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Analysis of petroleum oil droplet behavior during a subsea release

A combined laboratory and modeling study determining the behavior of oil droplets when breaching the sea surface after a subsea release

Master's thesis

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SINTEF

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Master's thesis in Environmental Chemistry
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Abstract

During a subsea blowout, millions of oil droplets will travel through the water column towards the sea surface. Their behavior upon reaching the surface will affect the optimal procedure to minimize the environmental impact. The droplets' behavior will determine the oil film thickness, emulsification, and persistence. Droplet behavior is necessary for oil spill contingency, especially regarding the clean-up and environmental impacts of the release. Different clean-up responses will be needed depending on whether the droplets breach the sea surface solidified or liquefy. There is a lack of knowledge on how surfacing droplets will behave, especially high pour point oil droplets. This study aims to close some of this knowledge gap by looking into how droplets with different pour points behave upon reaching the surface, especially regarding the solidification process.

Experiments and simulations were used in this study to determine the droplet behavior when reaching the surface. OSCAR was used to simulate subsea blowouts to find accurate rising times of the droplets, while Stokes law calculations were used to find appropriate droplet sizes. The experimental part was done using the Inverted Cone, where the droplets were kept under water for a pre-decided time and filmed upon reaching the water surface.

By using the inverted cone, it was determined that a droplet with more than 10ºC higher pour point than seawater temperature would be solid upon reaching the sea surface. It was further concluded that a droplet with more than 10º centigrade lower pour point than seawater temperature would liquefy immediately upon reaching the surface. It was also concluded that a middle phase exists where the droplets undergo a more complicated process. This thesis was not able to conclude what happens in this interval. However, deconstruction of the droplets was observed in the middle phase.

Sammendrag

Under et undervannsutslipp flyter millioner av oljedråper gjennom vannkolonnen og opp mot havoverflaten. Hvordan dråpene oppfører seg når de når overflaten vil avgjøre både oljefilmtykkelsen, emulgeringen og livsløpet til dråpen. Oppførselen til dråpene vil være avgjørende for oljevernberedskap, spesielt når det gjelder opprydding og miljøpåvirkninger av utslippet. Oljen vil mest sannsynlig trenge forskjellige opprydningsmetoder avhengig av om dråpen er størknet eller flytende når den når overflaten. I dag er det mangel på kunnskap rundt dette feltet. Hvordan overflatedråper vil oppføre seg, og da spesielt dråper fra oljer med høyt stivnepunkt, er det ikke mange som har forsket på tidligere. Denne studien tar sikte på å lukke noe av dette kunnskapsgapet ved å se på hvordan dråper med forskjellige stivnepunkt oppfører seg når de når overflaten, med et spesielt fokus på hvordan de størkner.

I denne studien er det blitt brukt både eksperimenter og simuleringer, OSCAR ble brukt til å simulere undervannsutslipp for å finne nøyaktige stigetider for dråpene, mens beregninger med Stokes lov ble brukt for å finne passende dråpestørrelser. Den eksperimentelle delen ble utført ved bruk av Inverted Cone, hvor dråpene ble holdt under vann i en forhåndsbestemt tid, før de ble sluppet opp til overflaten. I det dråpene nådde overflaten ble de filmet for å kunne observere dråpens oppførsel.

Konklusjonen ble at en dråpe med mer enn 10º celsius høyere stivnepunkt enn sjøvannstemperaturen ville være i fastfase når den nådde havoverflaten. Det ble videre konkludert med at en dråpe med mer enn 10º Celsius lavere stivnepunkt enn sjøvannstemperaturen ville bli flytende umiddelbart når den nådde overflaten. Det ble også konkludert med at det er en midtfase hvor dråpene gjennomgår en mer komplisert prosess. Det ble observert dekonstruksjon av dråpene i denne midtfasen, men oppgaven var ikke i stand til å komme til en konklusjon av hva som skjer i dette intervallet.

