, oil-in-water-in-oil (o/w/o) emulsions and water-in-oil-in-water (w/o/w) emulsions. As single emulsions, the multiple emulsions are also thermodynamically unstable and will phase separate over time. [23, 24]

Double emulsions can be prepared in a one-step or two-step method. In the lab the two-step method gives better control during preparations of double emulsions and also better stability of the emulsion. Using two different emulsifiers, surfactants, are required when preparing multiple emulsions using the two-step method. A combination of both hydrophilic surfactants (in o/w emulsions) and hydrophobic surfactants (in w/o emulsions) are often used to stabilize multiple emulsions. [17, 23, 24] Considering an o/w/o emulsion, in the first step, the inner o/w emulsion will be prepared using a hydrophilic surfactant and high intensity emulsification conditions. Thereafter the emulsion is added to a solution of a hydrophobic surfactant in oil phase, then emulsified gently to create the final double emulsion.

The concentration and ratio of the different surfactants, as well as the ratio of the oil and water phases, are important in order to achieve stable multiple emulsions. Too high surfactant concentrations would lead to a decrease in the interfacial film strength between the different phases in the multiple emulsions. Creaming and sedimentation are phenomena which occurs in multiple emulsions due to the surfactants, and also as a result of flocculation and rise of large droplets in the samples. [23]

Potential applications of multiple emulsions are several, such as in agriculture, chemistry, cosmetics, food and pharmaceutical industry. [25] The multiple emulsions are for instance desired for controlled-release drug delivery system for slow and persistent release of active material from the internal emulsion droplets and into the continuous phase. [12, 25] Multiple emulsions have been observed in crude oil, but little is known. [26]

2.2.3 Emulsification

Preparation of emulsions, or emulsification, is the process where the bulk phase is broken into small droplets. The process requires an energy input in order to disperse the phases. The interfacial tension will provide a spherical droplet shape to minimize the surface area. This can be related to the Laplace pressure (see equation (3)), which is the force acting across the interface. The Laplace pressure represents the energy barrier, which has to be overcome to disrupt the droplet. [17]

$$\Delta P = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \qquad (3)\ [17]$$

Here ΔP is the pressure difference inside and outside the droplet, γ is the interfacial tension and R_1 and R_2 are the radii of curvature. For spherical droplets, the Laplace equation can be reduced to:

$$\Delta P = \frac{2\gamma}{R} \qquad (4)\ [17]$$

The emulsification process requires an energy input. Several emulsification methods are based on the stator-rotor principle, and can be mechanical stirring, e.g. using an Ultra Turrax or a propeller. Other emulsification methods can be ultra sound or homogenizers. If smaller droplets are wanted, a larger energy input is needed. [17]

2.2.4 Stability of Emulsions

Since emulsions are thermodynamically unstable, the kinetic stability can be adjusted in order to increase the time before the emulsion breaks. The system exists in a metastable phase where the energy barrier to prevent aggregation of the droplets can be high enough to resist the emulsion breaking process. [27]

Several mechanisms can affect the kinetic stability, and one can adjust some parameters to prevent the emulsion from breaking: [17]

- Increase the electrostatic repulsion in o/w emulsions.
- Increase the mechanical strength of the interfacial film by strong intermolecular forces of surface active components adsorbed to the surface.
- Increase the elasticity of the interfacial film (Gibbs-Marangoni effect).
- Lower the interfacial tension, but there is no direct relationship between interfacial tension and stability to coalescence.

- Lower the volume fraction of the dispersed phase, which reduces the frequency of droplet collision.
- Decrease the droplet sizes in order to resist molecular diffusion.
- Increase the viscosity of the continuous phase in order to reduce the mobility of the droplets.

In an emulsion, the droplets move due to Brownian motion, sedimentation, and creaming. Brownian motion are random movements of for example particles in a solution, or gas molecules in a gas. The direction and rate of the movement changes when particles collide with each other or with the wall of the container they are in. The rate of the Brownian movement decreases as the mass of particles increases. Droplets and particles larger than 1 µm does not have Brownian motion, but move due to gravitational forces which can cause sedimentation and creaming. [17]

When two droplets are approaching each other, attractive and repulsive forces will start to affect their motion. The attractive forces, i.e. van der Waals forces, are promoting aggregation and destabilizing of the emulsion, while repulsive forces, electrostatic and steric forces, enforce stability. [28] The stability of a droplet can be observed in a potential energy curve as a function of the separation distance between the droplets, as shown in Figure 4. The energy barrier which droplets has to overcome in order to merge as the electrical double layer overlaps, is also shown in the figure as V_T.

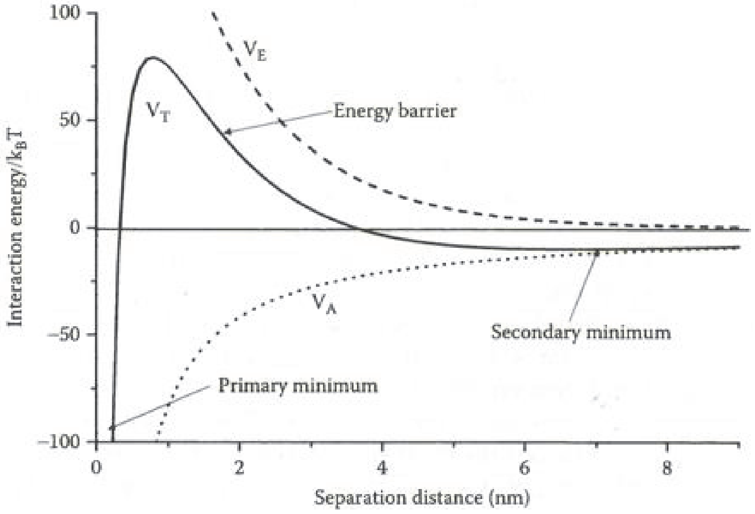


Figure 4: Example of a potential energy curve as a function of the droplet distance. V_E is the repulsive double-layer interactions, and V_A is the attractive van der Waals forces. [29]

There are several stabilizing components, which are promoting different stability mechanisms. Both surface-active agents (surfactants) and particles adsorb to the surface of the droplets. It is important to understand what happens on the surface of droplets, an on the interface between oil and water. The droplets in an emulsion will try to reduce the interfacial area, and make an interfacial surface film.

2.2.5 Destabilization Mechanisms

Because emulsions are thermodynamically unstable, they tend to phase separate over time. There are several destabilization mechanisms for breakage of emulsions, as illustrated in Figure 5. The destabilization mechanisms can be divided into two main steps: Firstly, a migration of the droplet due to gravitational forces; and secondly, an increase of the droplet size due to Oswald ripening, coalescence or flocculation.

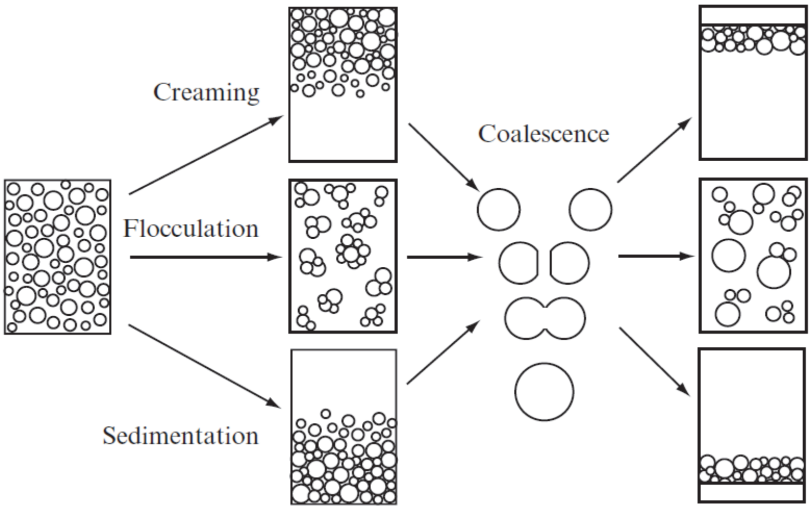


Figure 5: Destabilization mechanisms of emulsions, including creaming, flocculation, sedimentation, coalescence and phase separation. [16]

Creaming and sedimentation are mechanisms based on gravitational force. These processes depends on the density difference between the two phases. Light droplets rises, resulting in creaming, as when $\rho_{\text{droplets}} < \rho_{\text{continous phase}}$. Heavy droplets sediments to the bottom of the samples when $\rho_{\text{droplets}} > \rho_{\text{continous phase}}$. Creaming and sedimentation are reversible phenomenon where the initial state can be obtained by agitation. [16]

Flocculation occurs if the attractive forces between the droplets are strong enough, the droplets are so close that they form energetically stable clusters where the droplets retain in their own shape and size. Flocculation is not always a reversible phenomenon, considering droplets close enough to each other, would lead to coalescence and a loss of their integrity. [16, 17]

By molecular diffusion, also called Ostwald ripening, and coalescence, the droplets in the emulsion grow in size and eventually separates into two phases. Ostwald ripening is the process where large droplets grow at the expense of small droplets. The process is driven by the high Laplace pressure difference in small droplets which forces the solvent present in the small droplets to diffuse into a larger droplet. [17] Coalescence is an irreversible process where two or more droplets merge into each other and form a larger droplet. [16] The phenomena is driven by thinning and disruption of the liquid film between the droplets. [30]

Foams can also be formed during emulsification. When there is high content of gas in the liquids, or more air is introduced, the contact area between gas and liquid increases during emulsification. A foam is a dispersion of gas in a liquid or a solid continuous phase. The stability of a foam can vary, and like emulsions they are thermodynamically unstable. Surfactants are great emulsifying agents, but they can also be good foaming agents, which can be a challenge when that is undesirable. Different surfactants can create more foam than others. The formation of foam leads to creaming, and as mentioned above, creaming can cause coalescence. [17]

Mechanical destabilization applies force by centrifuges, cyclones, and/or membranes to separate the emulsions, and are often combined with thermal methods. Chemical methods increases the probability of coalescence of droplets by rupturing and weakening the rigid film. The electrical double layer in o/w emulsions is compressed by addition of salt, which leads to a reduction in the repulsive (stabilizing) force between droplets. [17, 22]

Electrical methods apply electrical fields in order to promote coalescence. The water droplets in a w/o emulsion will be polarized by applying an electrical field. Due to the positive and negative charges inside the water molecules and the creation of dipoles, attractive and repulsive forces between the water droplets makes them line up between the electrodes, as seen in Figure 6. When water molecules are covering the field between the electrodes, droplets will coalescence. [17, 22]

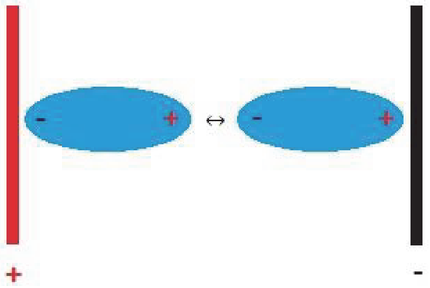


Figure 6: Polarization of water droplets in an electrical field.

2.2.6 Crude Oil Emulsions

When crude oil is flowing through the porous system in an oil reservoir, emulsions can be formed or destabilized. In some reservoirs, stable emulsions can be destabilized when crude oil is passing through the reservoir during oil production, or on the other hand, stable emulsions can be formed. Formation of emulsions in the reservoirs or during oil production can cause problems in the oil industry. The formation and stability of the crude oil emulsions are dependent of how they are stabilized, i.e. by surface active components, the adsorption method, interfacial properties (interfacial tension and viscosity) [31], and the presence of stabilizing components in the crude oil, like asphaltenes, naphthenic acids, resins and solid particles (sand, clay and scale products with adsorbed asphaltenes). Other stabilizing components in the oil reservoirs can be particles and chemicals from drilling fluids or injection water. The crude oil emulsion are destabilized by mechanical, chemical and electrical methods. [22]

2.3 Filtration of Emulsions

A filter or a membrane is normally used to separate different components by letting some pass through and other remain on top of the filter. There are several types of filtration methods, filters and membranes. [32] In this project, a porous glass filter is used. The idea is that the pore size of the filter can selectively separate different droplets of different sizes. Droplets smaller than the pore diameter of the filter can easily pass through the pores and the emulsion will not be demulsified. Large, rigid droplets have to deform to be able to pass the pores: They are dependent of their flexibility, since they can be squeezed, broken and collide. [31, 32] Both flocculation and coalescence are processes that can take place during filtration through a porous system. [31, 33]

Darcy's law, equation (5), describes the flow of an incompressible fluid with constant viscosity through a homogenous porous media.

$$Q = \frac{\kappa A(p_1 - p_2)}{\mu L} \quad (5)\ [34]$$

The equation shows the relation between flow rate through a porous media, Q, viscosity of the fluid, μ, and pressure drop (p_1-p_2) over a given distance. κ is the permeability of the media. A is the cross-sectional area of the flow and L is the length over which the pressure drop is taking place.

According to Darcy's law, there needs to be a pressure gradient over the distance the liquid is going to flow because of hydrostatic conditions. If there is a pressure gradient, the flow will occur from high to low pressure. The greater the pressure gradient, the greater the flow rate. The flow rate will differ through different materials, even if the pressure gradient is the same. [34]

An oil reservoir works as a filter since it consist of a huge network of pores in different sizes and shapes. The porosity of the reservoir states how close and dense the pores are packed, and the ability to let a fluid flow through a porous material is called permeability. High permeability is important for a fluid to flow easily through a porous media. [34] The most common reservoir rocks are sandstone and limestone, which have pores in the micrometer scale. High quality sandstone has a pore size greater than 30 µm, called macropores. [5] Table 4 shows some pore sizes in porous media. Reservoirs and pores are normally filled with both oil and water. In an oil reservoir with a water wetting surface, the oil needs to overcome the strength and properties of the water film to be able to flow through the reservoir.

Table 4: Pore size in some porous media. [5]

Porous media	**Pore size [µm]**
Sandstone	2-30 µm
Tight sandstones	0.03-2 µm
Shales	0.003-0.1 µm

2.4 Experimental Techniques

Several methods can be used to characterize emulsions. In this study, the stability of emulsions are analyzed by low-field NMR, microscopy, and bottle testing.

2.4.1 Evaluation of Emulsion Stability by Bottle Testing

The stability of emulsions can be studied visually using the bottle test methodology, and different parameters can be obtained. Phase separation and occurrence of free oil or free water can be followed visually in a graduated conical cylinder over time. Disadvantages can be the difference in perception of height of the interface between the emulsion and the oil or water phase by different persons, and the process to observe in the bottle test tube is time consuming. [35]

From weighing the samples before and after filtration, a mass balance can be obtained, and the percentage recovered amount of sample can therefore be calculated (equation (6)) in order to see how much was left in the filter or lost.

$$\% \, Recovered = \frac{Mass\,recover}{Mass\,initial} \cdot 100\ \% \tag{6}$$

The initial oil or water content can be calculated based on the preparation of emulsions: The weight and density of the different components, as in equation (7).

$$\% \, oil/water\ initial = \frac{V_{oil/water}}{V_{tot.initial}} \cdot 100\ \% = \frac{\frac{m_{oil/water}}{\rho_{oil/water}}}{\frac{m_{oil}}{\rho_{oil}} + \frac{m_{water}}{\rho_{water}}} \cdot 100\ \% \tag{7}$$

The percent amount of free oil or water formed immediately after filtration can be calculated based on the bottle test (equation (8)), using the total amount of sample in the bottle test tube and the free oil/water observed.

$$\% \, free\ oil/water = \frac{V_{free\ oil/water}}{V_{tot.in\ bottle\ test\ tube}} \cdot 100\ \% \tag{8}$$

2.4.2 Optical Microscope

The optical microscope is used for direct observation of a sample, and can be used to study characteristic of colloidal particles, e.g. the droplet sizes, and droplet stability considering flocculation and coalescence.

The light passes through a lens system which distinguishes the details in the sample and magnifies the image to the observer. Objects down to 1 µm can be observed, although this is limited by the resolution capability of the microscope, optical contrast between the droplets, the environment, and the light source. [17, 36]

Limitations by using optical microscope for observation include that only a small part of the sample is analyzed, which would not be representative. The sample may need to be diluted or spread on the microscope slides, which can break or destabilize the emulsion droplets. [37] The droplet sizes obtained using microscopy are number based, compared to for example droplet sizes obtained by NMR which are volume based, and makes the two not entirely comparable.

2.4.3 Nuclear Magnetic Resonance (NMR)

By using low-field nuclear magnetic resonance (NMR), parameters like droplet size distribution, oil profile and water profile in an emulsion can be determined. Advantages by using NMR to examine the emulsions is that the whole sample is considered. The light absorption of the sample is not relevant in the NMR, and the sample can be analyzed immediately after preparation without need of dilution or spreading. [37]

In order to calculate the droplet size distribution, in the case of w/o emulsions, only the signal of the dispersed phase, i.e. the water phase, must be recorded and processed. To separate the oil and water signals, relaxation times, mobility, and difference in temperature dependency on the viscosity, are considered by low-field NMR. The principle of the method uses a magnetic field where a nuclei from a hydrogen atom is excited to a higher energy level, and the relaxation back to the equilibrium state can be measured after exposing it for a radio frequency pulse, depending on the molecular mobility of protons in the liquid. [19]

The signal from the continuous phase, the oil phase in w/o emulsions, is suppressed because oil and water have different relaxation times, both the longitudinal (T_1) and the transverse (T_2) relaxation times. [24] The relaxation time is the time the oil signal uses to return to equilibrium and the z-storage time is the time the NMR signal is located along the z-axis and is subjected to the T_1 relaxation process. The oil signal returns to equilibrium, and the water signal is left. By inserting the water signal back in the xy-plane, the diffusion and T_2 can be measured, which gives the droplet size distribution and a profile which indicates the water profile. The signals are separated due to the different molecular mobility, because the mobility of oil is normally much lower than for water. [37]

In o/w emulsions the relaxation times cannot separate the signals from oil and water, as the oil viscosity approaches the water viscosity (i.e. overlapping of T_1, T_2 and diffusion coefficients). Therefore a RMSD (Root of mean squared displacement) separation approach is applied, where the difference in the RMSD is dependent of the restricted mobility of the droplet phase and unrestricted mobility of the continuous phase. A diffusion measurement suppresses the signal from the continuous phase with gradients before the measurement starts. Observation times that produces significant different RMSD between the continuous phase and the droplets are then used to suppress the continuous phase. Consequently, the RMSD measured is larger for the continuous phase, than for droplets, where the RMSD is confined by the dimensions of the droplet. [38]

There are several important parameters obtained by NMR, like the droplet size distribution (DSD), the S/V profile and the oil and water profiles.

2.4.3.1 *Droplet Size Distribution (DSD)*

From the droplet size distribution (DSD) the average droplet diameter, the mode diameter, total size range and half width can be found or calculated. Figure 7 shows an example of a droplet size distribution, including the average droplet diameter, mode, total size range of the droplets and the half width. The intensity of the droplet diameters are proportional to the volume of the droplets, and therefore is the distribution obtained by the NMR measurement a volume distribution.

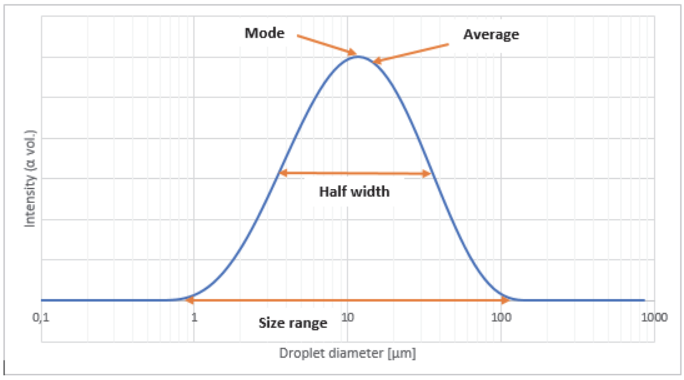


Figure 7: Example of a droplet size distribution (DSD) for an emulsion obtained by NMR, where the average droplet diameter, mode, total size range and half width size range are included.

There are some uncertainties with largest detected droplet sizes and the total size range of the droplets. Therefore is the half-value of the width, the half width, used to compare the samples instead of the total size range.

The average droplet size and the mode can be the same, but not always, and therefore are both included in this report. The mode is the point at the curve where the occurrence of droplets of one particular size is the largest, the vertex. The average droplet size can be calculated as in equation (9), where I is the percentage intensity and d is the droplet diameter in micrometers. The average droplet size is volume based.

$$\overline{d_v} = \frac{\sum_{i=1}^{n} I_i\, d_i}{\sum_{i=1}^{n} d_i} \tag{9}$$

The DSD measurement is containing two sequences which both are divided into two parts. One part where the continuous phase (the bulk phase) is suppressed. In o/w emulsions, the water signal is suppressed, and in w/o emulsions the oil signal is suppressed. The other part of the sequences are the experimental measurement and differs from each other in the two sequences. The second part in the first sequence is a diffusion measurement (Figure 8) where the diffusion of the dispersed phase, the droplet phase, is measured. The average droplet size can be obtained by the surface-to-volume ratio (S/V) of the droplets. The second part in the second sequence is called a CPMG experiment, a T_2 measurement where the distribution of the droplet size is made (Figure 9). By combining the two sequences, the droplet size distribution is obtained. [38]

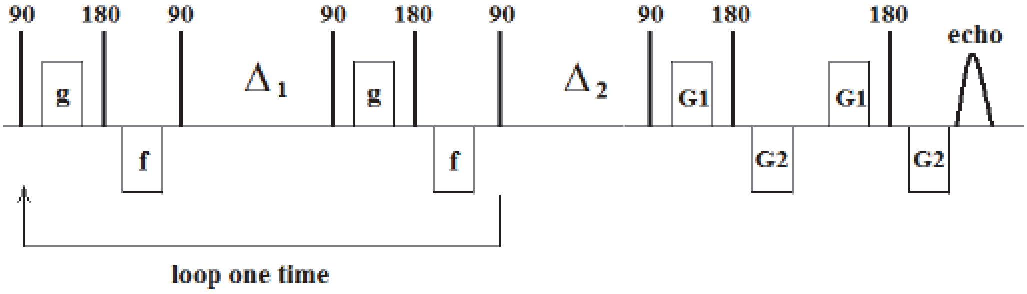


Figure 8: NMR sequence that is called the combined oneshot-diffusion experiment. First the continuous phase is suppressed and then a diffusion measurement is performed. [38]

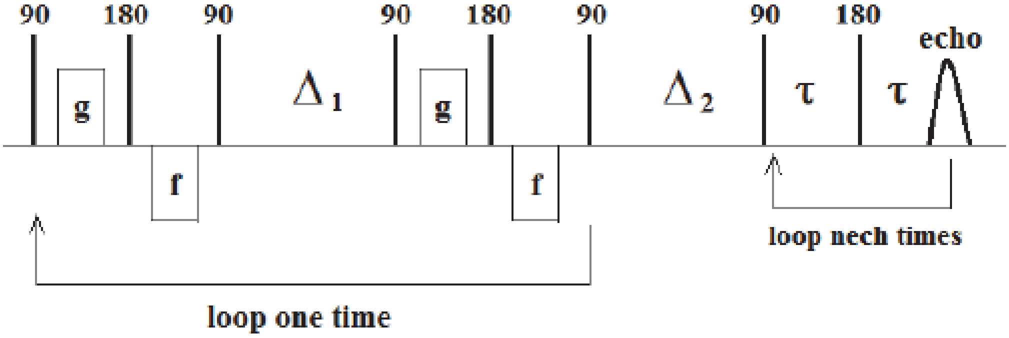


Figure 9: NMR sequence that is called the combined oneshot-CPMG experiment. First the continuous phase is suppressed and then a T_2 measurement is performed (where the distribution of the droplet size is made). [38]

The different parameters in the NMR sequences are described below: [38]

- g and f are the G1_suppression values in the NMR program, which are the strength of the suppressing gradients suppressing the continuous phase. Increased suppression gradients would result in obtaining a diffusion coefficient from the dispersed droplets.

If the continuous phase was not properly suppressed it would contribute to the NMR signal together with the dispersed droplets. When measuring w/o crude oil emulsions, a low G1_supression value would be best because the water signal is then only suppressed by the relaxation time.