Acknowledgements

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List of abbreviations

Abbreviation	Meaning
DSD	Droplet size distribution
EPA	Environmental protection agency
GLR	Gas to liquid ratio
HSE	Health Safety and Environment
OSCAR	Oil Spill Contingency And Response, a tool developed by SINTEF for simulating oil spills.
PP	Pour point, The temperature where the oil ceases to flow
PPD	Pour Point Depressants, Chemicals that will lower the pour point if added to oil

1. Introduction

According to Norwegian law, any industry that could potentially pollute the environment must have emergency preparedness measures in place proportional to the likelihood and severity of the event (Brekne; et al., 2004). Throughout history, the oil industry has had a record of oil releases, which have resulted in significant environmental consequences. A significant blowout such as Deepwater Horizon released 200,000 tons of oil into the environment, negatively impacting marine life, such as dolphins and deep-sea coral, as well as marine and shoreline ecosystems (Beyer et al., 2016).

Each crude oil field contains a different type of oil regarding its properties, and each oil would behave differently if it were released into the environment. High-wax oil, a type of oil with a high wax concentration and a high pour point, has been produced more in recent years. Due to its sticky nature, the clean-up methods used for low pour point oils was rendered ineffective (Moldestad, 2006). There has been a focus on high-wax clean up methods the last 25 years, and high-wax oil clean-up methods have been significantly developed. However, it seems like they focus on cleaning up oil that is released as a liquid slick. A different behavior of the oil, where solid droplets reach the surface, might therefore create a problem for clean-up measures, as well as the fate of the rest of the oil spill(Davies et al., 2019).

The inverted cone has been developed by SINTEF and the university of Hawaii to be able to look at oil droplets suspended underwater for a set amount of time. This makes it possible to see how the droplets behave in the water column after a subsea release, and how a droplet will behave when reaching the surface.

1.1 Objectives

The objective of this study is to use the inverted cone to do the following: (1) determine whether an oil droplet with a high pour point will solidify during a subsea release, (2) determine what happens with the droplets between a complete solidification and a complete liquidation, and (3) use oil spill contingency and response (OSCAR) and Stokes' law calculations to simulate a subsea release to determine droplet size and time underwater.

2. Theory

In this thesis, the inverted cone is used to see if a difference in pour point and time underwater can make the droplets from a subsea release solidify when reaching the surface.

A subsea blowout can release tons of oil into the environment. For example, about 200,000 tons of oil were released into the environment during the Deepwater Horizon(Beyer et al., 2016). Furthermore, due to the oils' varying chemical composition, their properties, when released, vary immensely. Every crude is composed of different chemical components and has different properties and reactions(Daling, 2015). Due to the differences in oil properties, the optimal method for clean-up in the event of a spill varies considerably; therefore, it is essential to map out clan-up responses for all new oil production sites.

Due to the oils' varying compositions, the research on different oils is unlimited. This section goes through the most critical research conclusions as of today. First, relevant organic chemistry definitions and the differences in oil compositions are discussed. However, this paper does not include details on naphthene, aromatics, and non-wax paraffins. By diluting the wax and asphaltenes all three contribute to the pour point, but as the compounds themselves do not have any known reactions to affect the pour point, they are merely mentioned.

Regarding the physical properties of the oils, extra care has been taken to present the pour point, as this is the essential variable of this experiment. Density, surface tension, and viscosity are often also presented in standard research articles to define the oils. These parameters are also explained in this thesis. Other physical properties, such as flash point and boiling point, are not described, as they do not directly affect the solidification process of the oil.

Oil weathering is significant for the optimal clean-up procedure. Most known weathering processes are described in this section, with extra emphasis on the ones in which the oil's viscosity is essential. A viscous liquid has similarities to a sold. Viscosity is therefore considered, in this thesis, as the parameter most closely related to solidification. Since spreading, drifting, and sedimentation relate more to where an oil travels than its change in chemical composition, these concepts are not described in detail.

All publicly known oil spill clean-up methods are described in this thesis, as they all are used to various extents and combinations.

Detection of oil is vital for reducing the impact of minor leaks and blowouts. Radars focus on the consistency of oil for detection and are one of the most widely used detection methods today(Fingas & Brown, 2014). The results from this thesis might affect detection of oils as well. Radars, as well as some of the other detection methods that might be affected by solidification are presented in this thesis. However, other detection methods, such as sonar detection and other acoustic methods, are not mentioned due to space restrictions.

Although a high-pour-point oil probably behaves differently than low-pour-point oils when released above water, this thesis focuses on discreet oil droplets. Discreet oil droplets are only formed in high concentrations in a subsea blowout. Surface releases, such as boat collisions, are not included in this thesis.