- Δ_1 is the D6 value and Δ_2 is a stabilizing time constant in the NMR program. D6 is the z-storage time delay, the time the oil signal uses to go back to equilibrium. In order to obtain the z-storage time for crude oil emulsions, the z-storage time needs to be increased so that there is no signal left when measuring just the crude oil (bulk crude oil) with the CPMG one-shot measurement.
- G1 and G2 are the G1_max or G1_min values in the different scans in the NMR program, which are the strength of the gradients. G1_min is set to 1000 for all the measurements, and G1_max is the maximum strength of the gradients applied when the diffusion coefficient is determined. Using a high G1_max value would result in measuring most of the small droplets in the sample, because a smaller slope and a smaller diffusion coefficient obtained (see Figure 11 below). The signal from large droplets would have a larger attenuation, which gives more signal from smaller droplets. On the other hand would a low G1_max value result in measuring more of the large droplets in the sample, but the uncertainty of the measurement would be higher using a low G1_max value due to noise in the signal of the measurement of the diffusion coefficient.
- The 2*τ is the inter echo spacing, which is the time between the echoes in the sequence, the time between the measuring points in a CPMG experiment.

The intensity of the NMR signal, I, obtained by the sequences is decreasing as a function of the echo signal, and is shown in equation (10) and (11). I_0 is the initial intensity of the NMR signal. γ is the gyromagnetic ratio, δ is the gradient pulse length and Δ is the z-storage time delay (D6 value). [24]

$$I = I_0 e^{-\gamma G_{max}^2 \delta^2 \left(\Delta - \frac{\delta}{6}\right) D} \qquad (10)\ [38]$$

$$ln \frac{I}{I_0} = -\gamma^2 G_{max}^2 \delta^2 \left(\Delta - \frac{\delta}{6}\right) D \qquad (11)\ [38]$$

Figure 10 shows the decrease of intensity. The intensity decreases as a function of the echo signal and the gradient strength applied. The slope in the graph is proportional to the intensity of the signal. The uncertainty of the slope (α) becomes larger the closer the G1_max is to G1_min (here 1000). [24]

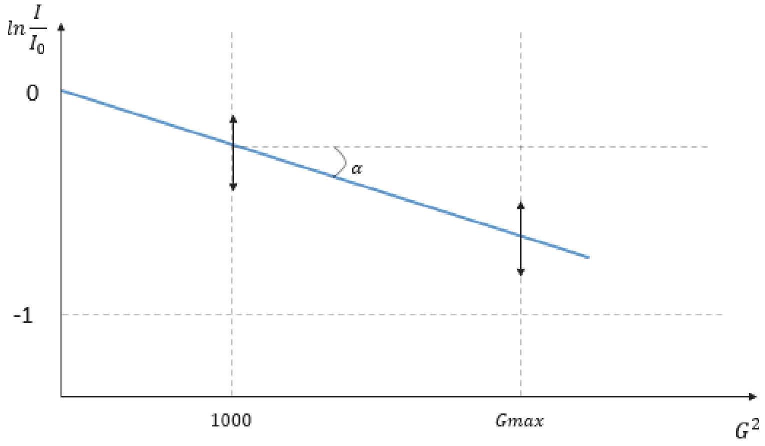


Figure 10: Graph of the intensity as a function of the gradient strength.

The diffusion coefficient, D, (equation (12)) is obtained by the intensity (equation (10) and (11)). Considering just the droplets, D(t) is the measured diffusion coefficient for the emulsion, and D_0 is the diffusion coefficient for the continuous phase, the bulk phase in the droplets. The bulk diffusion coefficient for water is $2.3 \cdot 10^{-10}$ m^2/s at 25 °C. t is the observation time of the sample. [24]

$$\mathrm{D(t)} = \mathrm{D_0} - \left(\frac{4}{9\sqrt{\pi}} D_0 \sqrt{D_0 t}\, \frac{S}{V}\right) \qquad (12)\ [38]$$

The diffusion coefficient as a function of the observation time is shown in Figure 11. The slope is proportional with the surface-volume ratio (S/V), and the D_0 is more important for large droplets than for small. [24]

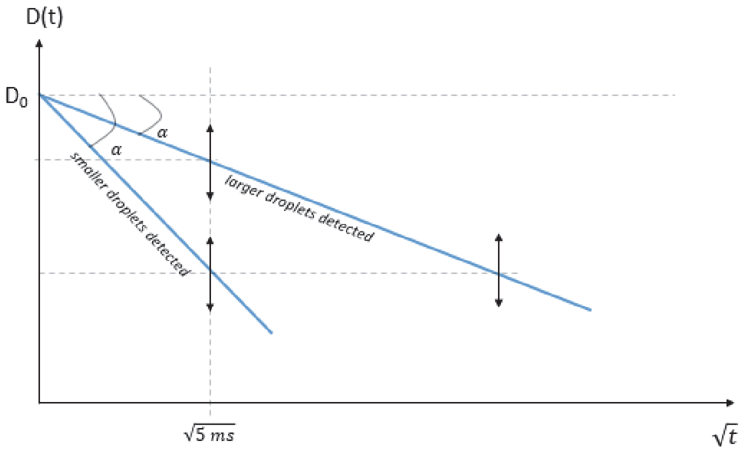


Figure 11: Graph of the diffusion coefficient as a function of the observation time.

By obtaining the diffusion coefficient (equation (12)), the relaxation time and the surface to volume ratio of the components, a distribution of the droplet size can be calculated by the NMR from these values in absolute length. [24] The DSD is given as a function of the intensity proportional to the volume of the droplet diameter.

2.4.3.2 S/V profile

An S/V profile gives a vertical variation of the average droplet diameter along the height of the sample. This method can be used when w/o emulsions forming free bulk water are analyzed.

The S/V profile measurement is containing a sequence which is divided into three parts (Figure 12). The first part is where the continuous phase (the bulk phase) is suppressed. The second part of the sequence is the experimental measurement, a diffusion measurement where the diffusion of the dispersed phase, the droplet phase, is measured. The average droplet size can be obtained by the surface-to-volume ratio (S/V). The third part of the sequence is the experimental profile measurement where the S/V profile is obtained. g and f are the G1_suppression values. Δ_1 is the D6-value, the z-storage time delay, and Δ_2 and Δ_3 are stabilizing time constants. g_p and g_r are the gradients which gives a position dependent frequency in the profile. [38]

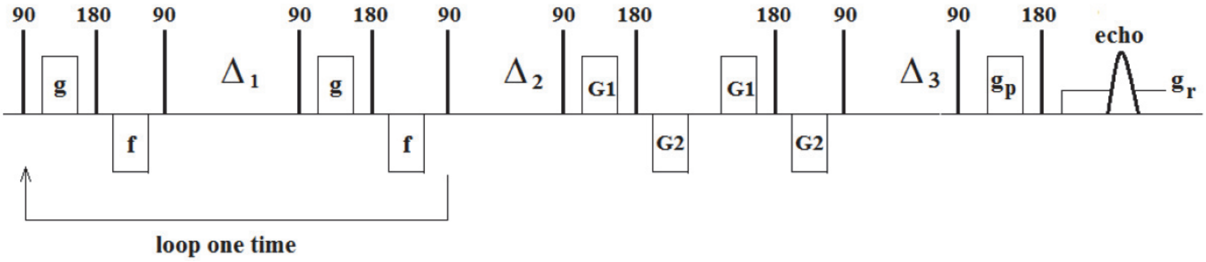


Figure 12: NMR sequence that is called the combined oneshot-diffusion-profile experiment. Firstly the continuous phase is suppressed, secondly a diffusion measurement is performed and finally the experimental profile measurement where the S/V profile is obtained. [38]

The S/V profile shows the average droplet diameter along the height of the sample, while DSD program is based on the whole sample, and not just parts in different heights. The DSD gives a quantitative view of the droplet size, and the average droplet size obtained by the DSD is based on a T_2 experiment, while the average droplet size obtained by an S/V profile is based on a $1/T_2$ experiment. The values on each side of the DSD leads to the average droplet size obtained by DSD to differ from the average droplet size obtained by the S/V profile. The average droplet size obtained by the DSD and the S/V profile are not comparable, and for that reason are both included. In order to obtain and calculate the average S/V, the T_2 distribution needs to be transformed to a S/V distribution. This can be done by finding an average value for $(1/T_2)$. The S/V profile gives the average (1/droplet diameter). [24]

An example of a S/V profile is shown in Figure 13. In this example the average droplet diameter along the height of the tube is constant and ~7 µm.

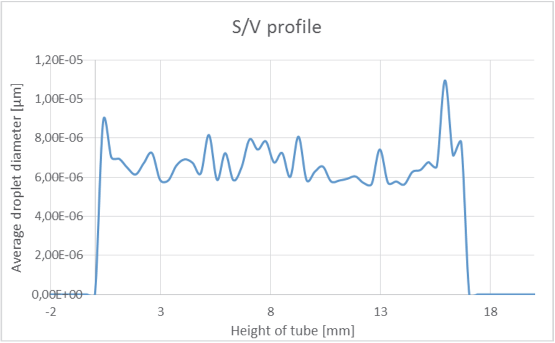


Figure 13: Example of a S/V profile for a w/o emulsion obtained by NMR, where the average droplet diameter along the height of the sample is given.

2.4.3.3 Oil and Water Profiles, and Oil and Water Contents

The oil profile (for o/w emulsions) and water profile (for w/o emulsions) gives the vertical variation of the dispersed phase composition in an emulsion. To follow the separation of oil and water from the emulsions, the profile can be measured over time and variation along the height of the NMR tube. [39]

The profile experiment is a two part sequence. One part where the continuous phase (the bulk phase) is suppressed. In o/w emulsions the water signal is suppressed, and in w/o emulsions the oil signal is suppressed. The other part of the sequence is the experimental measurement where the profile is obtained (Figure 14). g and f are the G1_suppression values. Δ_1 is the D6-value, the z-storage time delay, and Δ_2 is a stabilizing time constant. g_p and g_r are the gradients which gives a position dependent frequency in the profile. [38]

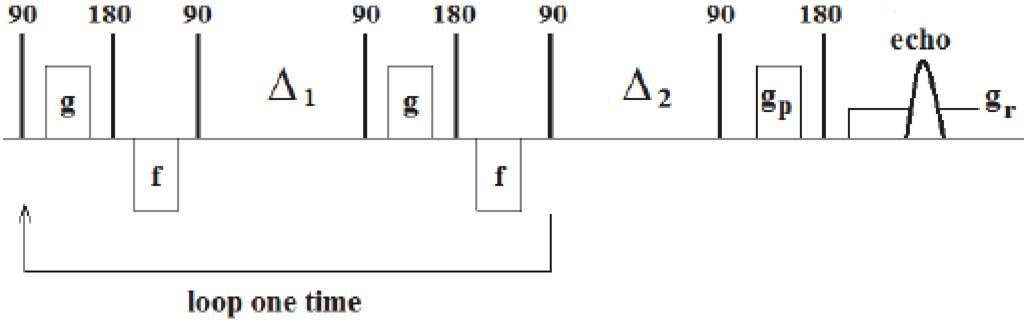


Figure 14: NMR sequence that is called the combined oneshot-profile experiment. First the continuous phase is suppressed and then the profile is obtained by the profile measurement. [38]

An example of a water profile is shown in Figure 15. In this example there is about 33 vol. % water at the bottom of a w/o emulsion sample, as seen in the figure. Occurrence of free water in a w/o emulsion would result in a peak of 100 vol. % at the bottom of the sample (0 mm) in the water profile obtained. Occurrence of free oil in an o/w emulsion would result in a peak of 100 vol. % at the top of the sample in the oil profile obtained.

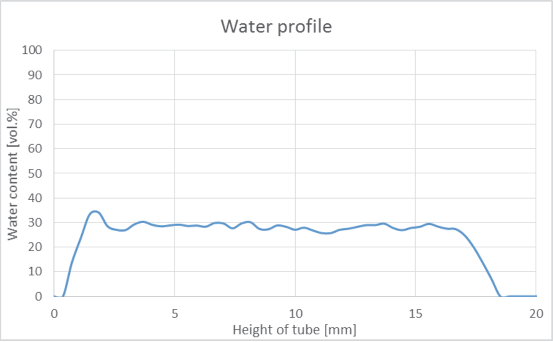


Figure 15: Example of a water profile for a w/o emulsion obtained by NMR, where the water content along the height of the sample is given.

The oil or water content is determined from the profile analyzed by NMR. The content is the average of the content of dispersed phase (vol. %) along the height of the sample, and can be calculated like this:

$$OC\ or\ WC\ [vol.\%] = \frac{\sum_{i=0}^{n=h} OC_i\ or\ WC_i}{n} \tag{13}$$

Where h is the height of the NMR tube, n is the total number of data, and OC or WC is the oil content or water content in volume percent.

3. Experimental

In this chapter, the experimental procedures that were used in this Master's thesis project are described. The o/w, w/o and o/w/o emulsion systems were tested and stabilized by different surface active components in order to create interfaces with different rigidity and flexibility. All the experiments were performed at room temperature.

The w/o emulsions were crude oil emulsions. O/W model oil emulsions were stabilized by the hydrophilic surfactant Tween80, or the hydrophilic silica particles, Aerosil R7200, in order to create different droplet interfaces in the emulsions. Filtration of particle dispersions was performed in order to determine how the particles behaved during filtration. Multiple o/w/o emulsions were also prepared using a two-step method, and filtrated to see what happened to the double emulsions during filtration.

3.1 Preparation of Emulsions

The w/o emulsion containing crude oil were simply mixed with water. O/W model oil emulsions were prepared by dissolving the surface active components in the water phase, and then adding the oil phase.

Different parameters such as mixing speed, mixing time, oil or water content, choice of crude oil for the w/o emulsions, choice of model oil for the o/w emulsions and o/w/o emulsions, choice of surface active components, and concentration of surface active components were examined in order to have parameters which gave stable enough emulsion systems to be analyzed with droplet size distributions similar to each other (4.1 – Review from 1st semester).

3.1.1 Choice of Components for W/O Emulsions

Two crude oils were tested and used as the continuous phase in the w/o emulsions. Both were North Sea crude oils, where Crude Oil A was an acidic heavy crude oil and Crude Oil B was an acidic heavy medium crude oil. Milli-Q water (18.2 MΩ at 25 °C) was the dispersed phase. Data about the different crude oils are given in Table 5.

Table 5: Density, viscosity and API value for w/o crude oil emulsion components at 20 °C. Numbers marked with * are obtained from "*The Handbook of Chemistry and Physics*" [40]. Densities marked with ** are measured by the density meter Anton Paar DMA 5000. Viscosities marked with *** are measured by rheometer Anton Paar MCR 301. API values are calculated based on densities measured at 15 °C obtained with the density meter Anton Paar DMA 5000.

Component	**Density [g cm^{-3}]**	**Viscosity [mPa s]**	**°API value**
Crude oil A	0.9346 **	315.4 ***	19.2
Crude oil B	0.8924 **	15.3 ***	26.5
50:50 wt. % Crude oil A and B mixture	0.9177 **	104.5 ***	22.1
Water	1.0000 *	1.002 *	10

First, the two crude oils were tested separately, and the emulsification conditions were determined in order to create stable emulsions. Maximum droplet size was reached for both w/o emulsions of pure Crude Oil A and pure Crude Oil B, but the droplets were too small compared to the filter pores. Therefore a mixture of the crude oils was tested and new emulsification conditions were determined. The mixture contained 50 wt. % Crude Oil A and 50 wt. % Crude Oil B.

3.1.2 Choice of Components for O/W Emulsions

Model oils, hexadecane and primol, were used as the dispersed phase of the prepared o/w emulsions, Milli-Q water was the continuous phase. More detailed data of the emulsion components are given in Table 6. Some of the mixing parameters tested gave unstable emulsions which formed free oil. In all the emulsions prepared there was observed creaming. Hexadecane was chosen for further analysis because primol had too low mobility and too high viscosity.

Table 6: Densities and viscosities for o/w model oil emulsion components at 25 °C. [40]. Densities marked with * are obtained using the density meter Anton Parr DMA 5000. Viscosities marked with ** are obtained using the rheometer Anton Parr MCR 301.

Component	**Density [g cm^{-3}]**	**Viscosity [mPa s]**
Hexadecane	0.7730	3.34 (at 20 °C)
Primol	0.8603*	133 **
Water	1.000	1.002 (at 20 °C)

Three different surface-active components were tested and used in this project. Two different hydrophilic surfactants, AOT and Tween80, were used to obtain flexible droplets, and hydrophilic silica particles, Aerosil R7200, was used to obtain rigid droplets. The concentration of surface-active components in the different samples could vary in weight percent of the continuous phase. The surfactant AOT was discarded because it created too much foam during emulsification.

In the preparation of the particle-stabilized o/w model oil emulsions, particles were added to the water phase and sonicated. Sonication was performed to ensure that the particles were completely dissolved in the continuous phase. Sonication of Aerosil R7200 lasted for about 1 hour and 30 minutes. This was in contrast to the preparation of surfactant-stabilized o/w model oil emulsions: The surfactants were highly viscous liquids which just needed some stirring to ensure that the surfactants were perfectly diluted in the water phase.

3.1.3 Multiple Emulsions

Multiple (double) o/w/o emulsions were prepared using a two-step method, containing primol as the oil phase and MQ-water as the water phase. The surfactant Tween80 was used to stabilize the inner o/w emulsion, and Span80 was used to stabilize the outer, double emulsion.

Different dyes were tested to determine the nature of the phases in the double emulsions. Two water soluble dyes, Methylene Blue and Congo Red, and an oil soluble dye, Sudan III. It was first prepared a 1000 ppm stock solution of each dye, afterwards they were diluted into 1, 10 and 100 ppm solutions.

3.1.4 Emulsification

The emulsions were emulsified using a four bladed propeller (developed in-house) or an Ultra Turrax with S25N18G shaft (IKA T25 Digital). Different mixing frequencies were used in order to create emulsions with desired droplet sizes. The four bladed propeller was used for mixing frequencies of 50 to 2000 rpm, and the Ultra Turrax for mixing frequencies higher than 3000 rpm, up to 24000 rpm. The emulsions were prepared in glass vials with a total liquid volume of 30 mL.

After emulsification, automate pipette was used to transfer some of the emulsion (~ 4 mL) to the NMR tube directly after emulsification, just a droplet was analyzed using microscopy, and the rest of the sample was filtrated.

In order to prepare multiple emulsions, the samples were mixed twice. First the inner emulsion was prepared by intense emulsification with the Ultra Turrax in order to create small droplets. The oil content was 30 vol. %, and the water phase was containing the hydrophilic surfactant Tween80. The single emulsion was analyzed using microscope to ensure that small droplets were formed. Then the outer emulsion was prepared by adding 30 vol. % emulsion into a primol oil phase, which was containing the hydrophobic surfactant Span80. The outer emulsion was then mixed gently using the propeller in order to create the double emulsion and preventing the inner emulsion from breaking. The multiple emulsion were then analyzed using microscopy.

While preparing emulsions, the vial was moved up and down continuously to ensure complete mixing of the entire sample the first 30 seconds of the emulsification.

The type of emulsion prepared during emulsification had to be taken into account when a new emulsion system was considered. This was done by having a droplet of the emulsion prepared into the pure dispersed phase and pure continuous phase, in order to see in which phase the droplet was dissolved. Crude oil w/o emulsions were confirmed because the crude oil emulsion droplet dissolved in the crude oil phase, and o/w surfactant- and particle-stabilized emulsions were confirmed when the droplets dissolved in the water phase and not in the pure hexadecane oil phase. The same was done and confirmed when preparing the multiple emulsions, first the o/w primol emulsion, and then the double o/w/o primol emulsion.

3.2 Filtration

The emulsions were filtrated through glass filters with a known porosity. The filtration set-up consisted of a filter funnel with a filter, placed on the top of a receiving filter flask, which was connected to a suction source, Figure 16.

Figure 16: Experimental set-up of the filtration.

Two different sintered borosilicate glass filters were used. Duran ® Filter discs, 4 mm in diameter, porosity number 3 and 4, with pore sizes of 10-16 µm and 16-40 µm respectively.

In order to obtain better control of the filtration, and to have constant and stable suction, a vacuum pump was preferred to use as suction rather than water jet suction. Automate pipette was used to transfer (~4 mL) emulsion to the NMR tube directly after filtration.

3.3 Emulsion Stability

NMR was used to analyze the stability of w/o crude oil emulsions and o/w model oil emulsions both before and after filtration. In addition, a bottle test was performed on the filtrate in order to observe immediate separation and the kinetics of the formation of free oil (in o/w emulsions) or free water (in w/o emulsions). In addition to NMR and bottle test, all emulsions prepared were also analyzed using microscope.

3.3.1 Analyzing by NMR

The NMR used in this experiment was a R4 21 MHz PFG-NMR instrument developed and supplied by Geir Sørland and Anvendt Teknologi. 21 MHz is the resonance frequency of hydrogen which corresponds to the magnetic field of 0.5 Tesla in the instrument. In this project, NMR tubes of 18 mm in diameter were used, and the sample amount was 3.65 mL.

3.3.2 Microscopy

The microscope used in this project was a Digital Video Microscope (DVM). The microscope was a Nikon Eclipse, and the camera was a CoolSNAP-Pro camera by Media Cybernetics. The software used to capture the images was called Image-Pro Plus 5.0. Magnification of the objectives available were 10x, 20x and 50x.

3.3.3 Bottle Testing

The cylindrical conical tubes used for the bottle tests were delivered from Brand ® Germany, called Blau Brand ® ASTM 100 mL centrifuge tube, as shown in Figure 17. The total volume of the tubes were 100 mL and the length of the tube was 203 mm, marked at every 25 mL in the cylindrical part of the tube.

Figure 17: Cylindrical bottle test tube with conical bottom.

3.4 Filtration of Particle Dispersions

Particle dispersions were prepared and filtrated in order to observe how the particles behaved during filtration. The idea was to find out if they would clog the filter or not. If they clogged the filter, it was interesting to find the critical concentration for the clogging.

Several dispersions of the hydrophobic silica particles Aerosil R972, with different concentrations (1-10 wt. % Aerosil R972), in primol or hexadecane were sonicated and filtrated through filter with porosity number 3. In order to have an indication of the size range for particles obtained in the dispersions, microscope was used to see if the particles were in the colloidal size range. If the particles were smaller than 1 µm, the particles would not be visible by eye.

4. Results and Discussion

The experimental results from low-field NMR analysis, microscopic imaging, bottle testing, and discussion about the results are shown in this chapter. The chapter is divided into five sections. Initially, the results from the 1st semester are summarized, secondly, filtration results of w/o crude oil emulsions are presented, thirdly, filtration results of o/w model oil emulsions: including surfactant- and particle-stabilized emulsions are presented, fourthly, the filtration results obtained in both 1st and 2nd semester are discussed, and finally, filtration results of multiple o/w/o model oil emulsions are presented.

All the data obtained by NMR before and after filtration of the different emulsions are included in the appendix. Firstly, the DSD for all the different emulsion system analyzed before and after filtration by NMR are included in Appendix A – Droplet Size Distribution. Secondly, Appendix B – S/V Profiles, shows the average droplet sizes along the height of the NMR tube before and after filtration of the w/o crude oil mixture emulsions, and finally, the oil and water profiles are given in Appendix C – Oil and Water Profiles, including the profiles before and after filtration analyzed by NMR. In Appendix D – Risk Assessment, is the risk assessment of the experimental work in this project given in Norwegian.

4.1 Review of 1st Semesters Results: Filtration of W/O Model Oil Emulsions Stabilized by Particles, Surfactants, and Particle-Surfactant-Mixtures

The specialization project "*Stability of Water-in-Oil Emulsions in Porous Media*" was performed at the Ugelstad Laboratory during the 1st semester, in the fall of 2015. W/O emulsions were prepared in order to analyze the stability during filtration through glass filters to determine how the droplet rigidity and flexibility influenced the stability during filtration. The different systems had similar droplet sizes before filtration in order to perform reasonable comparisons of the systems behavior during filtration. The droplet size and the water content were determined by NMR. Half width of the droplet size range before filtration were 2-70 µm in diameter, a mode of ~13 µm in diameter and the average droplet diameter was ~17 µm.

W/O emulsions stabilized with different stabilizing components were prepared. Model oil (primol) was used as oil phase and pure water was used as water phase. Several model oils were tested first, and primol was concluded to be most applicable for these experiments. The emulsions were stabilized by the hydrophobic silica particles Aerosil R972, the hydrophobic surfactant Span80, and two different mixtures of both particles and surfactants: One containing 0.5 wt. % Aerosil R972 + 0.5 wt. % Span80, and the other 0.25 wt. % Aerosil R972 + 0.75 wt. % Span80.

The particle-stabilized emulsions created rigid droplets which broke and coalesced during filtration: The NMR experiments showed that the droplet sizes was about halved, with a decrease in the mode from 16 μm to 8 μm in diameter. This reduction was caused by droplets coalescence and forming free water. The emulsified water content was also halved during filtration, which was due to the free water formed during filtration was not included in the NMR sample after filtration. The surfactant-stabilized emulsions created flexible droplets which passed through the filters without variations in droplet sizes during filtration, with a mode of ~9 μm in diameter both before and after filtration. There was no change in the emulsified water content during filtration.

The results obtained with emulsions stabilized by two different mixtures of particles and surfactants were not completely consistent. The mixture of 0.5 wt. % particles and 0.5 wt. % surfactants seemed to be controlled by the surfactant: There was no change in the droplet sizes during filtration, with a mode of ~11 μm in diameter, and no free water formed. But the mixture of 0.25 wt. % particles and 0.75 wt. % surfactants did not just show the effect of surfactant-stabilized emulsions after filtration, but also the effect of particle-stabilized emulsions: There was no free water formed, but there was a slight decrease in the droplet size during filtration, where the mode shifted from 11 to 8 μm during filtration.

4.2 W/O Emulsions: Crude Oil Emulsions

Different crude oil emulsions were prepared in order to achieve stable emulsions. In addition droplets comparable to the 1st semesters droplets in the w/o model oil emulsions prepared were aimed for.

4.2.1 Crude Oil A Emulsions

A heavy acidic North Sea crude oil, here named Crude Oil A, was tested first.

4.2.1.1 Determination of Emulsification Conditions for Crude Oil A

Several mixing speeds were tested in order to prepare stable emulsions with droplets in the same size range as the particle- and surfactant-stabilized w/o model oil emulsions from the 1st semester. Crude Oil A was emulsified by hand, 1000 rpm, and 1500 rpm for five minutes, and also 500 rpm for three minutes. The DSD obtained using the different emulsification conditions for Crude Oil A emulsions are shown in Figure 18.

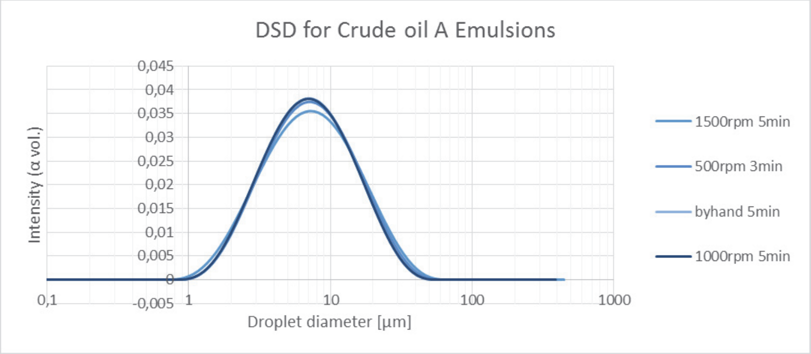


Figure 18: DSD for Crude Oil A and water emulsions (30 vol. % water cut) prepared with different emulsification conditions.

There was no free water formed within one hour after emulsification for any of the samples, and it could be concluded that the samples were stable for at least one hour after emulsification. Visual observations indicated small amounts of free water at the bottom in some vials after one hour. Most free water was observed in Crude Oil A emulsion emulsified at 500 rpm for three minutes, and after one day there was about 10 % free water formed in the vial. The emulsification conditions had low impact on the droplet sizes in Crude Oil A emulsions, and it was irrelevant if the emulsion was emulsified by hand or high mixing speed. Emulsification at 1000 rpm for five minutes was chosen as mixing parameters for the filtration experiments.

By comparing the DSD for Crude Oil A with the DSD obtained in the 1st semesters different w/o model oil emulsions, Crude Oil A emulsions tended to contain smaller droplets, as shown in the figure below, Figure 19. The droplets were too small to perform a reasonable comparison with the systems prepared in the 1st semester. The droplets were also significantly smaller than the filter pores of the smallest filter which had a pore size of 10-16 µm.

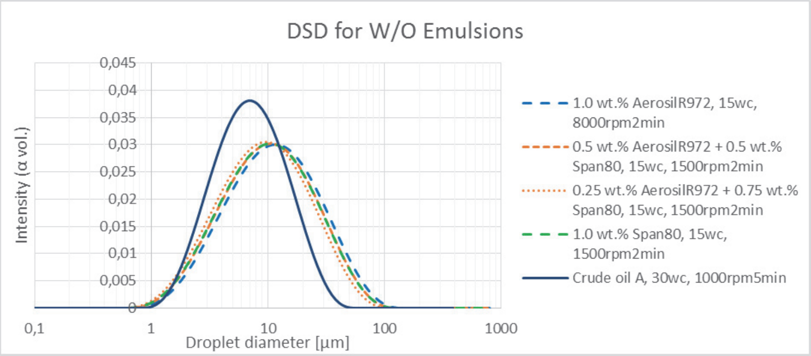


Figure 19: Comparison of DSD for w/o emulsions: Crude Oil A emulsion compared to the different w/o model oil emulsion systems analyzed in the 1st semester.

4.2.1.2 Filtration of Crude Oil A

W/O emulsions of Crude Oil A and water, containing 30 vol. % water cut, were filtrated through filter with porosity number 3. Free water was formed in the bottle test tubes immediately after filtration due to coalescence for several of the samples, as shown in Figure 20. This was not included in the NMR sample after filtration. The NMR results and filtration analysis before and after filtration of the Crude Oil A emulsions are shown in Table 7. Free water observed in the bottle test tubes within three minutes after filtration was determined, calculated by equation (8) and included in the table. The mode and the average droplet sizes were 7 and 9 µm in diameter, respectively, both before and after filtration.

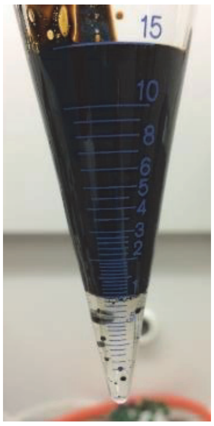


Figure 20: Bottle test tube containing a filtrated Crude Oil A emulsion. Free water was formed after filtration through filter with porosity number 3. Parallel 2

Table 7: NMR results and filtration analysis of Crude Oil A emulsions, containing 30 vol. % water cut, emulsified at 1000 rpm for five minutes. Filtrated through filter no. 3. Water contents marked with * are assumed because height measurement of the samples was not performed. Free water observed in the samples are measured within three minutes after filtration.

	Half width [µm]		**Mode [µm]**		**Average [µm]**		**Water content [%]**		**Mass balance, % recov.**	**Filtration time**	**Free water observed [%]**
	Before	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**			
1	3-19	3-19	7	7	9	9	27*	31*	89.6	9 min	Not measured
2	3-18	3-19	8	7	9	9	25*	27*	84.6	13 min	6.67
3	3-19	3-21	7	7	9	10	22	22	87.7	10 min 30 sec	0.67
4	3-18	2-21	7	7	9	10	20	16	87.3	23 min 45 sec	14.3

As shown in the table above and in the figure of the DSD below (Figure 21), the droplets were small, and did not change in size during filtration. The droplets had a mode of 7 µm in diameter and an average droplet diameter of 9 µm, both before and after filtration. This was also smaller than the filter pores of filter 3 which was used, as well as the pores of the smallest filter, filter 4.

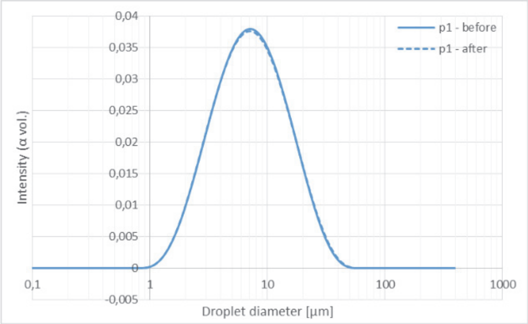


Figure 21: DSD for a w/o crude oil emulsion of Crude Oil A and water, containing 30 vol. % water cut, emulsified at 1000 rpm for five minutes, before (solid line) and after (dashed line) filtration with filter no. 3. Parallel 1.

By comparing the microscope images of emulsions before and after filtration (Figure 22 a and b respectively) and the NMR results before filtration, it can be concluded that most of the droplets were smaller than the filter pores, and could therefore pass through the filter easily. Because droplet sizes obtained using microscopy are number based, and volume based obtained using NMR, the droplet sizes obtained with the different instruments were not completely comparable, but could give an indication of differences and similarities of the droplet sizes. The droplets were on average ~5 µm in diameter before filtration, and most droplets ~3 µm in diameter after filtration, observed using microscope. This was just a small decrease in droplet size, and therefore it could be concluded that there was no change in the droplet size during filtration and the results obtained by NMR were confirmed. The filtration was not size specific since the droplet sizes were undersized compared to the filter pore size.

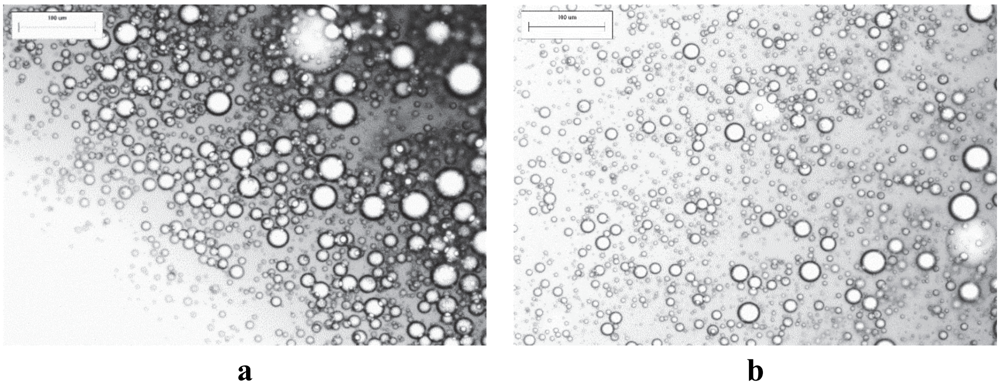


Figure 22: Microscope images of Crude Oil A emulsions, 30 vol. % water cut, emulsified at 1000 rpm for five minutes, before (a) and after (b) filtration through filter no. 3. Parallel 4. Magnification 10x. Size mark: 100 µm.

The free water formed in the bottle test tubes might be due to coalescence and breakage of droplets, and the volume of free water formed varied a lot in the different samples. This was not entirely consistent because there were no change in droplet sizes during filtration, but the recovered amount of sample during filtration was approximately 87 % for all the samples. This would be a result of sample material lost in the filter, and free water formed was most likely due to breakage of droplets during filtration.

Only one of the parallels (parallel 4) showed a decrease of water content during filtration. The decrease of 20 % in water content during filtration obtained by NMR was due to the free water formed in the bottle test tubes within three minutes after filtration (~15 %) which was not included in the sample for the NMR after filtration. There was small amounts of free water observed in parallel 3 (~1 %), which was consistent to the NMR results where no change in the water content during filtration was determined. The water content determined by NMR for the two first parallels, both before and after filtration, were not reliable: There were made some assumptions in the calculations because height measurements of the samples were not performed. The initially low water contents obtained for the samples by NMR were due to uncertainties and sensitivity of the NMR instrument.

4.2.2 Crude Oil B Emulsions

In addition to Crude Oil A, the heavy medium acidic North Sea crude oil, here named Crude Oil B, was tested in order to create emulsions with larger droplets. The desire was to create droplets similar in size as in the emulsions analyzed in the 1st semesters particle- and surfactant-stabilized w/o model oil emulsions, and larger than the droplets obtained in the Crude Oil A emulsions.

4.2.2.1 Determination of Emulsification Conditions for Crude Oil B

To determine the emulsification conditions for Crude Oil B, several mixing speeds were tested. Free water was observed in some samples within 15 minutes after emulsification, as can be seen in Table 8. This was due to low mixing speed for this heavy medium crude oil, which needed more intense emulsification.

Table 8: Emulsification conditions and stability of Crude Oil B emulsions.

Emulsification conditions	**Stability observations**
500 rpm 5 min	Free water observed after 15 minutes.
1500 rpm 5 min	Free water observed after 15 minutes.
4000 rpm 2 min	Free water observed within one hour.
6800 rpm 2 min	Stable, no free water formed within one hour.

The DSD for the stable Crude Oil B emulsions are shown in Figure 23. By comparing the DSD for Crude Oil B emulsions with the DSD obtained for Crude Oil A emulsions, it can be determined that the droplets in Crude Oil B emulsions were still small and not significantly larger than the droplets obtained using Crude Oil A. Therefore filtration of Crude Oil B emulsions was not performed.

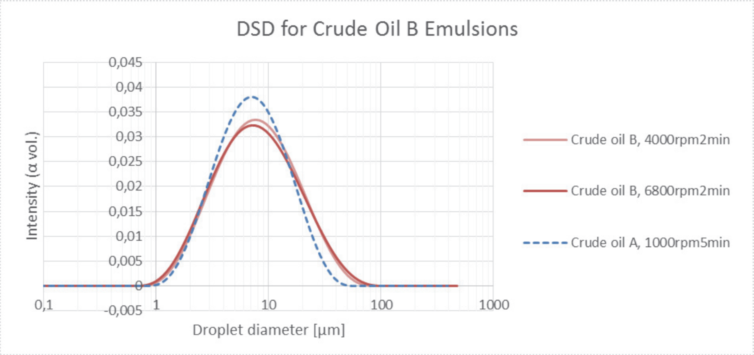


Figure 23: DSD for Crude Oil B and water emulsions (30 vol. % water cut) prepared with different emulsification conditions, compared to Crude Oil A and water emulsions (30 vol. % water cut).

4.2.3 Emulsions of Mixture of 50 wt. % Crude Oil A and 50 wt. % Crude Oil B

Because of the small droplets obtained while emulsification of pure Crude Oil A w/o emulsions and pure Crude Oil B w/o emulsions, also including free water formed during filtration of pure Crude Oil A w/o emulsions, larger droplets and optimization of the NMR program was needed. A 50:50 wt. % mixture of the Crude Oils A and B was made in order to achieve stable emulsions containing larger droplets. By mixing two different crude oils with different viscosities and different surface properties, larger droplet sizes would hopefully be obtained during emulsification.

4.2.3.1 Determination of the Emulsification Conditions for 50:50 wt. % Crude Oil A and B Mixture Emulsions

To determine the emulsification conditions for the 50:50 wt. % Crude Oil A and B mixture emulsion, several mixing speeds were tested. This was in order to prepare stable emulsions, emulsions within the same size range as the particle- and surfactant-stabilized w/o model oil emulsions from the 1st semester, and droplets larger than previously obtained using pure Crude Oil A or pure Crude Oil B. The emulsions were not stable if free water was formed during the first hour after emulsification, and some of the emulsion was then broken due to coalescence. The different emulsification conditions and stability of the emulsions are shown in Table 9.

Table 9: Emulsification conditions and stability for the 50:50 wt. % Crude Oil A and B mixture emulsions.

Emulsification conditions	**Stability observations**
300 rpm (shaker) 48 hours	No free oil formed within one day after emulsification, long emulsification time.
1000 rpm 15 min	No free oil formed within one hour after emulsification, long emulsification time.
4000 rpm 5 min	No free oil formed within one day after emulsification.
6800 rpm 2 min	No free oil formed within one day after emulsification, but too small droplets observed using microscopy (number based average droplet diameter ~7 µm).

The 50:50 wt. % Crude Oil A and B mixture emulsion were emulsified at 4000 rpm for five minutes. Emulsification at 1000 rpm for 15 min was too time consuming, and 6800 rpm for two minutes was too intense and created smaller droplets than the filter pores. The DSD of the 50:50 wt. % Crude Oil A and B mixture emulsions compared to emulsions prepared with pure Crude Oil A and pure Crude Oil B are shown in Figure 24. Both the pure Crude Oil A w/o emulsion and pure Crude Oil B w/o emulsion had a considerably lower DSD than the 50:50 wt. % Crude Oil A and B mixture emulsion, and larger droplets were then successfully prepared in the w/o crude oil emulsion mixture. The emulsions in the figure below, except one, contained a 30 vol. % water content/cut (wc). The emulsion with the dashed line contained a 15 vol. % wc. Emulsions with 30 vol. % wc had larger droplets than the emulsions prepared with 15 vol. % wc when the same oil phase was used. It is consistent that the droplets prepared using high water contents are larger than the droplets prepared using a lower water content, because there are more total surface area available of the dispersed phase to create droplets using a higher water content.

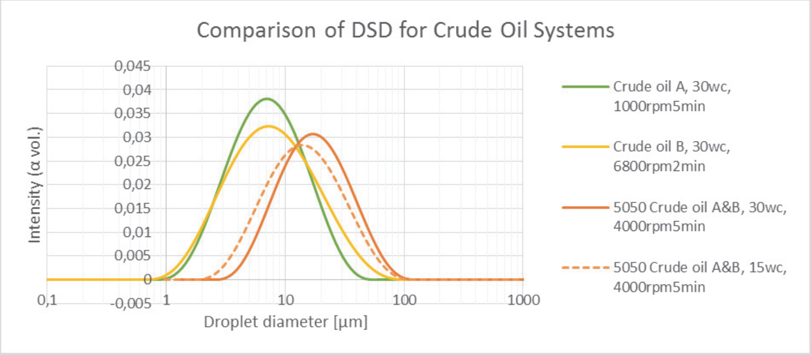


Figure 24: Comparison of the DSD obtained for the w/o crude oil emulsion systems, including pure Crude Oil A emulsions, pure Crude Oil B emulsions, and the 50:50 wt. % Crude Oil A and B mixture emulsions.

Further optimization to reduce the emulsification time was performed since stable emulsions with as low energy input as possible was desired to create optimally sized droplets in the 50:50 wt. % Crude Oil A and B mixture emulsions. Figure 25 below shows the DSD of the 50:50 wt. % Crude Oil A and B mixture emulsions during further determination of the emulsification conditions, where both 2000 and 4000 rpm with different emulsification times were analyzed.

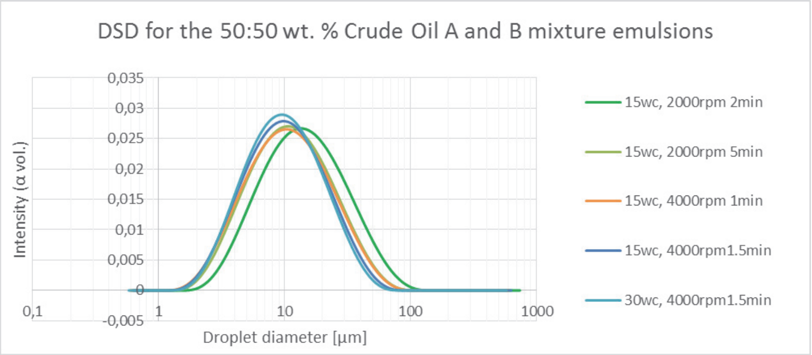


Figure 25: DSD for the 50:50 wt. % Crude Oil A and B mixture emulsions prepared with different emulsification conditions.

The different emulsification conditions created similar droplet sizes. 4000 rpm for 1.5 minutes seemed to be a good compromise in order to achieve stable emulsions and small droplets. By comparing the DSD obtained for the 50:50 wt. % Crude Oil A and B mixture emulsions with the values obtained in the 1st semesters different w/o model oil emulsions stabilized with both particles and surfactants as shown in the figure below (Figure 26), it can be seen that the droplets obtained from the crude oil mixture were similar to the droplets obtained in the different emulsions prepared in the 1st semester. It was therefore chosen to continue with the crude oil mixture, and filtration of these emulsions could be performed.

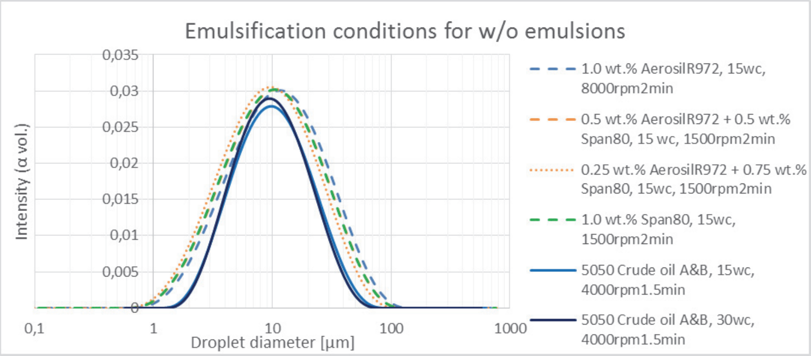


Figure 26: Comparison of the DSD for w/o emulsions. The 50:50 wt. % Crude Oil A and B mixture emulsions compared to the different w/o model oil emulsion systems prepared in the 1st semester.

4.2.3.2 Optimization of the NMR Program for W/O Crude Oil Emulsion

The NMR program was first optimized for the mixture of the different crude oils because it had to be taken into account that this emulsion was containing both a heavy (Crude Oil A) and a medium heavy (Crude Oil B) crude oil. The suppression value, D6 (z-storage time), was optimized using the difference in relaxation time between water and crude oil. This was done by adjusting the z-storage time (D6) to a value that caused no signal from the pure crude oil when the 50:50 wt. % Crude Oil A and B mixture was measured alone (not in an emulsion). The z-storage time delay was set to 650 ms (milliseconds). The relaxation time was also used to separate the oil and water signals in the crude oil emulsions.

The second problem was that the 50:50 wt. % Crude Oil A and B mixture emulsions tended to phase separate quite fast after filtration. Free water was formed in the bottle test tube immediately after filtration, but this water phase was not included in the sample for the NMR experiment after filtration. In some of the samples free water was detected during the NMR experiment. Due to the free water formed it was difficult to separate the bulk water and water in the droplets. As the DSD program considers the whole sample at once, the free water would give a negative effect on the results obtained. In order to have reliable results considering the droplet sizes, extensive improvement and optimization of the NMR program was performed, and the S/V profile program was therefore included.

The S/V profile program was included and optimized for the crude oil emulsions in order to be able to consider the droplet sizes even if free water was formed during measurement, after filtration. The S/V profile showed the average droplet diameter along the height of the sample, and did not consider the whole sample all at once as the DSD program. The free water did not affect the water profile program, and the free water formed in the samples influenced only the numbers considering the droplet sizes obtained by the DSD program.

Root of mean squared displacement (RMSD) separation approach could also have been applied. The RMSD separation approach is affected by turbulence and mobility in the sample, and therefore it would have taken some time to have a stable temperature of the sample and also stable measurements of the water profile. The relaxation time is not affected by the mobility, turbulence in the sample, or the temperature, and the results obtained using the S/V profile program would be more reliable than using an RMSD separation approach.

The S/V profile program was made and added to the NMR program by Geir Sørland. By including the S/V profile, data considering the droplet size of the filtrated crude oil emulsions could be included and analyzed. The numbers based on the DSD program and the S/V profile program could not be compared, and both needed to be handled and analyzed separate, both before and after filtration.

4.2.3.3 Filtration of 50:50 wt. % Crude Oil A and B Mixture Emulsions

Filtration of the 50:50 wt. % Crude Oil A and B mixture emulsions was performed on emulsions prepared at 4000 rpm for 1.5 minutes. Emulsions containing both 15 and 30 vol. % wc were filtrated through filters with porosity number 4, pores at 10-16 µm.

Free water was formed in the bottle test tubes after filtration. The amount of free water formed within three minutes was determined, but this was not included in the NMR sample after filtration. The free water appearance kinetics for the samples after filtration was also observed. For a few samples, free water could also be observed in the filtration flask during filtration, seen as the lighter brown colored liquid in the filtration flask in Figure 27. Free water could also be observed in the NMR tubes after measurement in some of the samples.

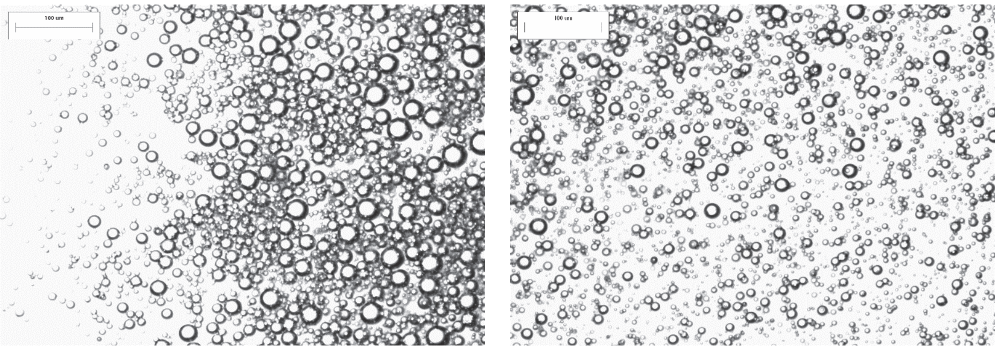
Figure 27: Free water formed in the filtration flask during filtration of the 50:50 wt. % Crude Oil A and B mixture emulsions.