The plume, and droplet size are important for how the droplets behave before reaching the surface. Extra care has therefore been taken to describe the parameters around a subsea release. Due to this thesis examining oil droplets, and gas releases not releasing oil, it will not be presented. However, both single-phase oil release and multi-phase release containing oil will be presented.

Finally, OSCAR is described. OSCAR is a tool developed by SINTEF to simulate a subsea blowout. It is used worldwide for contingency planning of oil platforms, among other things. This thesis uses OSCAR to find realistic time frames to be used in the experiment.

2.1 Organic chemistry

Petroleum is usually composed of various organic compounds. It is essential to have a general understanding of the different organic compounds that exist to understand the different compositions of oils. Organic compounds are a combination of carbon chains with or without the addition of various atoms. The different subgroups of organic compounds are explained in this section.

2.1.1 Hydrocarbons

Most of the compounds found in oil are hydrocarbons. Hydrocarbons are compounds containing only hydrogen and carbon. Hydrocarbons range from compounds with as few carbon atoms as methane (CH_4) to compounds with as many carbon atoms as hectane ($C_{100}H_{202}$). Compounds can have a single, double, or triple bond between the carbon atoms. These bonds determine the saturation level of the compound. Compounds having pure single bonds are saturated compounds, while those with more than one double or triple bond are non-saturated compounds. As each carbon is surrounded by hydrogen, all hydrocarbons are

nonpolar. Hydrocarbons can be further divided into chains and cycloalkenes. (Brandvik & Daling, 2015a)

2.1.1.1 Chained alkenes

A chained alkene is a compound that does not contain any carbon-rings. It can be further divided into straight-chain alkenes and branched alkenes. In straight-chain alkenes, all carbon atoms are connected to a maximum of two other carbon atoms. In branched alkenes, one or more carbon atoms are connected to three or four other carbon atoms. (Brandvik & Daling, 2015a) See Figure 2-1 for examples of chained alkenes.
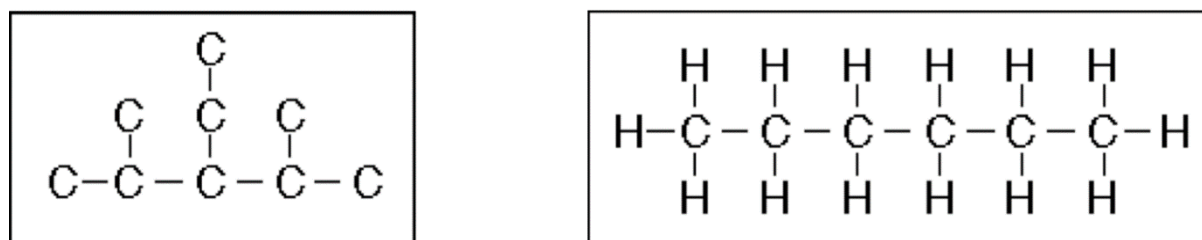
Figure 2-1: Example of branched alkene (on the left) and straight-chain alkene (on the right). Reprinted with permission from Brandvik, P. J., & Daling, P. S. (2015a). Crude oil composition, properties and laboratory methods to characterise crude oils [Lecture compendium KJ3050].

2.1.1.2 Cycloalkenes

Cycloalkenes are hydrocarbons containing one or more carbon rings. These rings can either be pure cycloalkanes or aromatic rings. A cycloalkane is made when three or more carbon atoms form a circle. The ring can be either wholly saturated or partially saturated. Furthermore, cycloalkanes can be attached to a carbon chain.(Brandvik & Daling, 2015a) See figure 2-2 for an example of a cycloalkene.
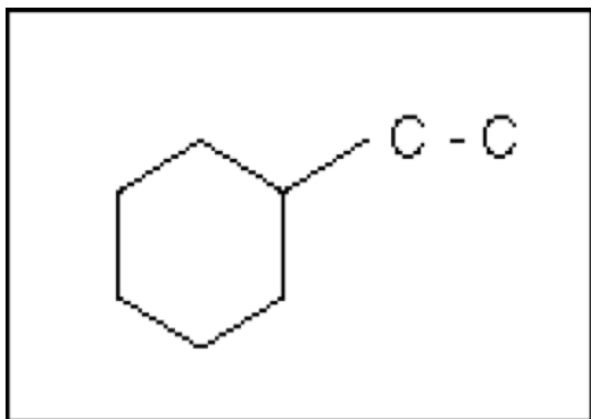
Figure 2-2: Drawing of a cycloalkane. Reprinted with permission from Brandvik, P. J., & Daling, P. S. (2015a). Crude oil composition, properties and laboratory methods to characterise crude oils [Lecture compendium KJ3050].(Brandvik & Daling, 2015a)