The NMR results and the filtration analysis before and after filtration of the different 50:50 wt. % Crude Oil A and B mixture w/o emulsions are shown in Table 10. The amount of free water observed in the samples within three minutes after filtration are included in the table. The free water was not included for the NMR sample after filtration, which might be due to the small decreases in water content for some of the 15 vol. % wc samples. The 30 vol. % wc emulsions had a small decrease for parallel 3, 4 and 5 considering the water content. The variation in the initial water content could be explained by the uncertainty and sensitivity of the instrument. There were no changes in the droplet sizes during filtration, neither for the 15 vol. % wc emulsions nor the 30 vol.% emulsions, and the droplet sizes were the same for both the 15 and 30 vol. % wc emulsion systems. The mode was 10 µm in diameter, the average diameter was 13 µm obtained by the DSD program and 7 µm obtained by the S/V profile program.

Table 10: NMR results and filtration analysis for the 50:50 wt. % Crude Oil A and B mixture w/o emulsions, emulsified at 4000 rpm for 1.5 minutes, both 15 and 30 vol. % water cut, filtrated through filter no. 4. The table is also including the percentage amount of free water formed during filtration, measured within three minutes after filtration.

	% WC	**Half width [µm] (obtained by DSD program)**		**Mode [µm] (obtained by DSD program)**		**Average [µm]**				**Water content [%]**		**Mass balance, % recovered**	**Filtr. time**	**Free water observed [%]**
						Obtained by DSD program		**Obtained by S/V profile program**						
		Before	After	Before	After	Before	After	Before	After	Before	After			
1	15	4-30	3-33	10	10	14	15	7	6	14	11	86.0	5min 40sec	0
2	15	4-31	4-34	11	11	14	15	7	7	13	9	87.4	5min 30sec	0
1	30	4-25	4-30	10	11	12	15	7	8	26	26	87.3	2min 40sec	0
2	30	4-27	4-30	10	11	13	14	7	8	26	25	87.9	2min 45sec	0.5
3	30	4-25	4-27	9	10	12	13	7	7	25	20	88.1	4min 30sec	0.6
4	30	4-24	4-26	9	9	12	12	7	7	31	25	89.2	3min	0
5	30	4-24	4-29	9	10	12	14	7	8	31	22	89.0	3min 20sec	0.5

In Figure 28 are the microscope images of a 50:50 wt. % Crude Oil A and B mixture emulsion before and after filtration shown. It can be seen that the droplet sizes were approximately the same during filtration. In this figure, it can also be observed that there were less large droplets in the sample after filtration compared to before, which might be due to some droplets breaking during filtration.



a **b**

Figure 28: Microscope images of a 50:50 wt. % Crude Oil A and B mixture emulsion, containing a 30 vol. % water cut, emulsified at 4000 rpm for 1.5 minutes, before (a) and after (b) filtration through filter no. 4. Parallel 1. Magnification 10x. Size mark: 100 µm.

The free water appearance kinetics was observed in the bottle test tubes after filtration. There was little to no free water formed immediately after filtration, but there was formation and appearance of free water over time. The free water formed in the bottle test tube during three hours after filtration was determined and the results are shown in Figure 29. During the first 40 minutes of the bottle test, the majority of free water was formed.

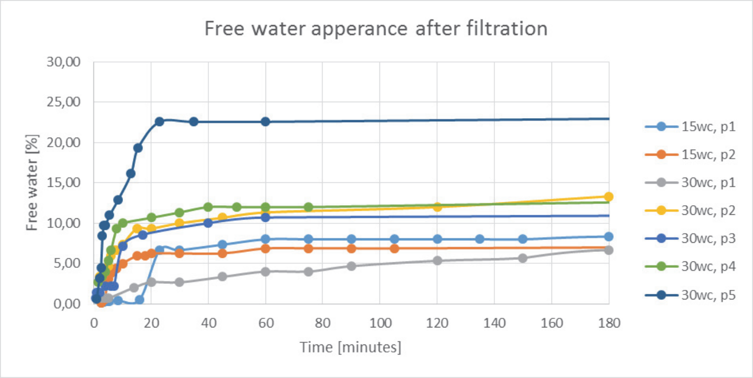
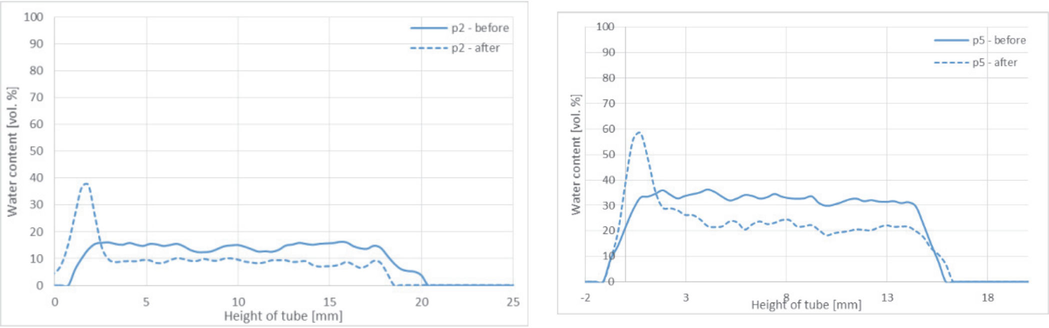


Figure 29: Free water appearance kinetics where free water observed within three hours after filtration of 50:50 wt. % Crude Oil A and B mixture emulsions are analyzed using bottle test.

There was a trend for most of the samples where they produced about 5-10 % free water each during the three hours bottle test. None of the samples produced much water immediately after filtration. This was consistent to the amount of free water observed within three minutes after filtration (included in the table above), which was about 0 % for all the samples.

Parallel 5, which produced about 23 % water during the first 20 minutes (see figure above), did also have the largest decrease in water content from before to after filtration determined by NMR (about a 30 % decrease).

There was a small decrease in water content for the 15 vol. % wc emulsions determined by NMR, although there was no free water formed immediately after filtration. The 30 vol. % wc emulsions had a decrease of about 20 % for parallel 3, 4 and 5, but no decrease for the two first parallels within three minutes after filtration. Examples of the water profile for both 15 and 30 vol. % wc emulsions are shown in Figure 30 a and b respectively.



a **b**

Figure 30: Water profile for w/o crude oil emulsions of a 50:50 wt. % Crude Oil A and B mixture and water, containing a 15 vol. % water cut (a, parallel 2) and a 30 vol. % water cut (b, parallel 5), emulsified at 4000 rpm for 1.5 minutes, before (solid line) and after (dashed line) filtration through filter no. 4.

The decrease in water content during filtration determined by NMR was not completely consistent to the amount of free water observed within three minutes after filtration. But this could be explained by the largest water droplets which were most likely to coalescence, may have sedimented to the bottom of the oil phase in the bottle test tube quite fast after filtration, and were therefore not included in the NMR sample. This might have caused the decrease in water content determined by NMR, and the appearance of free water in the bottle test tube over time.

The S/V profile program was included since free water was observed in some of the NMR samples after filtration, after measurement. The measurement after filtration run for 1-1.5 hours. By looking at a graphical picture of the water profiles for these samples, showing the evolution over time of water content along the height of the NMR tube (Figure 31), there was no free water formed during the first 30 minutes. A small sedimentation of droplets was observed (as yellow/green/light blue in the figure below), but there was no free water formed (should have been darker blue/purple in the figure below). Therefore could the DSD data obtained within 30 minutes after filtration be included in the report, and for that reason both the droplet size data obtained from the DSD program and the S/V profile program were considered.

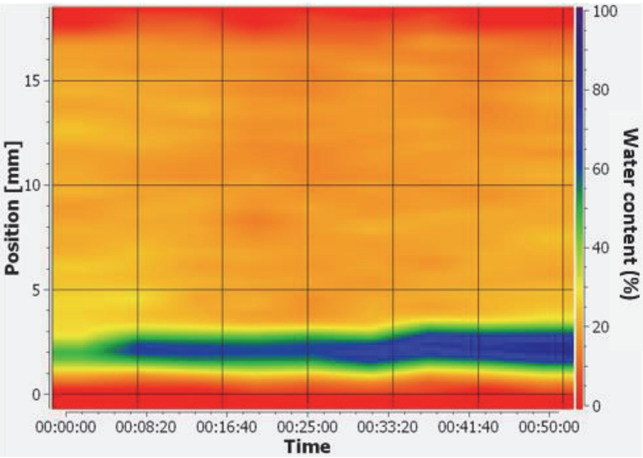


Figure 31: Example of a graphical view of the evolution over time of the water content in a w/o crude oil emulsion of a 50:50 wt. % Crude Oil A and B mixture emulsion, containing a 30 vol. % water cut, emulsified at 4000 rpm for 1.5 minutes, after filtration through filter no. 4. Parallel 2.

There were no changes in droplet sizes during filtration for both the 15 vol. % wc and 30 vol. % wc emulsions, neither considering the half width, mode, average obtained by the DSD program, nor the average obtained by the S/V profile program. The mode and both the average droplet sizes were more or less the same in the different samples from before to after filtration, and therefore it could be concluded that there were no changes during filtration. The mode was 10 µm in diameter both before and after filtration for all the samples. The average diameter obtained by the DSD program was 13 µm both before and after filtration, and 7 µm obtained by the S/V profile program both before and after filtration. This can be seen in Figure 32, which is representing the DSD, both before (solid line) and after (dashed line) filtration, and in Figure 33, which is representing the S/V profile, which shows the average droplet diameter along the height of the sample, both before (solid line) and after (dashed line) filtration.

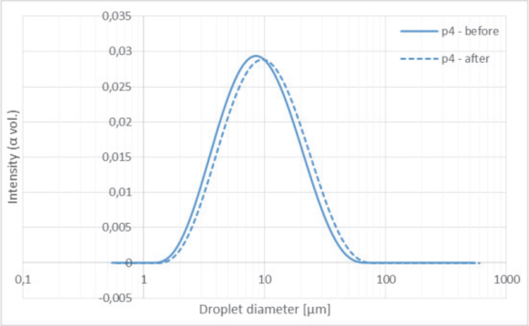


Figure 32: DSD for a w/o crude oil emulsion of a 50:50 wt. % Crude Oil A and B mixture and water, containing 30 vol. % water cut, emulsified at 4000 rpm for 1.5 minutes, before (solid line) and after (dashed line) filtration through filter no. 4. Parallel 4.

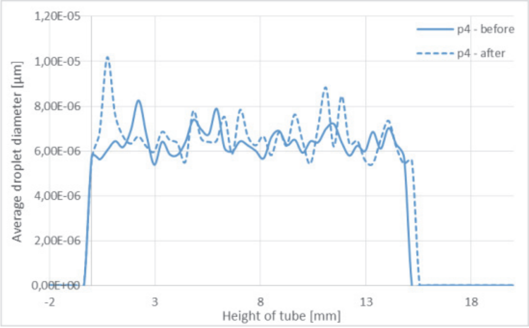


Figure 33: S/V profile for a w/o crude oil emulsion of a 50:50 wt. % Crude Oil A and B mixture and water, containing 30 vol. % water cut, emulsified at 4000 rpm for 1.5 minutes, before (solid line) and after (dashed line) filtration through filter no. 4. Parallel 4.

The crude oil emulsions were initially stable, but as mentioned earlier, there was free water appearance over time after filtration. This might be due to coalescence and breakage of the largest droplets in the samples and was not included in the NMR samples after filtration. The recovered amount for all the samples was about 88 %, which means that most of the sample passed the filters during filtration, but some of the sample might be left on top of the filter. The crude oil emulsions were stabilized by their own stabilizing components such as asphaltenes, naphthenic acids, resins or solid particles. Because the appearance of free water over time, it could be concluded that the crude oil emulsions were destabilized during filtration.

4.3 O/W Emulsions

Two different o/w model oil emulsion systems were prepared: stabilized by surfactants and particles. The aim was to prepare stable emulsions where no free oil was formed, and emulsions with the same droplet sizes as the w/o model oil emulsions prepared in the 1st semester.

4.3.1 O/W Emulsions Stabilized by Surfactants

As mentioned in the experimental section, hexadecane was chosen as the dispersed oil phase in surfactant stabilized o/w model oil emulsions. Primol was chosen initially, but the low mobility and high viscosity was undesirable. Initially both the hydrophilic surfactants AOT and Tween80 were tested, but AOT was discarded because it created too much foam during emulsification.

4.3.1.1 Determination of Emulsification Conditions for Surfactant-Stabilized O/W Emulsions

Several mixing speeds were tested when preparing o/w model oil emulsions of hexadecane and water, stabilized with surfactants, using 0.5 wt. % Tween80. This was in order to get stable emulsions for at least one hour after emulsification and droplets in the same size range as the w/o model oil emulsions prepared in the 1st semester. Mixing speeds of 1500, 2000, 3400 and 4000 rpm were tested, for a duration of five minutes. The DSD for determination of the emulsification conditions are shown in Figure 34. Optimization and calibration of the NMR program was time consuming in order to give reliable results while determining the emulsification conditions.

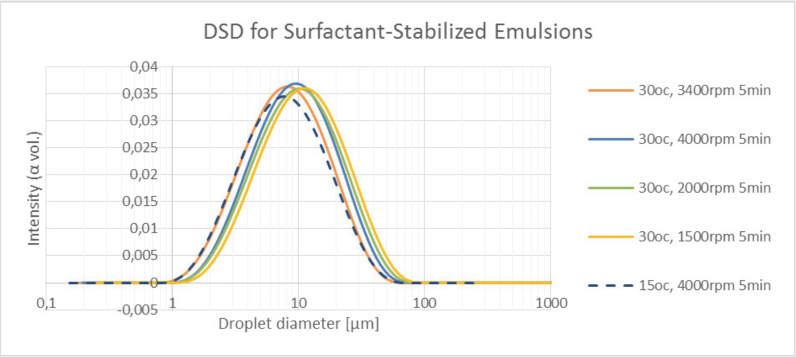


Figure 34: DSD for surfactant-stabilized o/w model oil emulsions of hexadecane and water, stabilized with 0.5 wt. % Tween80, prepared with different emulsification conditions.

The emulsions were stable and no free oil was formed over night. The emulsification conditions created emulsions containing droplets with similar sizes. Slower mixing speed did not create any larger droplets. It was decided to continue with emulsification at 4000 rpm for five minutes, because stable emulsions were formed, and properly emulsified.

By comparing the DSD for o/w model oil (hexadecane) emulsions stabilized with 0.5 wt. % Tween80 with the 1st semesters w/o model oil (primol) emulsions stabilized with 1.0 wt. % Span80, the DSD were quite similar, as seen in Figure 35. The 1st semester w/o model oil emulsions were containing a 15 vol. % water content/cut (wc) and in the 2nd semester, o/w model oil emulsions were containing both 15 and 30 vol. % oil content/cut (oc).

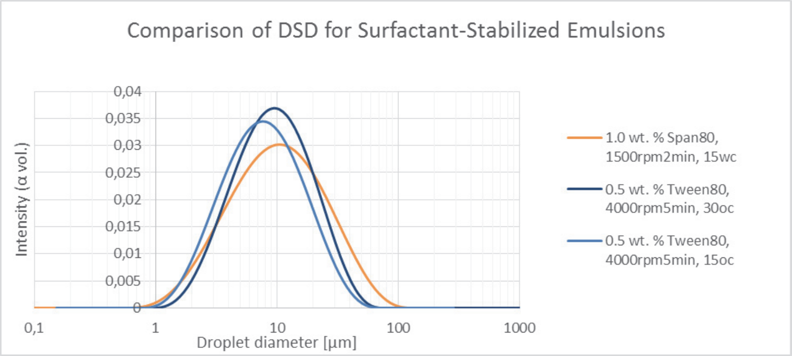


Figure 35: Comparison of the DSD for surfactant-stabilized emulsions (both o/w and w/o), stabilized with 1.0 wt. % Span80 (1st semester) and 0.5 wt. % Tween80.

As can be seen from the figure above, the mode of the DSD for the 30 vol. % oc emulsions was slightly higher than for the 15 vol. % oc emulsions (10 µm vs.7 µm in diameter). This was consistent due to emulsions obtained using a higher oil cut have more dispersed phase to be emulsified in the continuous phase. A greater total surface area were available to create droplets, and therefore were the droplets larger by using a higher content of the dispersed phase.

In order to achieve a larger initial droplet size, a lower concentration of the surfactant was tested. While determining the emulsification conditions for o/w model oil emulsions stabilized with 0.1 wt. % Tween80, it was found that there was insignificant differences using a low surfactant concentration than using a higher concentration. As seen in Table 11, emulsifying emulsions stabilized with 0.1 wt. % Tween80 at 2000 rpm for five minutes gave unstable emulsions which formed free oil immediately after emulsification, but emulsifying at 4000 rpm for five minutes gave a stable emulsion. Comparing the DSD for the emulsion stabilized with 0.1 and 0.5 wt. % Tween80, both emulsified at 4000 rpm for five minutes (Figure 36), it could be concluded that the concentration was not the critical parameter in order to be able to prepare larger droplets. Therefore filtration was not performed for low concentrated surfactant emulsions, only for the 0.5 wt. % Tween80-stabilized emulsions.

Table 11: Emulsification conditions and stability of o/w model oil emulsions stabilized with 0.1 wt. % Tween80.

Emulsification conditions	Stability observations
2000 rpm 5 min	Free oil observed immediately.
4000 rpm 5 min	Stable (no free oil formed within one day).

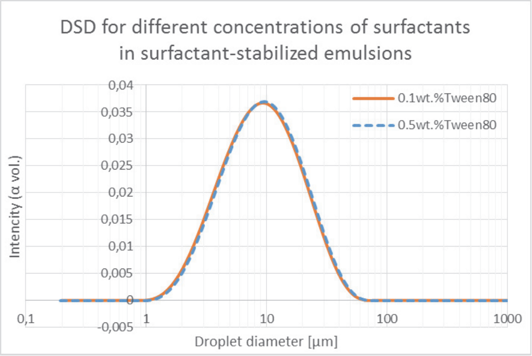


Figure 36: Comparison of the DSD for different surfactant concentrations (0.1 and 0.5 wt. % Tween80) used in surfactant-stabilized o/w model oil emulsions of hexadecane and water, 30 vol. % oil cut, emulsified at 4000 rpm for five minutes.

4.3.1.2 Filtration of Surfactant-Stabilized O/W Emulsions

The NMR results and filtration analysis for filtration of the o/w model oil emulsions of hexadecane and water stabilized with 0.5 wt. % Tween80, before and after filtration through filter with porosity number 4, are shown in Table 12. The surfactant-stabilized emulsions were emulsified at 4000 rpm for five minutes using the Ultra Turrax (both 15 and 30 vol. % oc) and at 2000 rpm for five minutes using the propeller (30 vol. % oc).

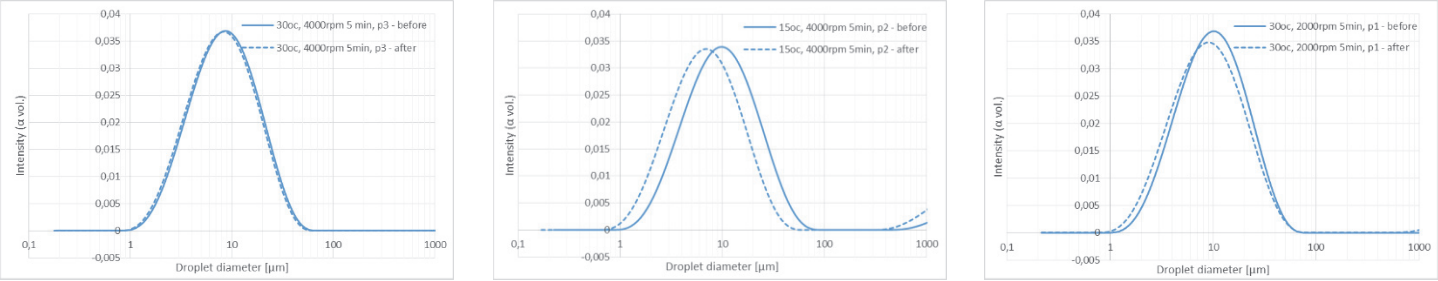
There was no free oil formed in the samples during filtration, but a foam layer could be observed on top of all the samples in the bottle test tubes immediately after filtration. The amount of foam in the samples was calculated the same way the amount of free oil in the samples could be calculated, using equation (8). The amount of foam observed was included in the table below and varied a lot for the different samples. The decrease in oil content for most of the samples during filtration, might be due to the foam layer not being included in the NMR sample after filtration. The droplet sizes did not change during filtration for most of the samples. The mode was ~10 µm in diameter and the average droplet diameter was ~12 µm, both before and after filtration, for the 30 vol. % oc emulsions. The 15 vol. % oc emulsions showed a small decrease in droplet size during filtration: The half width size range of the droplet diameter decreased from 4-30 µm before filtration to 2-20 µm after filtration.

Table 12: NMR results and filtration analysis for the surfactant-stabilized o/w model oil emulsions of hexadecane and water, containing 0.5 wt. % Tween80, both 15 and 30 vol. % oil cut, filtrated through filter no. 4.

	Stirring	**Oil cut [%]**	**Half width [µm]**		**Mode [µm]**		**Average [µm]**		**Oil content [%]**		**Mass balance, % recov.**	**Foam obs. [%]**	**Filtr. time**
			Before	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**			
1	4000rpm 5min	30	3-24	3-21	9	8	11	10	29	22	96.8	9.8	30 sec
2	4000rpm 5min	30	4-25	3-25	10	9	12	11	32	17	94.0	20.0	45 sec
3	4000rpm 5min	30	3-24	3-22	9	9	11	11	29	30	94.2	8.0	45 sec
4	4000rpm 5min	30	4-27	3-24	10	9	13	11	30	18	97.5	21.6	1:30 min
1	4000rpm 5min	15	3-25	3-21	9	8	11	10	12	11	95.7	20.0	15 sec
2	4000rpm 5min	15	4-30	2-18	11	7	14	8	16	11	95.6	20.0	45 sec
3	4000rpm 5min	15	5-39	3-20	15	7	18	9	13	8	94.7	4.0	45 sec
1	2000rpm 5min	30	4-26	3-25	10	9	11	12	29	16	94.7	4.2	40 sec
2	2000rpm 5min	30	4-26	3-20	10	7	12	9	28	13	Not meas.	4.0	40 sec

There was no change in droplet size during filtration using different emulsification conditions, but a small decrease was determined using different oil contents. There was no change in the mode (10 µm) and the average droplet diameter (12 µm) for the 30 vol. % oc emulsions (emulsified at 2000 and 4000 rpm for five minutes) during filtration. Flexible droplets which were able to pass the filter pores were formed.

The 15 vol. % oc emulsions (emulsified at 4000 rpm for five minutes) showed some variations: The mode and the average droplet diameter varied for all the samples. The average droplet sizes were about halved in both parallel 2 and 3, where it decreased from 15 to 7 µm in diameter for parallel 3. The half width of the size range did also show significant decreases during filtration for these samples, since the size range was 4-30 µm before filtration, and decreased to 2-20 µm after filtration. In the 15 vol. % oc emulsion, flexible droplets were also formed, but the largest droplets may have been broken and coalesced causing the decrease in droplet sizes. Examples of the DSD for surfactant-stabilized emulsions before (solid lines) and after (dashed lines) filtration are shown in Figure 37.



a b c

Figure 37: DSD for o/w emulsions of hexadecane and water stabilized, with 0.5 wt. % Tween80, before (solid line) and after (dashed line) filtration through filter no. 4. a) contain 30 vol. % oil cut, emulsified at 4000 rpm for five minutes, parallel 3. b) contain 15 vol. % oil cut, emulsified at 4000 rpm for five minutes, parallel 2. c) contain 30 vol. % oil cut, emulsified at 2000 rpm for five minutes, parallel 1.

The microscope images of the o/w surfactant-stabilized emulsions from the filtration, Figure 38 a and b, show that there were no variations in droplet sizes during filtration for the 30 vol. % emulsions emulsified at 4000 rpm for five minutes. Since no free oil was formed in the bottle test tube, it could be concluded that coalescence had not occurred.

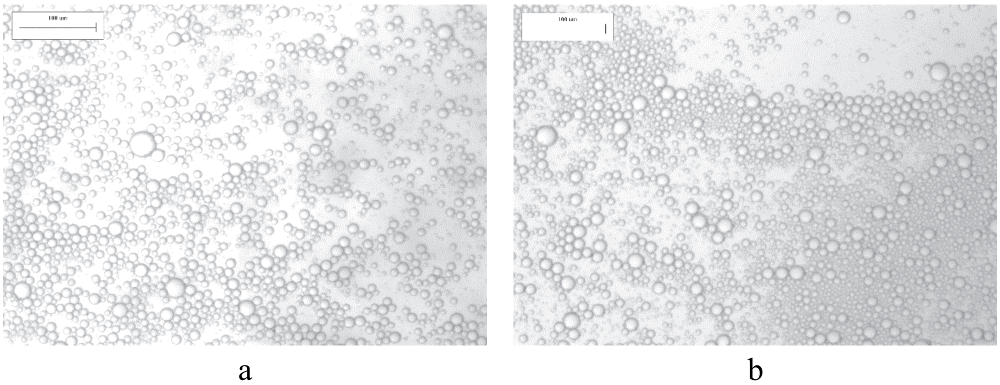


Figure 38: Microscope images of surfactant-stabilized o/w emulsion of hexadecane and water, 30 vol. % oil cut, 0.5 wt. % Tween80, emulsified at 4000 rpm for five minutes, before (a) and after (b) filtration through filter no. 4. Magnification 10x. Size mark: 100 µm.

As mentioned above, there was no free oil formed in the bottle test tube immediately after filtration, but a small foam layer on top of the samples was observed, as shown in Figure 39. This foam was not included in the NMR sample. The foam layers were forming free oil after one day. As seen from the table above, there was a decrease in oil content for all samples, which could be due to presence of oil in the foam layers. The foam was formed due to creaming of the largest oil droplets in the samples, causing coalescence and formation of free oil after one day.

Figure 39: Bottle test tube containing a filtrated surfactant-stabilized o/w model oil emulsion, filtrated through filter no. 4. No free oil formed in the bottle test tubes immediately after filtration, but a foam layer containing larger droplets was observed.

The oil content in the samples was determined from the oil profile analyzed by NMR. An example of an oil profile before and after filtration is shown in Figure 40, which indicates creaming in the samples. Both the 15 and 30 vol. % oc emulsions emulsified at 4000 rpm for five minutes had a decrease of about 30 % in oil content during filtration, and the 30 vol. % oc emulsified at 2000 rpm for five minutes had a 50 % decrease in oil content during filtration. Because of this large decrease in oil content, some of the oil was probably left on top of the filter as well as in the foam layer in the bottle test tube in the different samples. Recovered sample after filtration was ~96 % for all the samples. This might indicate that just a small amount was left on top of the filter, and therefore most of the decreased oil content during filtration was due to the foam layer in the bottle test tube.

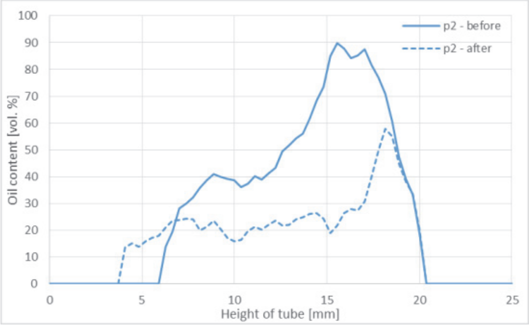


Figure 40: Oil profile for an o/w model oil emulsion of hexadecane and water, stabilized with 0.5 wt. % Tween80, 30 vol. % oil cut, emulsified at 4000 rpm for five minutes, before (solid line) and after (dashed line) filtration through filter no. 4. Parallel 2.

4.3.2 O/W Emulsions Stabilized by Particles

4.3.2.1 Determination of Emulsification Conditions for Particle-Stabilized O/W Emulsions

O/W emulsions stabilized by the hydrophilic silica particles Aerosil R7200 tended to make large droplets during emulsification. The emulsions creamed fast, and were very stable, i.e. no free oil was formed within one day. The average droplet diameter of o/w particle-stabilized emulsions obtained with different oil phases and emulsification conditions determined by microscopy are shown in Table 13. Average droplet diameters obtained using microscopy are number based, where at least 200 droplet diameters were measured for each of the different emulsification conditions using the microscope computer software Image-Pro Plus 5.0.

Table 13: Determination of emulsification conditions for particle-stabilized o/w model oil emulsions based on microscope imaging.

Oil phase	Emulsification conditions	Average droplet diameter [µm]
Primol	4000 rpm 5 min	126 µm
	8000 rpm 2 min	118 µm
	8000 rpm 5 min	53 µm
	18000 rpm 2 min	44 µm
	22000 rpm 2 min	33 µm
Hexadecane	8000 rpm 5 min	34 µm
	20000 rpm 2 min	35 µm
	24000 rpm 2 min	33 µm

The large droplets were first observed using microscope. Emulsified at 18000 rpm for two minutes using primol as oil phase, emulsions stabilized with 0.25 wt. % Aerosil R7200, both 15 and 30 vol. % oc, had most droplets ~50 µm in diameter. By increasing the particle concentration to 0.5 wt. % Aerosil R7200, most of the droplets observed in the microscope were ~30 µm in diameter using primol as oil phase. As mentioned earlier, primol was discarded because of the low mobility and high viscosity, and therefore it was continued to work with hexadecane instead.

By preparing particle-stabilized hexadecane emulsions at maximum speed of the Ultra Turrax (24000 rpm) for two minutes, large droplets (~30 µm in diameter) were observed using microscope, as seen in Figure 41. The DSD obtained by the NMR program was not adequate. A mode of 26 µm in diameter and an average droplet diameter of 19 µm could be indicated after some adjustments of the NMR program, while using the microscope an average droplet diameter of 33 µm was obtained. Droplet sizes obtained by NMR should always be larger than obtained by microscopy, since the droplet sizes obtained by NMR are volume based, and number based obtained by microscopy. Because the opposite was observed, this was not completely consistent. The NMR program was made for smaller droplets than the particle-stabilized emulsions observed by microscope, and therefore optimization of the program was needed in order to continue and have reliable results.

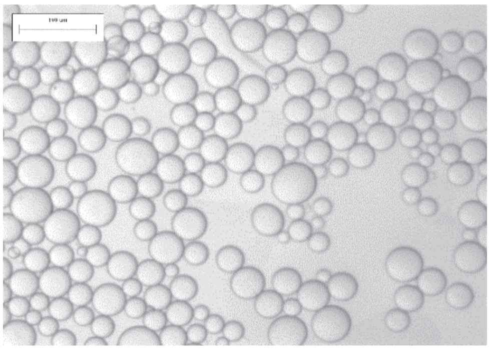


Figure 41: Microscope image of a particle-stabilized o/w model oil emulsion of hexadecane and water, containing 30 vol. % oil cut hexadecane, stabilized with 0.5 wt. % Aerosil R7200, emulsified at 24000 rpm for two minutes. Magnification 10x. Size mark: 100 µm.

4.3.2.2 Optimization of the NMR Program for O/W Particle-Stabilized Emulsions

As mentioned above, the particle stabilized o/w emulsions tended to contain large droplets even if the emulsions were prepared at maximum mixing speed of the Ultra Turrax. The emulsions were stable (no free oil was formed), and because of the large droplets, creaming took place in the samples quite fast after preparation. The results of the DSD obtained by the NMR were spread, and the accuracy was not sufficient. NMR results showed both smaller and larger droplets than observed in the microscope by just adjusting the suppression gradients and the maximum strength of the gradients, before concluding to fully optimize the NMR program. The NMR program was originally designed to measure DSD of emulsions with average droplet sizes of ~10 µm in diameter. In order to optimize the NMR program to be able to detect droplets in the real size range, the bulk diffusion coefficient for the phase found as droplet, the calibration values, suppression gradients and observation time needed to be considered.

The measured diffusion coefficient for the emulsions were higher than it should be, and the measured diffusion resulted in large droplet sizes, which were not observed in the microscope. This could be due to the water in the emulsion had not been suppressed properly, making water contribute in the diffusion coefficient obtained for the emulsion. Another reason for the high diffusion coefficient measured could be that the diffusion measurement was not convection compensating, which was needed due to an accelerated creaming process in the emulsions.

Several tests were performed in order to find out if the water was participating. Insignificant differences were obtained in the diffusion coefficient during the tests, and therefore it could be concluded that the water did not contribute to the high diffusion coefficient for the o/w hexadecane emulsions. If the diffusion coefficient for bulk hexadecane was set too low in the NMR program (~3.8 e-10 m^2/s), the large droplets in the samples and the noise in the experiment would result in droplet sizes much larger than the actual droplet size.

Because of convection and movements in the bulk hexadecane during calibration, and also movements due to the creaming process in the emulsions, the bulk diffusion coefficient for hexadecane was difficult to obtain. To be able to get reliable results, the diffusion coefficient for the bulk hexadecane was crucial, and had a massive impact on large droplets. The large shifts in the position of the DSD obtained was because the diffusion coefficient for the emulsion, D, was too close to the bulk diffusion coefficient for the hexadecane droplets, (D_0). This may also have caused disturbance in the measurements. At a given observation time, t, there was little variation in the measured diffusion coefficient for the emulsion from the bulk diffusion coefficient for the droplets. By increasing the observation time, a larger difference in the diffusion coefficients would be obtained, as shown in Figure 11 in the theory part, and the results would then be more realistic and reliable.

Because large droplets in the emulsions, a small change in the diffusion coefficient for the droplets in the emulsion would result in a large change in the average droplet size obtained by the NMR program. By increasing the observation time from 5 to 50 ms, there would be more signal to work with and the resolution improves. A longer observation time would result in:

- That we are further out on the observation time axis (x-axis) in Figure 11 in the theory part, chapter 2.4.3.1 – NMR, Droplet Size Distribution (DSD).
- A smaller diffusion coefficient for the emulsions than for the bulk diffusion.
- Variations due to noise in the diffusion measurement would be less important, and the DSD measurement would be more stable.

The diffusion coefficient for the bulk hexadecane, D_0, was then set to 4.0 e-10 m^2/s. When the emulsion droplet sizes were ~30 μm in diameter, the increase of the observation time had to be changed to acquire the same accuracy as with emulsions of smaller droplets. The mode and the average droplet size obtained by the optimized NMR program seemed more reliable, because a mode of 29 μm in diameter and an average of 34 μm in diameter was obtained. These numbers were more similar to the number based droplet sizes obtained by microscopic analyzing. Several tests of the new program was performed, and it could be concluded that the optimized program was reliable, and the filtration of the particle-stabilized emulsion could be performed.

4.3.2.3 Filtration of Particle-Stabilized O/W Emulsions

Filtration was performed on o/w model oil emulsion of hexadecane and water stabilized with 0.5 wt.% Aerosil R7200, 30 vol. % oil cut, emulsified at 24000 rpm for two minutes. The emulsions were filtrated through filter with porosity number 3. The filter was clogged during filtration, and therefore could only the data from before the filtration be obtained by NMR. It was not possible for the NMR to analyze the sample after filtration because there were no emulsion to analyze, almost only water was left in the filtration flask after filtration. The NMR results from before filtration of the o/w particle-stabilized emulsions, are shown in Table 14. Large droplets with an average droplet diameter of 34 μm were indicated. The recovered mass was about 60.9 % for both parallels, and almost no free oil was observed in the bottle test tube after filtration.

Table 14: Filtration analysis obtained by NMR for the particle-stabilized o/w model oil emulsions of hexadecane and water, containing 0.5 wt. % Aerosil R7200, 30 vol. % oil cut, emulsified at 24000 rpm for two minutes, filtrated through filter no. 3. n/a: not applicable.

	Half width [μm]		**Mode [μm]**		**Average [μm]**		**Oil content [%]**		**Mass balance,% recovered**	**Free oil observed [%]**	**Filtration time**
	Before	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**			
1	9-71	n/a	27	n/a	34	n/a	26	n/a	61.1	0	3 min 30 sec
2	9-73	n/a	28	n/a	34	n/a	24	n/a	60.7	3.33	3 min

Examples of the DSD and the oil profile for particle-stabilized emulsions before filtration, for the two parallels, are shown in Figure 42 and Figure 43. As mentioned earlier, the droplets were large compared to the previous w/o model oil emulsions from the 1st semester or the surfactant-stabilized o/w model oil emulsions. The droplet sizes were similar for both the parallels as shown in both the table above and the DSD figure below. The oil profiles were also similar for the two parallels. The oil profiles indicated that there were fast creaming in the samples because there were no oil at the bottom of the NMR tubes (at 0 mm in the oil profile). The oil contents obtained by NMR for the two parallels divided a little from the calculated oil content for the samples (32 vol. % oil), and the difference from 32 vol. % to 25 vol. % could be due to the uncertainty and sensitivity of the NMR instrument.

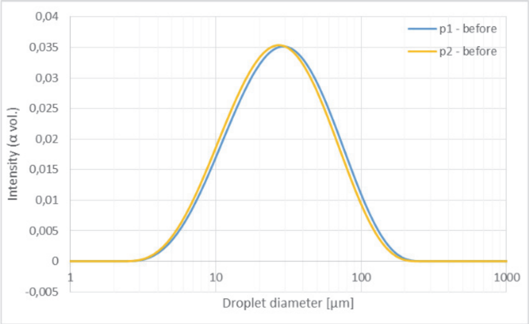


Figure 42: DSD for o/w model oil particle-stabilized emulsions of hexadecane and water emulsions, containing 30 vol. % oil cut, stabilized with 0.5 wt. % Aerosil R7200, emulsified at 24000 rpm for two minutes. Two parallels: Parallel 1 and 2, before filtration.

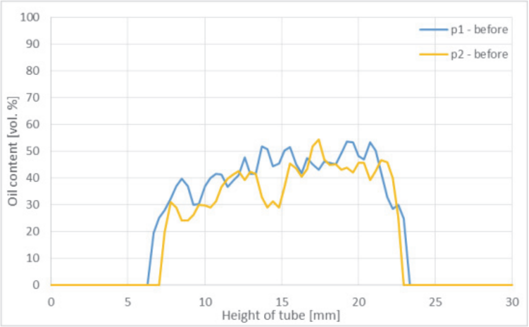


Figure 43: Oil profile for the o/w model oil particle-stabilized emulsions of hexadecane and water emulsions, containing 30 vol. % oil cut, stabilized with 0.5 wt. % Aerosil R7200, emulsified at 24000 rpm for two minutes. Two parallels: Parallel 1 and 2, before filtration.

After filtration it was not possible to analyze the filtrate by the NMR program. Almost all the particles were left on top of the filter forming a 1 cm thick filter cake, as shown in Figure 44. Most of the oil phase was also left on top of the filter together with the particles. Visual observations of the filtrate did barely show any emulsion or oil in the samples. The filter cake was a concentrated dispersion of particles in oil. A microscope image of the filter cake is shown in Figure 45. No droplets were shown in the microscope images, and it could be concluded that the droplets in the emulsion have been broken and left on top of the filter during filtration. The rigid droplets in the emulsions prepared may have flocculated, were then not able to pass the filter, and broke during filtration.

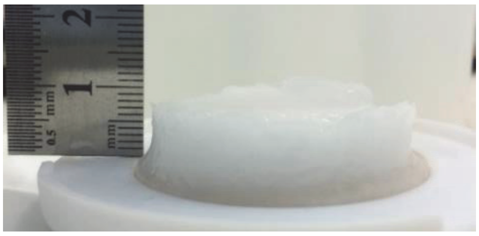


Figure 44: Gel layer formed on top of the filter when filtrating particle-stabilized o/w model oil emulsions of hexadecane and water, containing 30 vol. % oil cut, stabilized with 0.5 wt. % Aerosil R7200, emulsified at 24000 rpm for two minutes.

Figure 45: Microscope image of the gel formed on top of the filter when filtration of particle-stabilized o/w model oil emulsions of hexadecane and water, containing 30 vol. % oil cut, stabilized with 0.5 wt. % Aerosil R7200, emulsified at 24000 rpm for two minutes. No existing droplets can be seen. Magnification 10x. Size mark: 100 μm.

4.3.2.4 Filtration of Particle Dispersions

The hydrophobic particles Aerosil R972 were used to stabilize w/o model oil emulsions of primol and water in the 1st semester using 0.25 and 1.0 wt. % Aerosil R972. Because the hydrophilic particles Aerosil R7200 used in this semester to stabilize o/w model oil emulsions of hexadecane and water, clogged the filter using just 0.5 wt. % Aerosil R7200 in the emulsions, it would be interesting to have an indication about how fast the hydrophobic particles Aerosil R972 would clog the filter. Particle dispersions of Aerosil R972 in primol were prepared and filtrated in order to see how fast the particles would clog the filter. This was done in order to observe how the particles were stabilizing the emulsions and how they behaved during filtration.

In order to have an indication of the particle size range in the hexadecane and primol dispersions, microscopy was performed first. The particles could not be seen after sonication in hexadecane or primol, and it could be concluded that the particles were smaller than 1 μm.

Therefore the particles sonicated in hexadecane were analyzed by the nano zetasizer, but the particles were too polydisperse to give good results.

Filtration through filter 3 was performed on dispersions of different concentrations of particles in primol. Filtration time for the dispersions of the different particle concentrations were determined. The results are shown in Figure 46 and in Table 15. Filtration of the two samples with the highest concentrations, 7 and 10 wt. % particles, were aborted after 1 and 1.5 hours respectively.

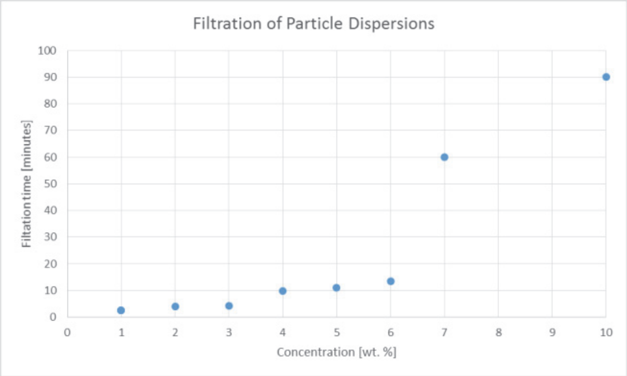


Figure 46: Filtration of particle dispersions in primol where the filtration time is given as a function of the particle concentration.

Table 15: Filtration data of the particle dispersions.

Concentration [wt. %]	Filtration time [minutes]	% recovered
1	2,5	94,7
1	2,5	94,0
2	4	93,3
3	4,25	92,0
4	9,75	93,6
5	11	90,8
6	13,5	89,3
7	60,1	37,5
10	90	9,0

The sonication gradually became difficult as the particle concentration increased. The highly concentrated particle dispersions were very thick after sonication for some hours, and the 10 wt. % particle dispersion was almost like a highly viscous gel before filtration. As can be seen from the table above, the recovered amount was small for 7 and 10 wt. % particle dispersions. This was due to residue left behind during filtration. A gel layer was formed on top of the filters which prevented the filtration, and therefore the filtrations were aborted.

As seen from the graph in the figure above, the graph made a huge leap in the filtration time. The critical concentration for clogging of the filter was between 6 and 7 wt. % particles. Using 6 wt. % particles there was no gel layer formed on top of the filter, only small, gel like droplets were observed (see Figure 47), with diameters ~0.5 cm. Using higher particle concentration in the dispersions, a gel layer covering the entire surface of the filter was formed. As mentioned above, the filtration was then aborted because nothing was able to pass the filters any more.

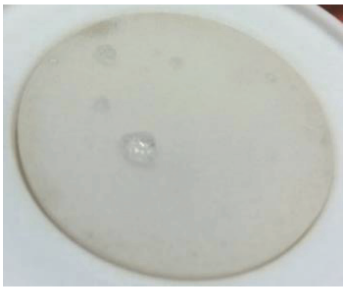


Figure 47: Gel droplet formed on top of filter no. 3 during filtration of a low concentrated particle-primol dispersion.

4.4 Overview of 1st and 2nd Semester's Filtration Results of O/W and W/O Emulsion Systems

In this chapter a qualitative comparison of the stability during filtration of the different emulsion systems studied in both the 1st and 2nd semester are presented. The table below (Table 16) gives an overview of the most important highlights and differences in the systems. The systems were prepared in order to have the same initial droplet sizes before filtration. Comparing the different emulsion systems, smaller droplet sizes were obtained in the w/o Crude Oil A emulsion, and larger droplet sizes were obtained in the o/w hexadecane emulsions stabilized with Aerosil R7200.

Table 16: Observations during filtration of different o/w and w/o emulsion systems stabilized by different stabilizing components. Coalescence during filtration was measured within three minutes after filtration.

Type	Oil component	Stabilization component	Coalescence during filtration	Observations
w/o	Primol	Particles, Aerosil R972	Free water formed.	Droplet size and water content halved.
		Surfactants, Span80	No free water formed.	No changes in droplet size or water content.
		0.5 wt. % Aerosil R972 + 0.5 wt. % Span80	No free water formed.	No changes in droplet size or water content.
		0.25 wt. % Aerosil R972 + 0.75 wt. % Span80	No free water formed.	No changes in water content, but small decrease in droplet size.
	Crude Oil A	Crude Oil A components	Free water formed.	No change in droplet size. A small decrease in water content for some samples. Smaller initial droplets than in the other systems.
	50:50 wt. % Crude Oil A and B	Crude Oil A and B components	No free water formed. Destabilization over time after filtration.	No change in droplet size. A slight decrease in water content for most of the samples. Free water appearance over time after filtration.
o/w	Hexadecane	Surfactant, Tween80	No free oil formed.	Foam layer on top of the samples forming free oil after one day. Small decrease in droplet size for some samples. Oil content almost halved.
		Particles, Aerosil R7200	Almost no oil present after filtration (left on top of the filter), just water.	Filter cake of 1 cm formed on top of the filter, all particles were left here. Larger initial droplets than in the other systems.

Considering the surface stabilizing components, the particles were quite different from the surfactants. The difference between the surfactant- and particle-stabilized emulsions can be linked to the rigidity and flexibility of the interfaces. Particles have a tendency to flocculate, and it can be assumed that the particles formed rigid interfaces where the majority of droplets broke during filtration of the emulsions. It can also be assumed that the surfactants formed flexible droplets which passed the filter pores with a greater efficiency during filtration.

In the w/o surfactant-stabilized emulsions there were neither changes in droplet size nor water content: The w/o emulsions were stable during filtration, where no free water was formed. Since there were no changes in droplet size during filtration of surfactant-stabilized w/o emulsions, it could be assumed that flexible droplets which were able to pass the filter pores were formed. The o/w surfactant-stabilized emulsions showed a different trend. There was no free oil formed within one day, only a foam layer on top of the samples. The oil content was halved for several of the samples after filtration. As mentioned in 4.3.1.2 – Filtration of Surfactant-Stabilized O/W Emulsions, the decrease in oil content in the o/w emulsions could be due to large droplets creaming and forming a foam layer, which was not included in the NMR sample after filtration. In the samples containing 30 vol. % oil content, the droplet size did not change during filtration, neither prepared at 2000 nor 4000 rpm for five minutes, which indicated that flexible droplets which were able to pass the filter pores were formed. Some of the samples containing 15 vol. % oil content, showed a small decrease in droplet size which could be due to the creaming of the largest droplets in the sample as described above.

While preparing particle-stabilized emulsions, sonication of the hydrophilic silica particles Aerosil R7200 was proved to be more challenging than sonication of the hydrophobic silica particles Aerosil R972. This could be explained as Aerosil R7200 has a higher tendency to flocculate than Aerosil R972 in their respective media. Particle dispersions of hydrophobic silica particles Aerosil R972 in primol were prepared in order to get an indication of the critical concentration for when they would clog the filter during filtration. Particle dispersions of Aerosil R972 clogged the filter using 7 wt. % particles.

The different particle-stabilized o/w and w/o emulsion systems showed two different limiting cases. A lot of free water was formed in the w/o emulsions stabilized with both 0.25 and 1.0 wt. % of the hydrophobic silica particles Aerosil R972. Droplet sizes and water content was halved in the w/o emulsions during filtration. This was due to several rigid droplets formed were unable to pass the filter pores, and broke during filtration forming free water. The o/w emulsions systems showed another situation. Using 0.5 wt. % of the hydrophilic silica particles Aerosil R7200, the filter was clogged during filtration, within three minutes. The initial droplets before filtration were large. The o/w emulsion broke during filtration, and almost only water went through the filter. The dispersed oil phase was left on top of the filter together with the particles. The microscope images of the filtration cake (Figure 45) showed that there were no droplets left on top of the filter and a gel was formed. The gel was a dispersion of particles in oil. It could be concluded that the hydrophilic silica particles Aerosil R7200 formed larger droplets in the continuous phase than the hydrophobic silica particles Aerosil R972, which lead to more coalescence and destabilization during filtration of emulsions.

Crude oil emulsion filtration was performed on two different w/o crude oil emulsion systems. Both the Crude Oil A emulsions and the 50:50 wt. % Crude Oil A and B mixture emulsions contained initially small droplets (7 and 10 μm in diameter respectively) compared to the filter pores of the different filters (10-16 and 16-40 μm). During filtration there was no change in droplet sizes for both the crude oil systems. A significant amount of free water was formed in some of the Crude Oil A emulsions during filtration, and a decrease in water content was determined by NMR.