Aromatics are a particular type of cycloalkene. These compounds have alternating single and double bonds around the ring, increasing their stability. Aromatics usually form rings of five or six carbon atoms but can, in theory, consist of any number of carbon atoms above three. An aromatic can exist on its own, be connected by one bond, or be connected to a longer alkane chain. (Brandvik & Daling, 2015a) See Figure 2-3 for examples of aromatic compounds.
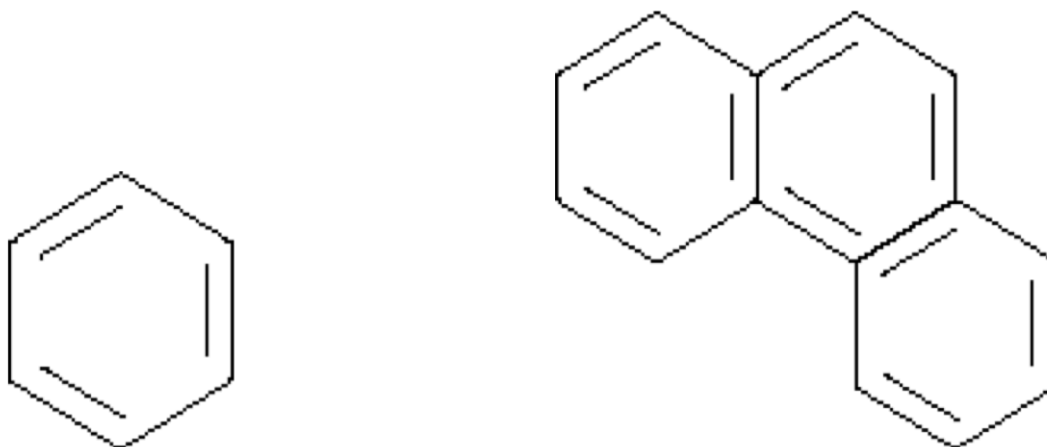
Figure 2-3: Example of aromatic compounds: a singular aromatic compound (benzene, to the left) and an interconnected compound (phenanthrene, to the right). Reprinted with permission from Brandvik, P. J., & Daling, P. S. (2015a). Crude oil composition, properties and laboratory methods to characterise crude oils [Lecture compendium KJ3050].

2.1.2 Non-hydrocarbons

Non-hydrocarbons are in petroleum organic chemical compounds that, in addition to hydrocarbons, contain small amounts of oxygen, nitrogen, sulfur, or trace metals such as vanadium or nickel. Non-hydrocarbons have a hydrocarbon base, but a hydrogen or carbon is

switched out with another atom. By switching out the hydrogen or carbon, the organic compound can transform to among other acids, esters, and nitrile compounds. Due to the difference in polarity force of the new atoms, small-chain compounds can be polar to semi-polar. (Brandvik & Daling, 2015a) See Figure 2-4 for examples of non-hydrocarbon compounds.
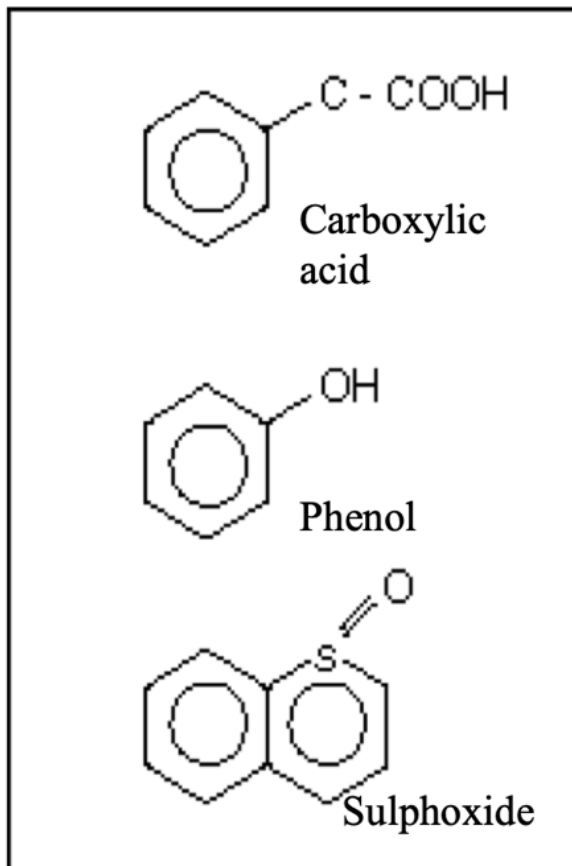
Figure 2-4: Examples of different non-hydrocarbon compounds. Reprinted with permission from Brandvik, P. J., & Daling, P. S. (2015a). Crude oil composition, properties and laboratory methods to characterise crude oils [Lecture compendium KJ3050].