Unlike Crude Oil A emulsions, there was no free water formed immediately after filtration of the 50:50 wt. % Crude Oil A and B mixture emulsions, though there was a decrease in water content during filtration determined by NMR. The free water appearance kinetics stated that the crude oil emulsions were destabilized after filtration, as ~5-10 % free water was formed in the bottle test tube during the first hour after filtration. The difference in the results obtained by NMR and the bottle test tube were not entirely comparable, but could be explained by the largest water droplets which were most likely to coalescence, may have sedimented to the bottom of the oil phase in the bottle test tube quite fast after filtration, and were therefore not included in the NMR sample. This might have caused the decrease in water content determined by NMR, and the appearance of free water in the bottle test tube over time.

Crude oil emulsions were stabilized by their own crude oil components. The w/o crude oil emulsions showed the same trend as the w/o particle-stabilized emulsions: The emulsions were destabilized during filtration where the droplets coalesced and formed free water. The behavior of crude oil emulsions was closer to particle-stabilized emulsions than surfactant-stabilized emulsions. Since the surfactant-stabilized emulsions, both the o/w and w/o emulsion systems, were not destabilize within one day after filtration, it could be stated that the surfactants were better stabilizing components than both the particles and the natural indigenous components in crude oil while filtrating/flowing through porous media.

4.5 Multiple Emulsions

Multiple (double) o/w/o model oil emulsions containing primol and water were made using the two-step method as introduced and described in the theory part, chapter 2.2.2 – Multiple Emulsions, and in the experimental chapters: 3.1.3 – Multiple Emulsions and 3.1.4 – Emulsification. The double emulsions were stabilized using the surfactants Tween80 and Span80, and analyzed using microscope. The inner o/w emulsion, Emulsion I, was prepared with a 30 vol. % oil cut, and stabilized with 1.0 wt. % Tween80. The double (outer) emulsion, Emulsion II, was containing 30 vol. % of Emulsion I, and stabilized with 1.0 wt. % Span80.

4.5.1 Determination of Emulsification Conditions for Double Emulsions

Using the two-step method, the inner o/w model oil emulsion, Emulsion I, was prepared first, using the Ultra Turrax. Several emulsification conditions were tested in order to create an emulsion with small droplets. The emulsification conditions tested when preparing Emulsion I are described in Table 17. The limitation was the foam produced during emulsification.

Table 17: Emulsification conditions for preparation of Emulsion I, the inner emulsion in double emulsions.

Emulsification conditions for emulsion I	**Stability**
24000 rpm 30 sec	Foam was coming out of the vial. Emulsification was aborted.
10000 rpm 1:10 min	Foam was coming out of the vial. Emulsification was aborted.
4000 rpm 10 min	Small droplets formed, most of ~5-30 µm in diameter.
6000 rpm 10 min	Small droplets formed, most of ~4-25 µm in diameter, average diameter ~10 µm. Great amount of foam produced the last minutes.
6000 rpm 5 min	Small droplets formed (most of ~4-20 µm in diameter, average diameter ~10 µm) and small amount foam produced.

Because higher emulsification conditions created too much foam, 6000 rpm for five minutes was chosen as the emulsification conditions for Emulsion I. Most droplets were in the size range of 10-15 µm in diameter, but there was also both smaller (~4 µm in diameter) and larger (~45 µm in diameter) droplets observed in Emulsion I, emulsified at 6000 rpm for five minutes. A microscope image of Emulsion I is shown in Figure 48.

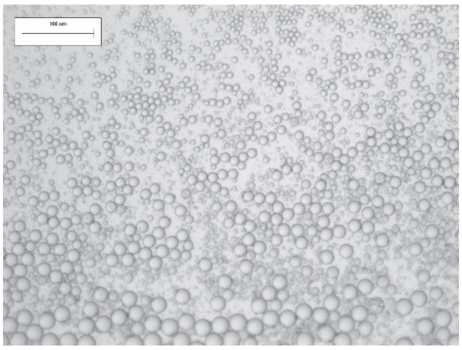


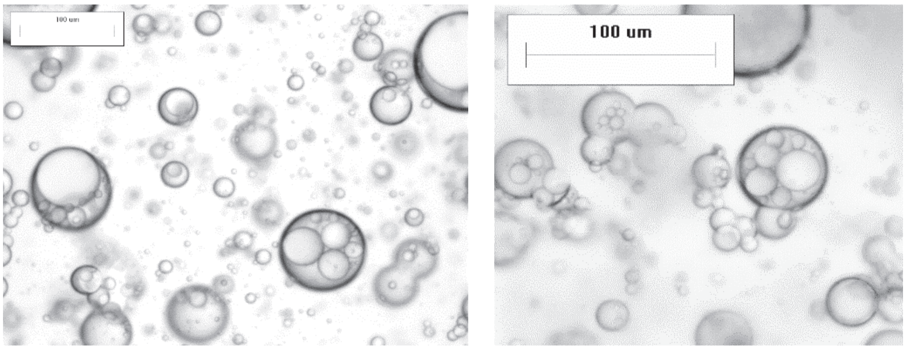
Figure 48: Microscope image of an o/w model oil emulsion of primol and water, containing 30 vol. % oil cut, stabilized with 1.0 wt. % Tween80, emulsified at 6000 rpm for five minutes. Magnification 10x. Size mark: 100 µm.

The outer (second) emulsion, Emulsion II, was prepared with different emulsification conditions than the inner emulsion. The emulsification conditions tested for emulsion II are described in Table 18. The limitation was to produce stable double emulsions, and not destroy the inner oil droplets. The emulsification was therefore performed gently using the propeller.

Table 18: Emulsification conditions for preparation of Emulsion II, the double emulsions.

Emulsification conditions for emulsion II	**Stability**
250 rpm 2 min	Double emulsion formed. Might be a too intense emulsification.
Three step program of 5 minutes: 50 rpm 1 min 100 rpm 3 min 150 rpm 1 min	Double emulsion formed. 50 rpm: Too little emulsification: Almost no mixing. 100 rpm: Difficult to mix the bottom and the top layer of the emulsion. 150 rpm: Top and bottom layer mixed.
125 rpm 5 min	Well mixed double emulsions formed.

Double emulsions were prepared successfully. The size range obtained of the droplets in the different emulsions varied. When preparing the double emulsion, Emulsion II, the outer droplets obtained were in the size range of 20-60 µm in diameter, but most of the outer droplets were ~35 µm. The droplets in the inner emulsion of Emulsion II varied depending on the size of the outer droplet. Many of the droplets in the inner emulsion of Emulsion II were ~3-10 µm in diameter. The droplet sizes in Emulsion I and in the inner droplets in Emulsion II were consistent because the droplet sizes of the inner emulsions in Emulsion II were in the same size range as the droplets created in Emulsion I. Examples of microscope images of double emulsions prepared are shown in Figure 49 a and b.



a b

Figure 49: Microscope images of double o/w/o emulsions of primol and water, 30 vol. % oil cut and 30 vol. % emulsion, stabilized with 1.0 wt. % Tween80 and 1.0 wt. % Span80, emulsified at 125 rpm for five minutes. Figure a) is taken with magnification 10x and figure b) is with magnification 20x. Size mark: 100 μm.

As shown in the figures above, the inner oil droplets are confined within the water droplet in the outer oil phase. When observing the double emulsions in the microscope, the outer emulsion/water droplets move around, and the oil droplets inside moves within the water droplet.

4.5.2 Filtration of Double Emulsions

Filtration of double emulsions was performed. The double emulsions were filtrated through filter with porosity number 3 in order to see what happened to the double emulsions during filtration. The filtration analysis of the filtration time and the recovered amount based on the mass balance for the double emulsions during filtration are shown in Table 19.

Table 19: Filtration analysis of double o/w/o emulsions of primol and water, containing 30 vol. % oil cut and 30 vol. % emulsion, stabilized with 1.0 wt. % Tween80 and 1.0 wt. % Span80, emulsified at 125 rpm for five minutes, filtrated through filter no.3.

Sample	% recovered	Coalescence	Filtration time
1	92.1	No free oil/water formed	3 min
2	92.6	No free oil/water formed	4 min 30 sec
3	92.8	No free oil/water formed	5 min 30 sec

The double emulsions were analyzed using the microscope while preparing Emulsion I, Emulsion II, and after filtration of Emulsion II. After filtration, there was no sign of double emulsions, as shown in Figure 50. Two different areas/zones were observed, containing clusters/flocs and single droplets. The clusters could be seen as the darkest spots in the figure below, circled by a dashed red line. The single droplets were spread around, some circled by a solid red line.

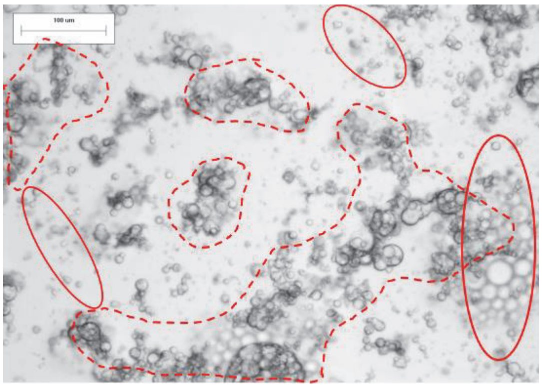


Figure 50: Microscope image of a filtrated double o/w/o emulsion, showing both the different zones: single droplets and clustered droplets. Magnification 10x. Size mark: 100 µm.

The different zones formed after filtration were due to the double emulsion breaking during filtration. No free oil or water was formed even though droplets have been broken. Pictures indicating both the zones are shown in the figures below.

Figure 51 shows single droplets. The droplets are separated and not clustered onto each other. The smallest droplets in the left lower part of the figure were in the range of ~8-38 µm in diameter, and the large droplets in the figure were in the range of ~60-130 µm in diameter.

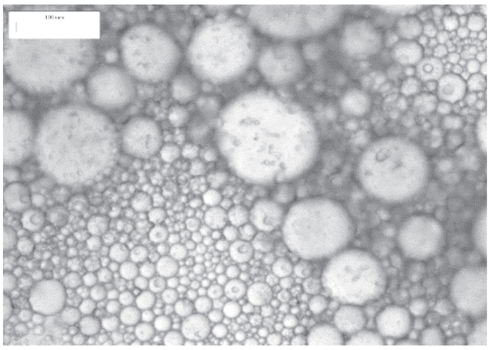


Figure 51: Microscope image of a filtrated double o/w/o emulsion, showing the single droplet zone. Magnification 10x. Size mark: 100 µm.

Figure 52 shows the clusters. The droplets in the clusters looked like clusters of single droplets and not double emulsions because while adjusting the focus on the microscope, it looked like the droplets also clustered in layers on top of each other. The figure also shows that there are some single droplets in between the large clusters.

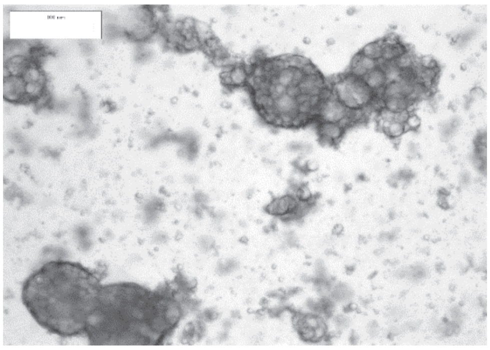


Figure 52: Microscope image of a filtrated double o/w/o emulsion, showing the zone of clustered droplets. Magnification 10x. Size mark: 100 µm.

A good example of the boundary between the zones of single droplets and clusters is shown in Figure 53, where the boundary line is clearly shown. The size range of the droplets inside the cluster were ~10-60 µm in diameter.

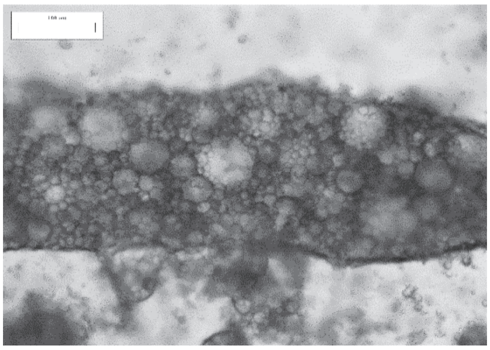


Figure 53: Microscope image of a filtrated double o/w/o emulsion, showing the distinction between the zones of single droplets and clustered droplets. Magnification 10x. Size mark: 100 µm.

4.5.3 Interpretation of Double Emulsions

In order to be able to differ the oil and water phases while using microscopy, the double emulsions were dyed. Several dyes were tested, but with no conclusion.

The water soluble dyes Methylene Blue and Congo Red were tested first on the inner emulsion, Emulsion I. Several concentrations of both were tested. Emulsions dyed with 1 ppm Methylene Blue was not a sufficient amount of dye to get a color contrast, and the concentration was increased to 10 ppm. No color contrast in the emulsions were observed in the microscope, and therefore Congo Red was tested. Emulsions dyed with both 10 and 100 ppm were prepared, but no red color contrast was observed. Using a water soluble dye to dye o/w emulsions (o/w/o emulsions) might not be suited because only the outline of the emulsions would be dyed blue or red in this case, and this was difficult to observe. In o/w/o emulsions, an oil soluble dye would probably work better because the droplet would contain color, not just the outline.

Sudan III was a red oil soluble dye. A stock solution of 1000 ppm Sudan III in primol was made. Emulsion I dyed with 10 ppm was prepared and analyzed, but no red droplets were observed using the microscope. But when observing dyed emulsion in the microscope, it seemed like some double emulsions also have been formed, where modification of the interfacial properties might have happened. The double emulsions were first found as darker (grey) droplets, as seen in the left bottom corner in Figure 54.

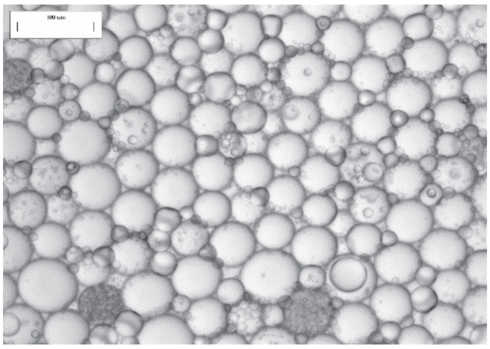


Figure 54: Emulsion I (inner/single emulsion) dyed with Sudan III. Magnification 10x. Size mark: 100 µm.

5. Conclusion

In this project, the stability during filtration through porous media of different o/w, w/o, and o/w/o emulsion systems were determined by NMR, microscopy and bottle testing. Emulsions were stabilized with different surface active components, such as surfactants, particles, and natural indigenous crude oil components. The results were compared to the w/o model oil emulsion systems studied during the 1st semester's specialization project.

The two different surfactant-stabilized emulsion systems (o/w and w/o) were not destabilized within one day after filtration. It could be assumed that flexible droplets were formed because there were no changes in droplet size for w/o emulsions, and just a small decrease was determined for some of the o/w emulsions. There was no decrease in water content for the w/o emulsions, but the oil content was roughly halved for the o/w emulsions due to foam layers forming on top of the samples which were not included in the NMR sample after filtration.

The particle-stabilized emulsion systems (o/w and w/o) were destabilized during filtration due to coalescence and breaking of rigid droplets. A significant amount of free water was formed in w/o emulsions where droplet size and water content were halved during filtration. The o/w emulsions initially formed larger droplets than w/o emulsions in the continuous phase, which led to increased coalescence, destabilization, and filter clogging during filtration.

W/O crude oil emulsions were destabilized during filtration even though the droplets were initially slightly smaller than the filter pores. Free water was formed immediately after filtration of Crude Oil A emulsions, and there was appearance of free water over time in the Crude Oil A and B mixture emulsions. Since the crude oil emulsions showed a similar trend as the different particle-stabilized emulsion systems, it could be concluded that the behavior of crude oil emulsions was closer to particle-stabilized than surfactant-stabilized emulsions.

Double o/w/o emulsions were prepared successfully and analyzed using microscopy. The double emulsions were destabilized during filtration: Double emulsions were not observed after filtration, but two different zones were formed. The different zones contained clusters or single droplets indicating coalescence of some droplets. Interpretation of the different emulsion components has not been possible yet.

6. Further Research

In the future, filtration of emulsions through bigger cores should be tested and analyzed by NMR. For further development of this experiments, analyzing emulsion droplets inside cores and the effect larger filter areas gives during filtration, could be beneficial. The experiments in this project have been performed at room temperature, and therefore should the filterability during higher temperatures be tested in order to better simulate real case conditions.

Until now, the microscopic properties during filtration, e.g. droplet sizes, have been determined by NMR and microscopy. In order to gain knowledge about what happens on the interface between oil and water, interfacial rheology could be performed. Interfacial rheology could be important in order to find out where the surfactants and particles go, how they adsorb and spread on interfaces. Interfacial rheology could also give an indication about the flexibility of surfactant-stabilized droplet interfaces. It could be beneficial to determine why there were almost no change in the droplet size during filtration of the surfactant-stabilized o/w and w/o emulsion systems.

Since hydrophilic silica particles Aerosil R7200 clogged the filter in o/w emulsions due to initially large droplets formed during emulsification, other particles could be tested out to counteract the clogging effect, possibly replacing Aerosil R7200 as the particles stabilizing o/w emulsions. Regarding the multiple emulsions, the behavior during filtration is not completely elucidated yet. A better characterization should be performed to be able to determine the type of emulsions formed after filtration.

7. References

1. Gilland, B., *Population, Economic Growth, and Energy Demand, 1985-2020.* Population and Development Review, 1988. **14**(2): p. 233-244.
2. Alvarado, V. and E. Manrique, *Enhanced Oil Recovery: An Update Review.* Energies, 2010. **3**(9): p. 1529.
3. Aurand, K.R., Dahle, G. S., Torsæter, O. , *Comparison of Oil Recovery for Six Nanofluids in Berea Sandstone Cores*. 2014, Norwegian University of Science and Technology.
4. McAuliffe, C.D., *Oil-in-Water Emulsions and Their Flow Properties in Porous Media.*
5. Nelson, P.H., *Pore-throat sizes in sandstones, tight sandstones, and shales.* AAPG Bulletion, 2009. **93**(3): p. 329-340.
6. Moulijn, J.A., M. Makkee, and A.E.v. Diepen, *Chemical Process Technology*. Vol. Second Edition. 2014: Wiley.
7. Petroleum.co.uk. *API Gravity*. 2015; Available from: http://www.petroleum.co.uk/api.
8. WebFinance, I.B. *API Gravity*. 2016; Available from: http://www.businessdictionary.com/definition/API-gravity.html.
9. Sizes, I. *Sizes: API degree*. 2003; Available from: http://sizes.com/units/hydrometer_api.htm.
10. Barrabino, A., *Phase Inversion, Stability and Destabilization of Model and Crude Oil Water-in-Oil Emulsions*. 2014, Norwegian University of Science and Technology, NTNU: Faculty of Science and Technology, Department of Chemical Engineering.
11. Silset, A., *Emulsions (w/o and o/w) of Heavy Crude Oils. Characterization, Stabilization, Destabilization and Produced Water Quality*. 2008, Norwegian University of Science and Technology, NTNU: Faculty of Science and Technology, Department of Chemical Engineering.
12. Sjoblom, J. and e. al., *Encyclopedic Handbook of Emulsion Technology*. 2001: Marcel Dekker, Inc.
13. Sjöblom, J., et al., *Our current understanding of water-in-crude oil emulsions.: Recent characterization techniques and high pressure performance.* Advances in Colloid and Interface Science, 2003. **100–102**: p. 399-473.
14. Simon, S., et al., *Rheological properties of particle-stabilized emulsions.* J. Dispersion Sci. Technol., 2010. **31**(5): p. 632-640.
15. Aveyard, R., Binks, B. P., Clint, J. H., *Emulsions stabilised solely by colloidal particles.* Adv. Colloid Interface Sci., 2003. **100-102**: p. 503-546.
16. Holmberg, K., Jönsson, B., Kronberg, B., Lindman, B., *Surfactants and Polymers in Aqueous Solution*. 2nd ed. 2003: John Wiley & Sons, LTD.
17. Mørk, P.C., *Overflate og kolloidkjemi: Grunnleggende prinsipper og teorier*. 8 ed. 2004: Department for Chemical Engineering, NTNU.
18. Hannisdal, A., et al., *Particle-stabilized emulsions: Effect of heavy crude oil components pre-adsorbed onto stabilizing solids.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2006. **276**(1–3): p. 45-58.
19. Benmekhbi, M., *Properties of Surfactant-Stabilized Liquid-Liquid Interfaces and the Relation to Emulsion Stability*. 2013, Norwegian University of Science and

Technology, NTNU: Faculty of Science and Technology, Department of Chemical Engineering.

20. Akil Ahmad, A.J., Siti Hamidah Mohd-Setapar, Siti Norazimah Mohamad-Aziz, Muhammad Abbad Ahmad-Zaini, Chuo Sing Chuong, *Effect of Parameter on Forward Extraction of Amoxicillin by using Mixed Reverse Micelles.* Research Journal of Biotechnology, 2013. **8**(10).
21. Mittal, K.L., *Polymer Surface Modification: Relevance to Adhesion*. Vol. 5. 2009: CRC Press Taylor & Francis Group.
22. Kokal, S.L., *Crude Oil Emulsions: A State-Of-The-Art Review.*
23. Jiao, J. and D.J. Burgess, *Rheology and Stability of Water-in-Oil-in-Water Multiple Emulsions Containing Span 83 and Tween 80.* AAPS PharmSci2003, 2003.
24. Sørland, G.H., *Dynamic Pulsed-Field-Gradient NMR*. 2014, Springer Series in Chemical Physics.
25. Kumar, R., M.S. Kumar, and N. Mahadevan, *Multiple Emulsions: A Review.* International Journal of Recent Advances in Pharmaceutical Research, 2012: p. 9-19.
26. Abdel-Raouf, M.E.-S., *Factors Affecting the Stability of Crude Oil Emulsions*, in *Crude Oil Emulsions- Composition Stability and Characterization*. 2012.
27. Sjöblom, J., *Emulsions and Emulsion Stability*. 2nd ed. Surfactant Science Series. Vol. 132. 2006: CRC Press.
28. Hiemenz, P.C., Rajagopalan, R., *Principles of Colloid and Surface Chemistry*. 3rd ed. 1997: Marcel Dekker.
29. Gregory, J., *Particles in Water, Properties and Processes*. 2006, Boca Raton FL, USA: CRC Taylor and Francis.
30. Tadros, T., *Coalescence*, in *Encyclopedia of Colloid and Interface Science*, T. Tadros, Editor. 2013, Springer Berlin Heidelberg. p. 84-84.
31. Sun, D., Duan, X., Li, W., Zhou, D., *Demulsification of water-in-oil emulsion by using porous glass membrane.* Journal of Membrane Science, 1998. **146**(1): p. 65-72.
32. Kocherginsky, N.M., Tan, C. L., Lu, W. F., *Demulsification of water-in-oil emulsions via filtration through a hydrophilic polymer membrane.* Journal of Membrane Science, 2003. **220**(1–2): p. 117-128.
33. Kukizaki, M., Goto, M., *Demulsification of water-in-oil emulsions by permeation through Shirasu-porous-glass (SPG) membranes.* Journal of Membrane Science, 2008. **322**(1): p. 196-203.
34. Tiab, D. and E.C. Donaldson, *Petrophysics : Theory and Practice of Measuring Reservoir Rock and Fluid Transport Properties*. 3rd ed. ed. Petrophysics - Theory and Practice of Measuring Reservoir Rock and Fluid Transport Properties. 2011, Burlington: Elsevier Science.
35. Opedal, N., Sørland, G., Sjöblom, J., *Emulsion Stability Studied by Nuclear Magnetic Resonance (NMR).* Energy & Fuels, 2010. **24**.
36. Solberg, J.K., *Lysmikroskopi*. 1984: Institutt for Fysikalsk Metallurgi, NTH Trykk.
37. Opedal, N., Sørland, G., Sjöblom, J., *Methods for Droplet Size Distribution Determination of Water-in-Oil Emulsions using Low-Field NMR.* diffusion-fundamentals.org, 2009. **7**: p. 1-29.
38. Sørland, G.H., *Characterisation of emulsions by PFG-NMR.*
39. Simon, S., Pierrard, X., Sjöblom, J., Sørland, G. H., *Separation profile of model water-in-oil emulsions followed by nuclear magnetic resonance (NMR) measurements: Application range and comparison with a multiple-light scattering based apparatus.* Journal of Colloid and Interface Science, 2011. **356**(1): p. 352-361.
40. Lide, D.R., *Handbook of Chemistry and Physics*. 71st ed. 1990: CRC Press.