2.2 Oil composition

Every crude is composed of different chemical components and has different properties and reactions. The considerable differences in properties lead to significant variation in optimal clean-up methods in the event of a spill, making it essential to map the responses of all new oil production sites.

The primary chemical groups in crude oil are paraffins, naphthenes, aromatics, resins, and asphaltenes. Paraffins and asphaltenes are the two groups that primarily affect an oil's solidification. This thesis takes a closer look at these two groups.

2.2.1 Definition of paraffin and wax

Paraffins are chained alkenes, and therefore completely hydrocarbonous and without any cycloalkenes. If a paraffin compound contains more than 20 carbon atoms, it is also defined as wax. Wax content is usually monitored and reported in wt%, where below 5–6 wt.% is considered average and above 10 wt.% is considered high (Brandvik & Daling, 2015a). The percentage of wax in an oil contributes to the behavior of the oil, especially the solidification process. The crystallization of wax is a highly discussed topic in science, especially regarding pipeline transportation of crude oil. Visintin et al. (2005) concluded that waxy oil behaves as a weakly attractive colloidal gel, which means that a solid (wax crystals) is dissolved in a liquid. Furthermore, although most of the substance is in a liquid form, the substance has the properties of a solid (Oxford-Colloid-Group, 2017). The solidity of the oil comes from the development of wax clusters due to interactions taking place between the wax particles; the wax aggregates and interacts until clusters span the whole material (Keshavarz et al., 2021).

First, the oil is weighed to find the wax content in crude oil. Then it is dewaxed before being weighed again. The difference between the weighings is the wax weight, which can be converted to wax-percentage by dividing the original weight of the oil. In SINTEF laboratories, the wax-determination method is based on Bridié et al. (Bridié et al., 1980). They mixed the oil with 2-methyl ketone and dichloromethane (1:1 ratio) and precipitated it at −10°C six times before weighing it (Sørheim et al., 2021).

2.2.2 Definition of asphaltenes

Asphaltenes, another major oil component, consists of condensed polycyclic aromatic compounds. Asphaltenes are the most polar parts of crude oil (Venkatesan et al., 2003). There is conflicting research about whether asphaltenes affect wax crystal formation and whether wax content affects an oil's solidification, and if so, how (Adebiyi, 2020; Joonaki et al., 2020). Different articles argue that the asphaltene content raises (García & Carbognani, 2001), lowers (Venkatesan et al., 2003), or does not affect a crude oil's pour point (Yang & Kilpatrick, 2005).

The asphaltene content in crude oil is determined by IP-143/90 or ASTM- D3279. Here, the heavy asphaltenes are found by seeing how much wt.% of the oil is soluble in n-heptane. First, the oil is weighed, then added to n-heptane. It is then shaken until all the dissolvable content is dissolved. The mixture is filtered, washed with heptane, dried, and weighed. The weight difference from the start is the weight of asphaltenes in the oil. The weight percentage

can be derived by dividing the asphaltene weight by the original weight.(Moradi et al., 2012; Petro-lubricant testing laboratories, 2020).

2.2.3 Asphaltenes' effect on pour point and wax crystal formation

Venkatesan et al. reasoned that the asphaltenes had similar structures and behaved as pour point depressants (PPD), which act by hindering wax crystal network formation, either by copolymer crystal modifiers or surfactants. The copolymer crystal modifier hinders the growth of wax formations by inserting itself into the network and breaking it up. The surfactant PPD surrounds the wax compounds, inhibiting them from reacting with one other. See Figure 2-5 for a drawing of how the different PPDs work.