Appendix A. Droplet Size Distribution

The droplet size distributions (DSD) obtained using low-field NMR are shown in this appendix. All the samples, without the samples included in the main report, are included here. An overview of the samples in this appendix is given in Table A 1.

Table A 1: Overview of the given DSD in this appendix. Samples marked with * are given in the main report.

Type	**Oil component**	**Stabilization component**	**Filter**	**Emulsification conditions**	**Oil/water cut [vol. %]**	**Figure**
w/o	Crude Oil A	Crude Oil A components	3	1000 rpm 5 min	30	*
						Figure A 1
						Figure A 2
						Figure A 3
	50:50 wt. % Crude Oil A and B	50:50 wt. % Crude Oil A and B components	4	4000 rpm 1.5 min	15	Figure A 4
						Figure A 5
					30	Figure A 6
						Figure A 7
						Figure A 8
						*
						Figure A 9
o/w	Hexadecane	0.5 wt. % Tween80	4	4000 rpm 5 min	30	Figure A 10
						Figure A 11
						*
						Figure A 12
					15	Figure A 13
						*
						Figure A 14
				2000 rpm 5 min	30	*
						Figure A 15

A. i. W/O Crude Oil Emulsions

Crude Oil A Emulsions

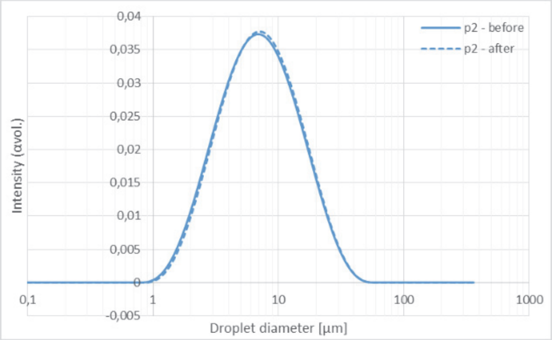


Figure A 1: DSD for a w/o emulsion of Crude Oil A and water, containing 30 vol. % water cut, emulsified at 1000 rpm for 5 minutes, before (solid line) and after (dashed line) filtration with filter no. 3. Parallel 2.

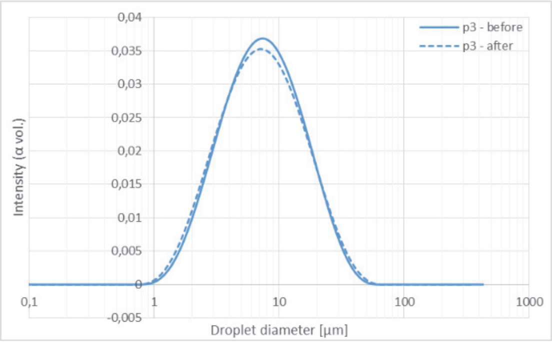


Figure A 2: DSD for a w/o emulsion of Crude Oil A and water, containing 30 vol. % water cut, emulsified at 1000 rpm for 5 minutes, before (solid line) and after (dashed line) filtration with filter no. 3. Parallel 3.

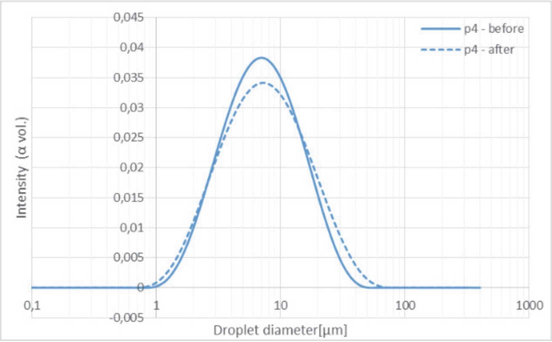


Figure A 3: DSD for a w/o emulsion of Crude Oil A and water, containing 30 vol. % water cut, emulsified at 1000 rpm for 5 minutes, before (solid line) and after (dashed line) filtration with filter no. 3. Parallel 4.

50:50 wt. % Crude Oil A and B Mixture Emulsions

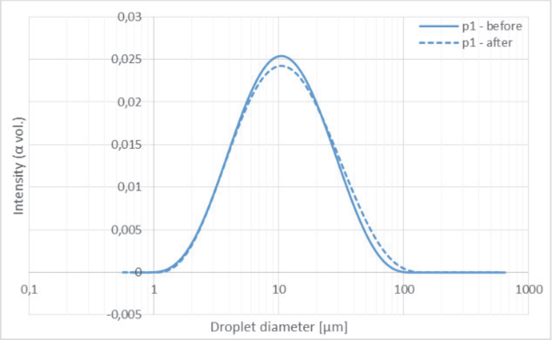


Figure A 4: DSD for an emulsion of a 50:50 wt. % Crude Oil A and B mixture and water, containing 15 vol. % water cut, emulsified at 4000 rpm for 1.5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 1.

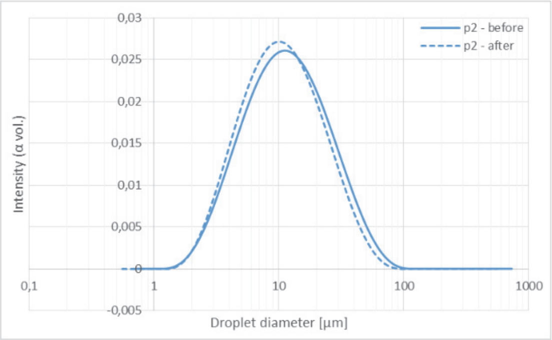


Figure A 5: DSD for an emulsion of a 50:50 wt. % Crude Oil A and B mixture and water, containing 15 vol. % water cut, emulsified at 4000 rpm for 1.5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 2.

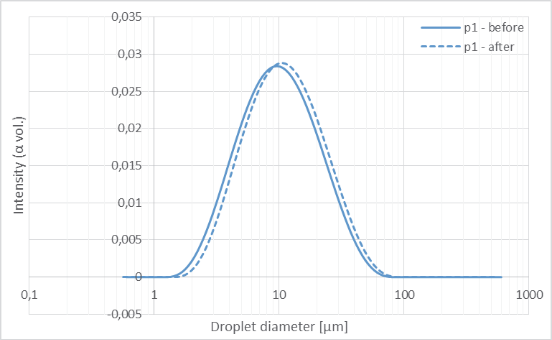


Figure A 6: DSD for an emulsion of a 50:50 wt. % Crude Oil A and B mixture and water, containing 30 vol. % water cut, emulsified at 4000 rpm for 1.5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 1.

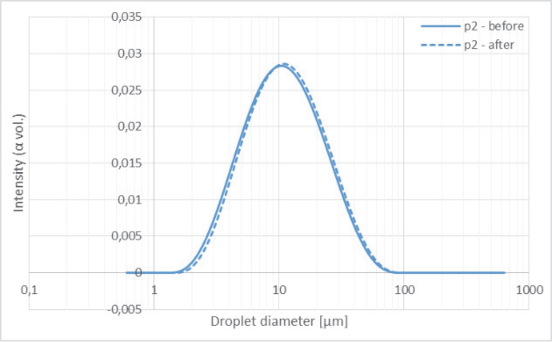


Figure A 7: DSD for an emulsion of a 50:50 wt. % Crude Oil A and B mixture and water, containing 30 vol. % water cut, emulsified at 4000 rpm for 1.5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 2.

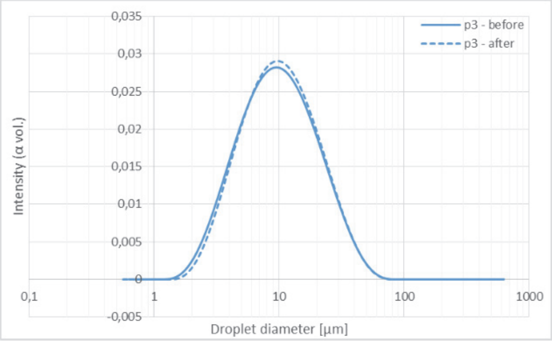


Figure A 8: DSD for an emulsion of a 50:50 wt. % Crude Oil A and B mixture and water, containing 30 vol. % water cut, emulsified at 4000 rpm for 1.5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 3.

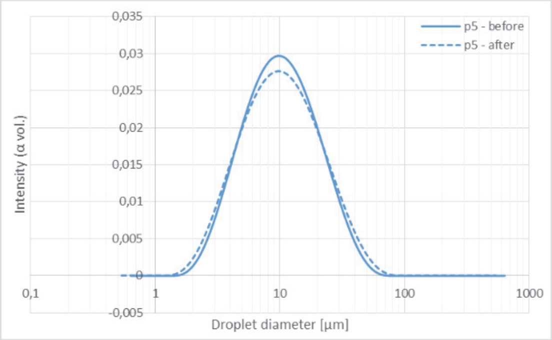


Figure A 9: DSD for an emulsion of a 50:50 wt. % Crude Oil A and B mixture and water, containing 30 vol. % water cut, emulsified at 4000 rpm for 1.5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 5.

A. ii. O/W Emulsions

Emulsions Stabilized by the Tween80 surfactant

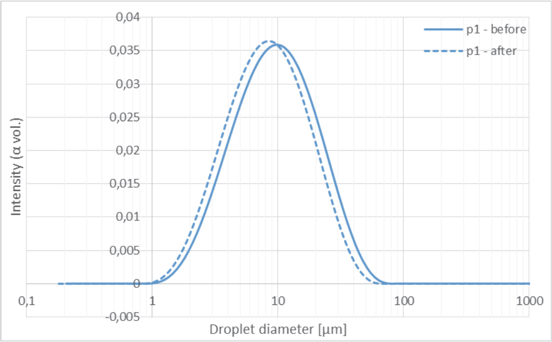


Figure A 10: DSD for an o/w emulsion of hexadecane and water stabilized with 0.5 wt. % Tween80, 30 vol. % oil cut, emulsified at 4000 rpm for 5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 1.

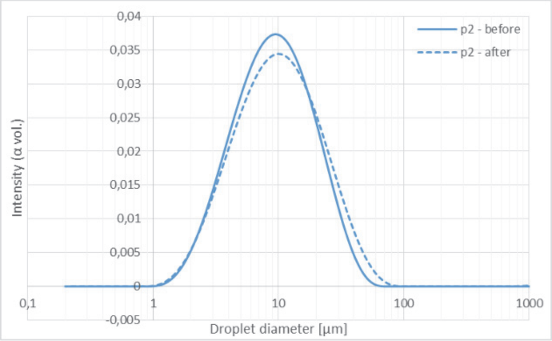


Figure A 11: DSD for an o/w emulsion of hexadecane and water stabilized with 0.5 wt. % Tween80, 30 vol. % oil cut, emulsified at 4000 rpm for 5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 2.

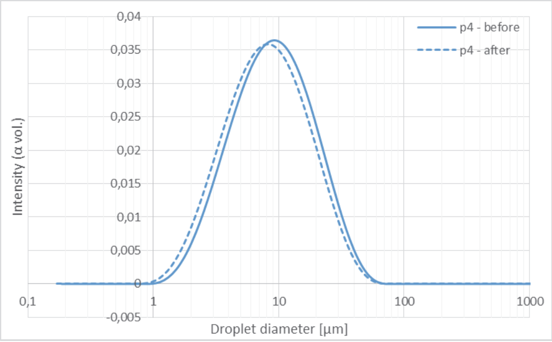


Figure A 12: DSD for an o/w emulsion of hexadecane and water stabilized with 0.5 wt. % Tween80, 30 vol. % oil cut, emulsified at 4000 rpm for 5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 4.

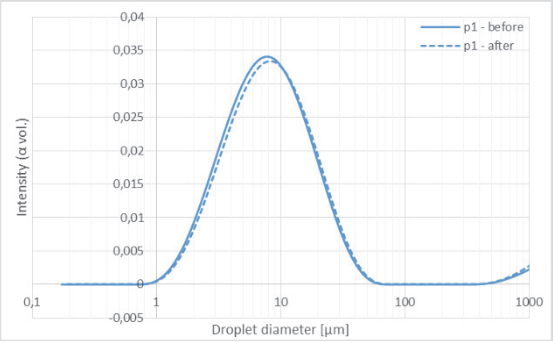


Figure A 13: DSD for an o/w emulsion of hexadecane and water stabilized with 0.5 wt. % Tween80, 15 vol. % oil cut, emulsified at 4000 rpm for 5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 1.

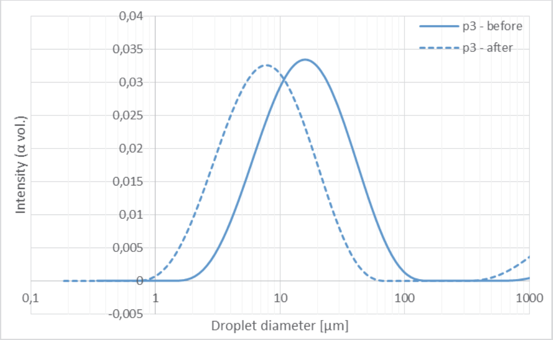


Figure A 14: DSD for an o/w emulsion of hexadecane and water stabilized with 0.5 wt. % Tween80, 15 vol. % oil cut, emulsified at 4000 rpm for 5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 3.

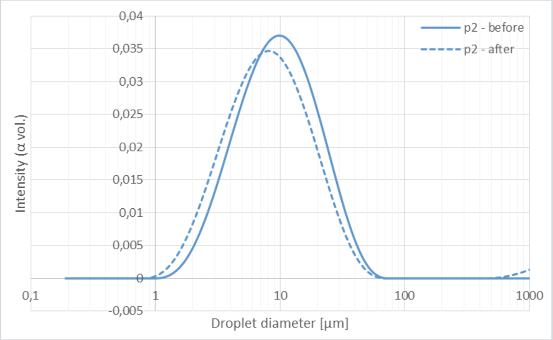


Figure A 15: DSD for an o/w emulsion of hexadecane and water stabilized with 0.5 wt. % Tween80, 30 vol. % oil cut, emulsified at 2000 rpm for 5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 2.

Appendix B. S/V Profiles

The S/V profiles of the 50:50 wt. % Crude Oil A and B mixture emulsions obtained using low-field NMR are shown in this appendix. All the samples, without the samples included in the main report, are included here. An overview of the samples in this appendix is given in Table B 1.

Table B 1: Overview of the given S/V profiles in this appendix. Samples marked with * are given in the main report.

Type	**Oil component**	**Stabilization component**	**Filter**	**Emulsification conditions**	**Water cut [vol. %]**	**Figure**
w/o	50:50 wt. % Crude Oil A and B	50:50 wt. % Crude Oil A and B components	4	4000 rpm 1.5 min	15	Figure B 1
						Figure B 2
					30	Figure B 3
						Figure B 4
						Figure B 5
						*
						Figure B 6

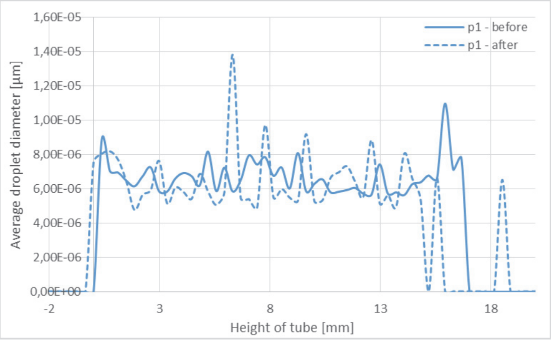


Figure B 1: S/V profile for an emulsion of a 50:50 wt. % Crude Oil A and B mixture and water, containing 15 vol. % water cut, emulsified at 4000 rpm for 1.5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 1.

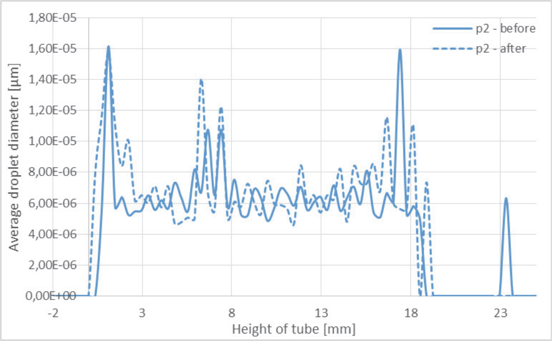


Figure B 2: S/V profile for an emulsion of a 50:50 wt. % Crude Oil A and B mixture and water, containing 15 vol. % water cut, emulsified at 4000 rpm for 1.5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 2.

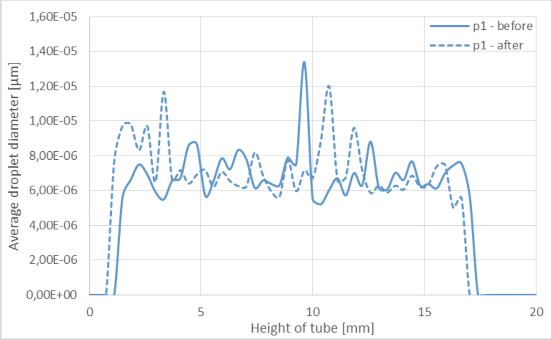


Figure B 3: S/V profile for an emulsion of a 50:50 wt. % Crude Oil A and B mixture and water, containing 30 vol. % water cut, emulsified at 4000 rpm for 1.5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 1.

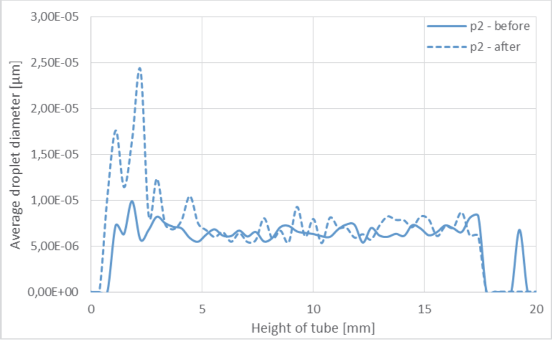


Figure B 4: S/V profile for an emulsion of a 50:50 wt. % Crude Oil A and B mixture and water, containing 30 vol. % water cut, emulsified at 4000 rpm for 1.5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 2.

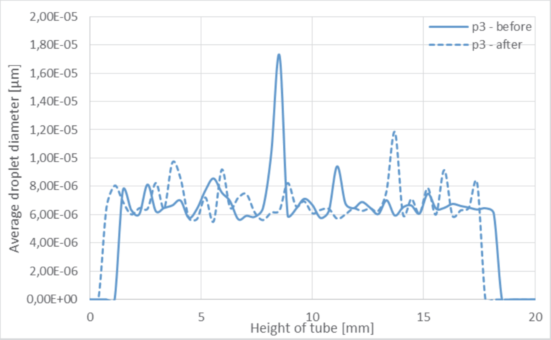


Figure B 5: S/V profile for an emulsion of a 50:50 wt. % Crude Oil A and B mixture and water, containing 30 vol. % water cut, emulsified at 4000 rpm for 1.5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 3.

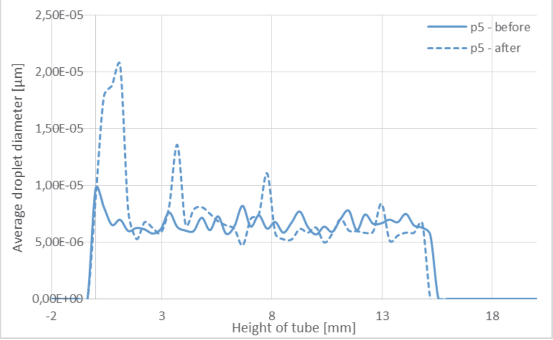


Figure B 6: S/V profile for an emulsion of a 50:50 wt. % Crude Oil A and B mixture and water, containing 30 vol. % water cut, emulsified at 4000 rpm for 1.5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 5.

Appendix C. Oil and Water Profiles

The oil profiles and water profiles obtained using low-field NMR are shown in this appendix. All the samples, without the samples included in the main report, are included here. An overview of the samples in this appendix is given in Table C 1.

Table C 1: Overview of the given oil and water profiles in this appendix. Samples marked with * are given in the main report.

Type	Oil component	Stabilization component	Filter	Emulsification conditions	Oil/water cut [vol.%]	Figure
w/o	Crude Oil A	Crude Oil A components	3	1000 rpm 5 min	30	Figure C 1
						Figure C 2
						Figure C 3
						Figure C 4
	50:50 wt. % Crude Oil A and B	50:50 wt. % Crude Oil A and B components	4	4000 rpm 1.5 min	15	Figure C 5
						*
					30	Figure C 6
						Figure C 7
						Figure C 8
						Figure C 9
						*
o/w	Hexadecane	0.5 wt. % Tween80	4	4000 rpm 5 min	30	Figure C 10
						*
						Figure C 11
						Figure C 12
					15	Figure C 13
						Figure C 14
						Figure C 15
				2000 rpm 5 min	30	Figure C 16
						Figure C 17

C. i. W/O Crude Oil Emulsions

Crude Oil A Emulsions

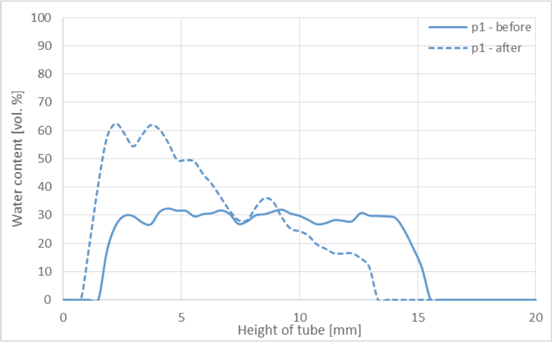


Figure C 1: Water profile for a w/o emulsion of Crude Oil A and water, containing 30 vol. % water cut, emulsified at 1000 rpm for 5 minutes, before (solid line) and after (dashed line) filtration with filter no. 3. Parallel 1.

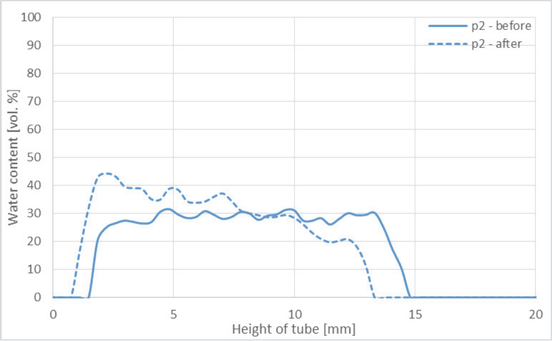


Figure C 2: Water profile for a w/o emulsion of Crude Oil A and water, containing 30 vol. % water cut, emulsified at 1000 rpm for 5 minutes, before (solid line) and after (dashed line) filtration with filter no. 3. Parallel 2.

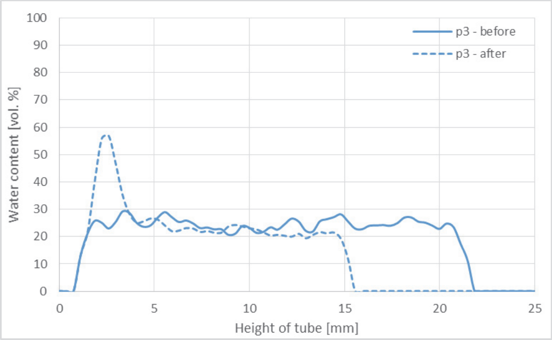


Figure C 3: Water profile for a w/o emulsion of Crude Oil A and water, containing 30 vol. % water cut, emulsified at 1000 rpm for 5 minutes, before (solid line) and after (dashed line) filtration with filter no. 3. Parallel 3.

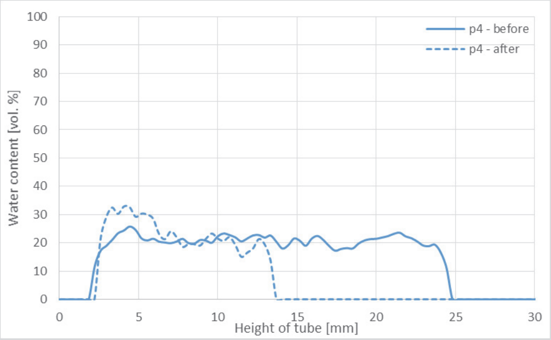


Figure C 4: Water profile for a w/o emulsion of Crude Oil A and water, containing 30 vol. % water cut, emulsified at 1000 rpm for 5 minutes, before (solid line) and after (dashed line) filtration with filter no. 3. Parallel 4.

50:50 wt. % Crude Oil A and B Mixture Emulsions

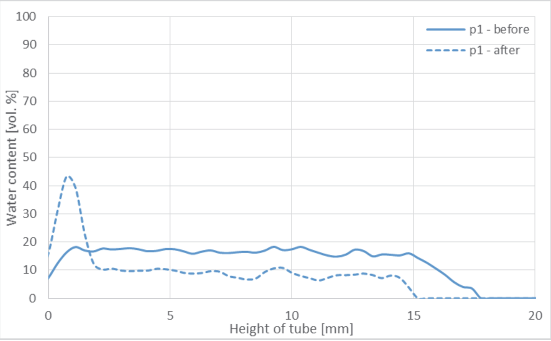


Figure C 5: Water profile for an emulsion of a 50:50 wt. % Crude Oil A and B mixture and water, containing 15 vol. % water cut, emulsified at 4000 rpm for 1.5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 1.

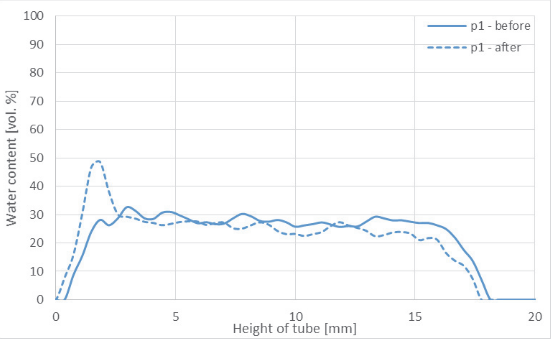


Figure C 6: Water profile for an emulsion of a 50:50 wt. % Crude Oil A and B mixture and water, containing 30 vol. % water cut, emulsified at 4000 rpm for 1.5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 1.

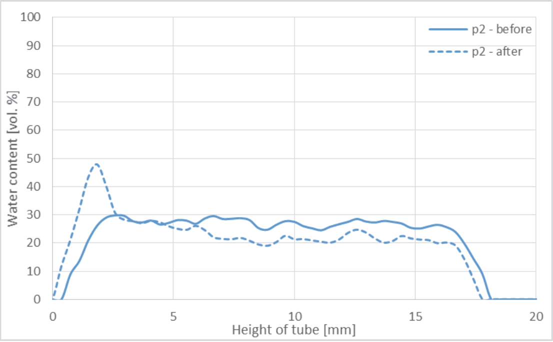


Figure C 7: Water profile for an emulsion of a 50:50 wt. % Crude Oil A and B mixture and water, containing 30 vol. % water cut, emulsified at 4000 rpm for 1.5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 2.

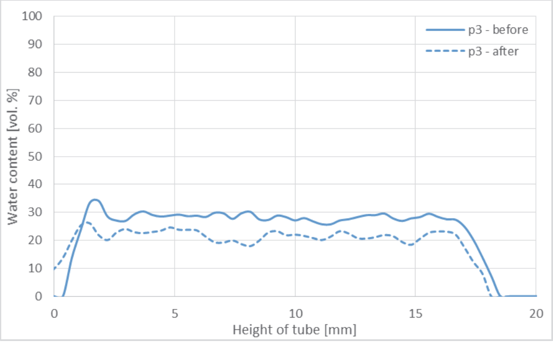


Figure C 8: Water profile for an emulsion of a 50:50 wt. % Crude Oil A and B mixture and water, containing 30 vol. % water cut, emulsified at 4000 rpm for 1.5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 3.

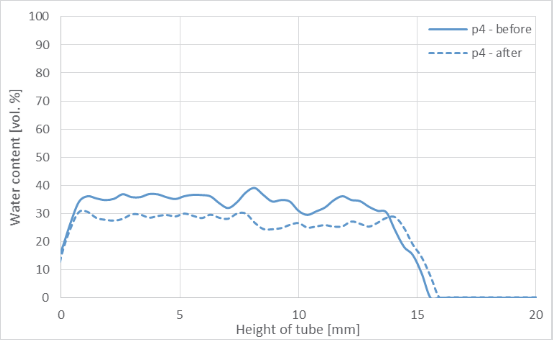


Figure C 9: Water profile for an emulsion of a 50:50 wt. % Crude Oil A and B mixture and water, containing 30 vol. % water cut, emulsified at 4000 rpm for 1.5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 4.

C. ii. O/W Emulsions

Emulsions Stabilized by the Tween80 Surfactant

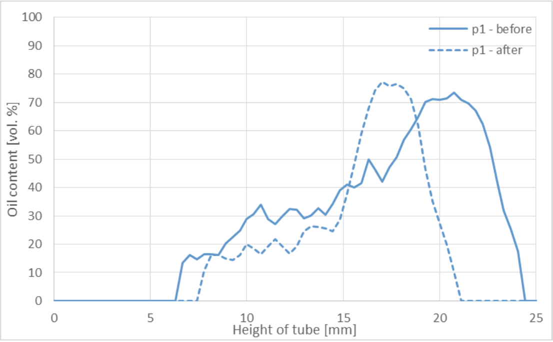


Figure C 10: Oil profile for an o/w emulsion of hexadecane and water stabilized with 0.5 wt. % Tween80, 30 vol. % oil cut, emulsified at 4000 rpm for 5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 1.

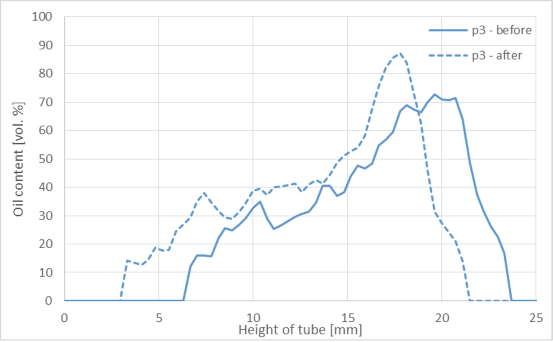


Figure C 11: Oil profile for an o/w emulsion of hexadecane and water stabilized with 0.5 wt. % Tween80, 30 vol. % oil cut, emulsified at 4000 rpm for 5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 3.

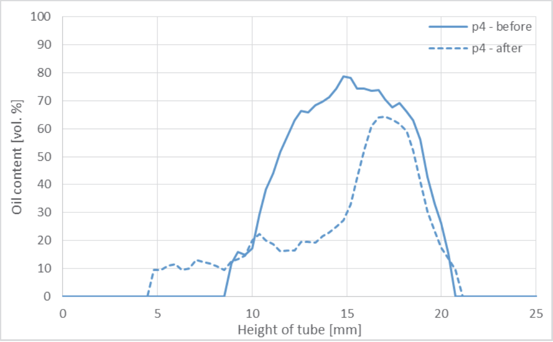


Figure C 12: Oil profile for an o/w emulsion of hexadecane and water stabilized with 0.5 wt. % Tween80, 30 vol. % oil cut, emulsified at 4000 rpm for 5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 4.

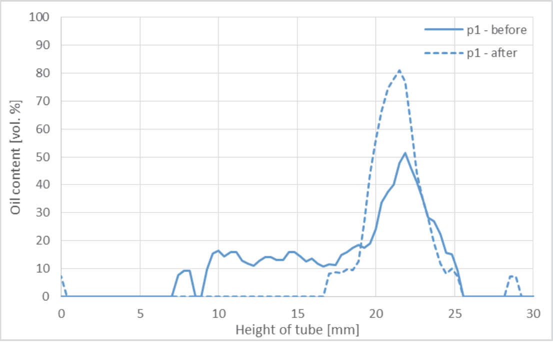


Figure C 13: Oil profile for an o/w emulsion of hexadecane and water stabilized with 0.5 wt. % Tween80, 15 vol. % oil cut, emulsified at 4000 rpm for 5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 1.

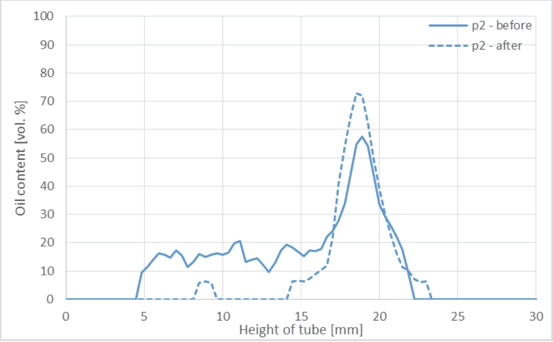


Figure C 14: Oil profile for an o/w emulsion of hexadecane and water stabilized with 0.5 wt. % Tween80, 15 vol. % oil cut, emulsified at 4000 rpm for 5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 2.

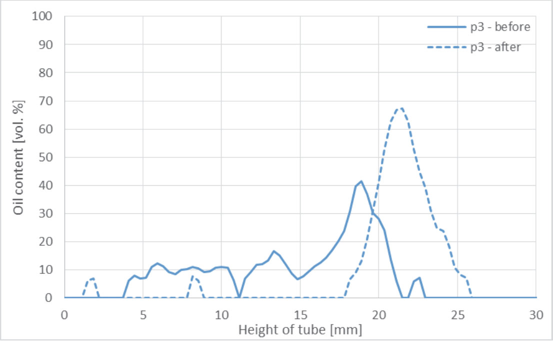


Figure C 15: Oil profile for an o/w emulsion of hexadecane and water stabilized with 0.5 wt. % Tween80, 15 vol. % oil cut, emulsified at 4000 rpm for 5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 3.

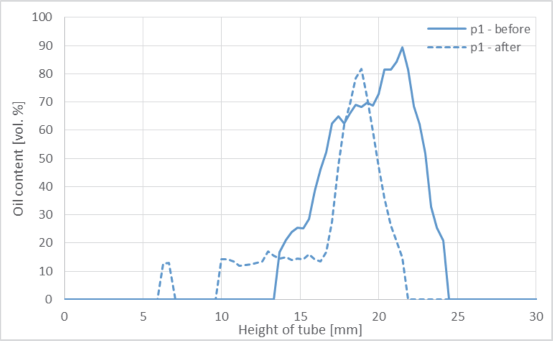


Figure C 16: Oil profile for an o/w emulsion of hexadecane and water stabilized with 0.5 wt. % Tween80, 30 vol. % oil cut, emulsified at 2000 rpm for 5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 1.

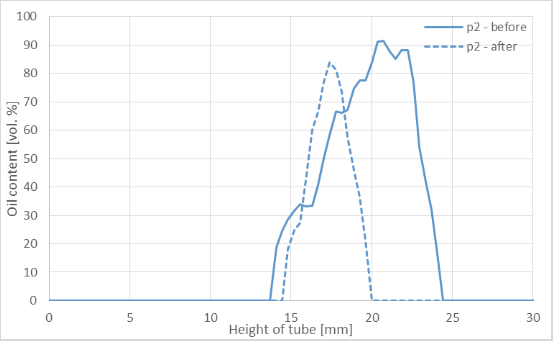
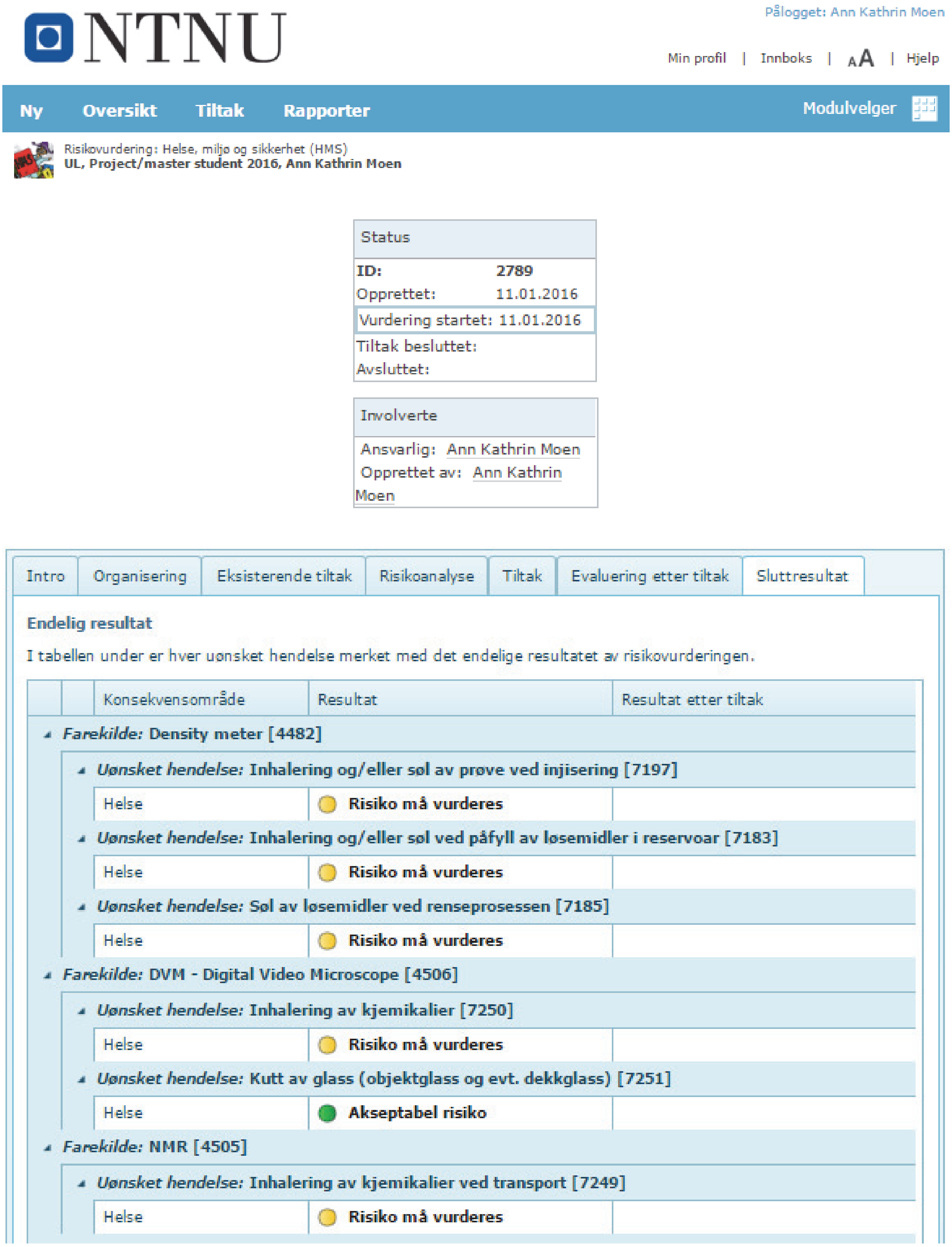


Figure C 17: Oil profile for an o/w emulsion of hexadecane and water stabilized with 0.5 wt. % Tween80, 30 vol. % oil cut, emulsified at 2000 rpm for 5 minutes, before (solid line) and after (dashed line) filtration with filter no. 4. Parallel 2.

Appendix D.Risk Assessment (in Norwegian)



Risikovurdering: Helse, miljø og sikkerhet (HMS)
UL, Project/master student 2016, Ann Kathrin Moen

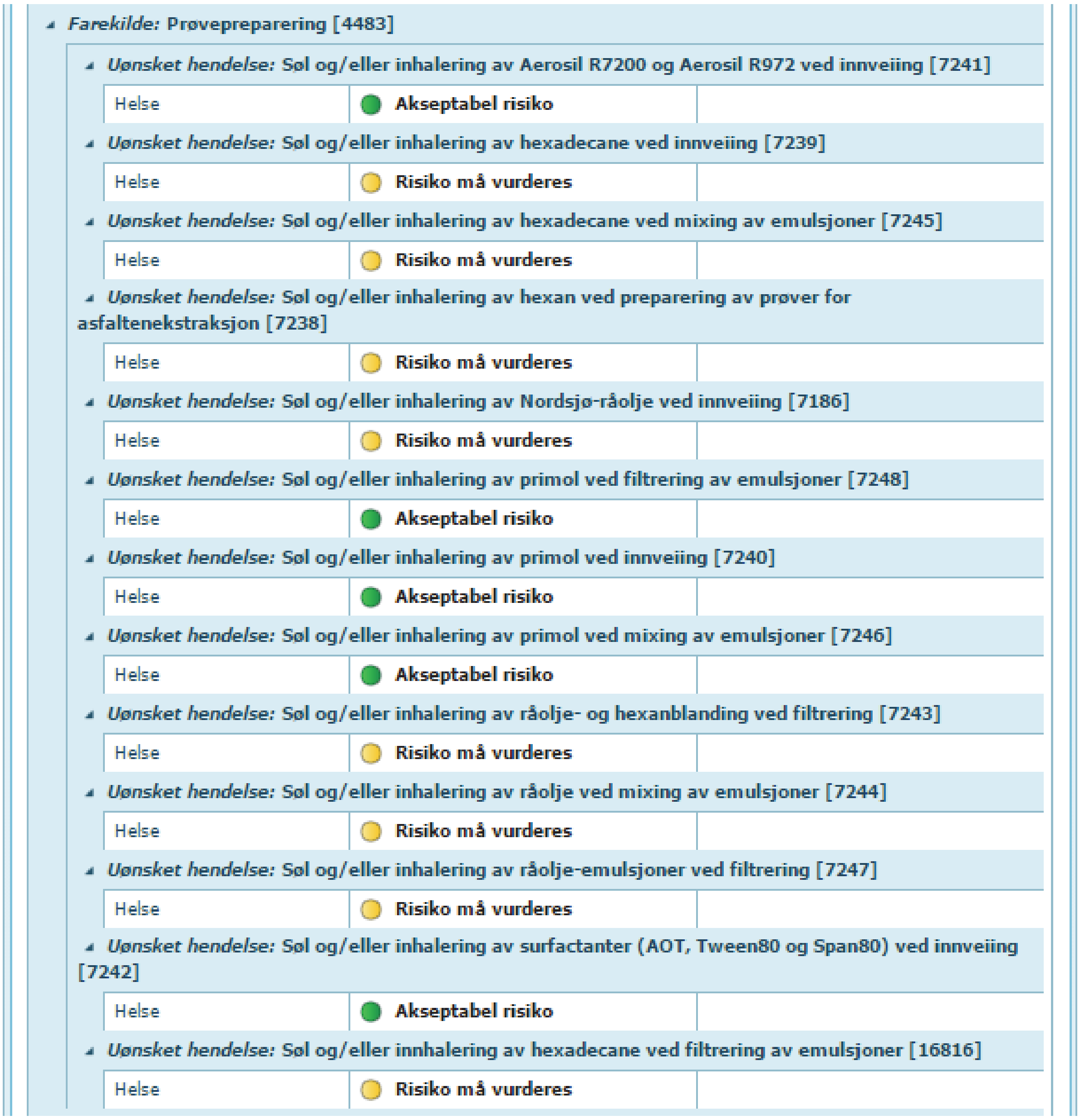
Status	
ID:	**2789**
Opprettet:	11.01.2016
Vurdering startet:	11.01.2016
Tiltak besluttet:	
Avsluttet:	

Involverte	
Ansvarlig:	Ann Kathrin Moen
Opprettet av:	Ann Kathrin Moen

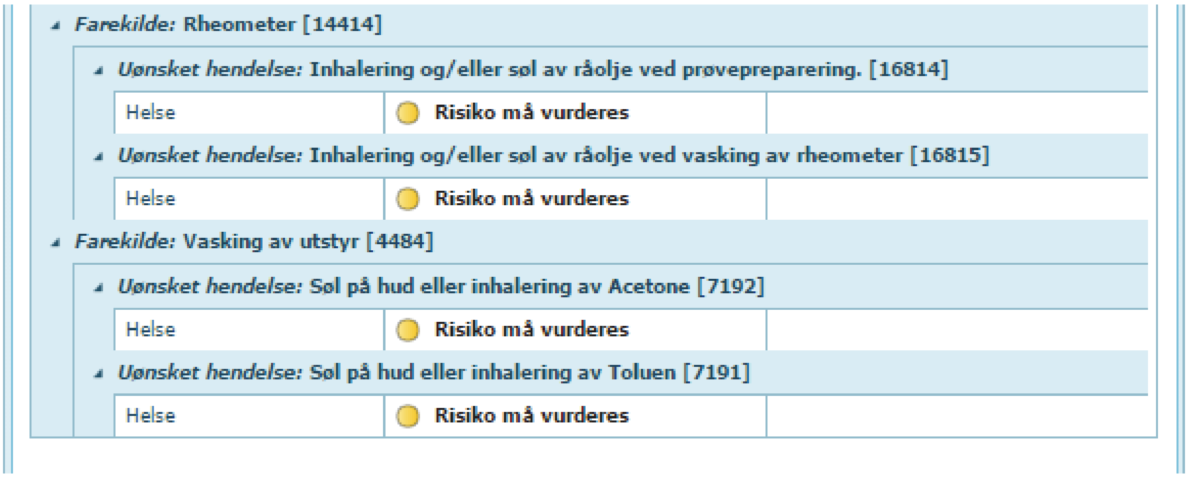
Endelig resultat

I tabellen under er hver uønsket hendelse merket med det endelige resultatet av risikovurderingen.

		Konsekvensområde	Resultat	Resultat etter tiltak
Farekilde: **Density meter [4482]**				
	Uønsket hendelse: **Inhalering og/eller søl av prøve ved injisering [7197]**			
		Helse	🟡 **Risiko må vurderes**	
	Uønsket hendelse: **Inhalering og/eller søl ved påfyll av løsemidler i reservoar [7183]**			
		Helse	🟡 **Risiko må vurderes**	
	Uønsket hendelse: **Søl av løsemidler ved renseprosessen [7185]**			
		Helse	🟡 **Risiko må vurderes**	
Farekilde: **DVM - Digital Video Microscope [4506]**				
	Uønsket hendelse: **Inhalering av kjemikalier [7250]**			
		Helse	🟡 **Risiko må vurderes**	
	Uønsket hendelse: **Kutt av glass (objektglass og evt. dekkglass) [7251]**			
		Helse	🟢 **Akseptabel risiko**	
Farekilde: **NMR [4505]**				
	Uønsket hendelse: **Inhalering av kjemikalier ved transport [7249]**			
		Helse	🟡 **Risiko må vurderes**	



- *Farekilde:* Prøvepreparering [4483]
  - *Uønsket hendelse:* Søl og/eller inhalering av Aerosil R7200 og Aerosil R972 ved innveiing [7241]
    - Helse — 🟢 **Akseptabel risiko**
  - *Uønsket hendelse:* Søl og/eller inhalering av hexadecane ved innveiing [7239]
    - Helse — 🟡 **Risiko må vurderes**
  - *Uønsket hendelse:* Søl og/eller inhalering av hexadecane ved mixing av emulsjoner [7245]
    - Helse — 🟡 **Risiko må vurderes**
  - *Uønsket hendelse:* Søl og/eller inhalering av hexan ved preparering av prøver for asfaltenekstraksjon [7238]
    - Helse — 🟡 **Risiko må vurderes**
  - *Uønsket hendelse:* Søl og/eller inhalering av Nordsjø-råolje ved innveiing [7186]
    - Helse — 🟡 **Risiko må vurderes**
  - *Uønsket hendelse:* Søl og/eller inhalering av primol ved filtrering av emulsjoner [7248]
    - Helse — 🟢 **Akseptabel risiko**
  - *Uønsket hendelse:* Søl og/eller inhalering av primol ved innveiing [7240]
    - Helse — 🟢 **Akseptabel risiko**
  - *Uønsket hendelse:* Søl og/eller inhalering av primol ved mixing av emulsjoner [7246]
    - Helse — 🟢 **Akseptabel risiko**
  - *Uønsket hendelse:* Søl og/eller inhalering av råolje- og hexanblanding ved filtrering [7243]
    - Helse — 🟡 **Risiko må vurderes**
  - *Uønsket hendelse:* Søl og/eller inhalering av råolje ved mixing av emulsjoner [7244]
    - Helse — 🟡 **Risiko må vurderes**
  - *Uønsket hendelse:* Søl og/eller inhalering av råolje-emulsjoner ved filtrering [7247]
    - Helse — 🟡 **Risiko må vurderes**
  - *Uønsket hendelse:* Søl og/eller inhalering av surfactanter (AOT, Tween80 og Span80) ved innveiing [7242]
    - Helse — 🟢 **Akseptabel risiko**
  - *Uønsket hendelse:* Søl og/eller innhalering av hexadecane ved filtrering av emulsjoner [16816]
    - Helse — 🟡 **Risiko må vurderes**



- *Farekilde:* Rheometer [14414]
  - *Uønsket hendelse:* Inhalering og/eller søl av råolje ved prøvepreparering. [16814]
    - Helse — 🟡 **Risiko må vurderes**
  - *Uønsket hendelse:* Inhalering og/eller søl av råolje ved vasking av rheometer [16815]
    - Helse — 🟡 **Risiko må vurderes**
- *Farekilde:* Vasking av utstyr [4484]
  - *Uønsket hendelse:* Søl på hud eller inhalering av Acetone [7192]
    - Helse — 🟡 **Risiko må vurderes**
  - *Uønsket hendelse:* Søl på hud eller inhalering av Toluen [7191]
    - Helse — 🟡 **Risiko må vurderes**