(a) Co-precipitation modifies structure

(b) Surfactants coat and disperse
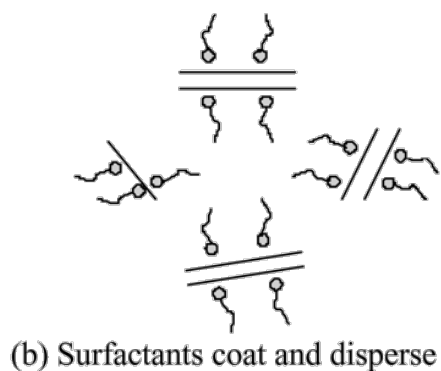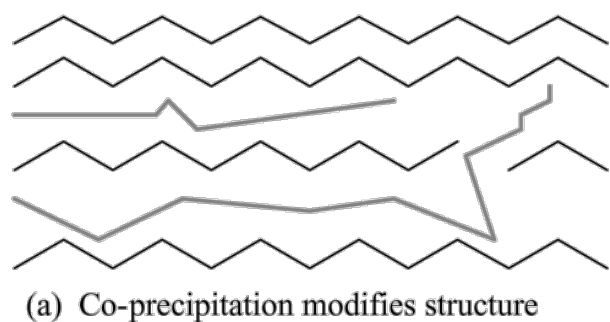
Figure 2-5: Shows how different pour point depressants interfere with wax crystal formation. A) How a co-precipitation modifies the crystal structure. And b) How surfactants break up the crystal structure. Reprinted with permission from The Effect of Asphaltenes on the Gelation of Waxy Oils, Ramachandran Venkatesan, Jenny-Ann Östlund, Hitesh Chawla, Piyarat Wattana, Magnus Nydén, and H. Scott Fogler, Energy & Fuels 2003 17 (6), 1630-1640 DOI: 10.1021/ef034013k Copyright 2003 American Chemical Society.

Additionally, Venkatesan et al. concluded that the polarity of the asphaltenes has an impact on an oil's solidification. Less polar asphaltenes decrease the gel point to a greater extent than

more polar asphaltenes. Therefore, the percentage of asphaltenes in a compound indicates the pour point, but different asphaltenes yield different percentages. (Venkatesan et al., 2003)

Yang & Kilpatrick argue that the asphaltene concentration does not affect the pour point. They concluded that the asphaltene concentration does not influence the wax formation; therefore, the solidification point is not affected. (Yang & Kilpatrick, 2005)

Garcia & Carbognani argue that "*flocculated asphaltenes in bulk crude oil behave like wax crystallization sites,*" which enhances the wax's crystallization and solidification. (García & Carbognani, 2001)

In more recent studies, it seems like the concrete molecular formula of the wax and asphaltene determines which of the three results arise: a reduced, increased, or unaffected oil solidification. It seems like there is no rule for whether the asphaltene will reduce, increase, or not affect the solidification of the oil (Taheri-Shakib et al., 2020).

2.3 Physical properties of oil

Crude oil has various physical properties affected by its components. This section defines the most critical parameters, including one way to measure those parameters. It should be noted that most of the physical properties also have other internationally accepted ways to be measured, but due to space restrictions, only one way of measuring is presented.

2.3.1 Pour point

The pour point is the temperature at which an oil ceases to flow when subjected to a slight movement after being cooled without disturbance (Brandvik & Daling, 2015a). The pour point is related to the oil's chemical composition, particularly its wax content.

The ASTM D97-17b procedure is the most recent standard American procedure to determine the pour point of any give(ASTM-international, 2018). See Figure 2-6 for a visual demonstration of determining the pour point. SINTEF has recently adopted ASTM D97 (Sørheim et al., 2021). The standard procedure for ASDM D97 is to have the oil in a water bath at a given temperature. Heat the oil to 9 °C above the expected pour point. The oil is lowered in 3 °C intervals and tilted until there is no observed movement for 5 s (Institute of petroleum, 2005). It is essential not to stir during the experiment. A wax web forms and makes the oil solidify, but when the oil is stirred, this web is destroyed, causing the oil to liquefy at a lower temperature.
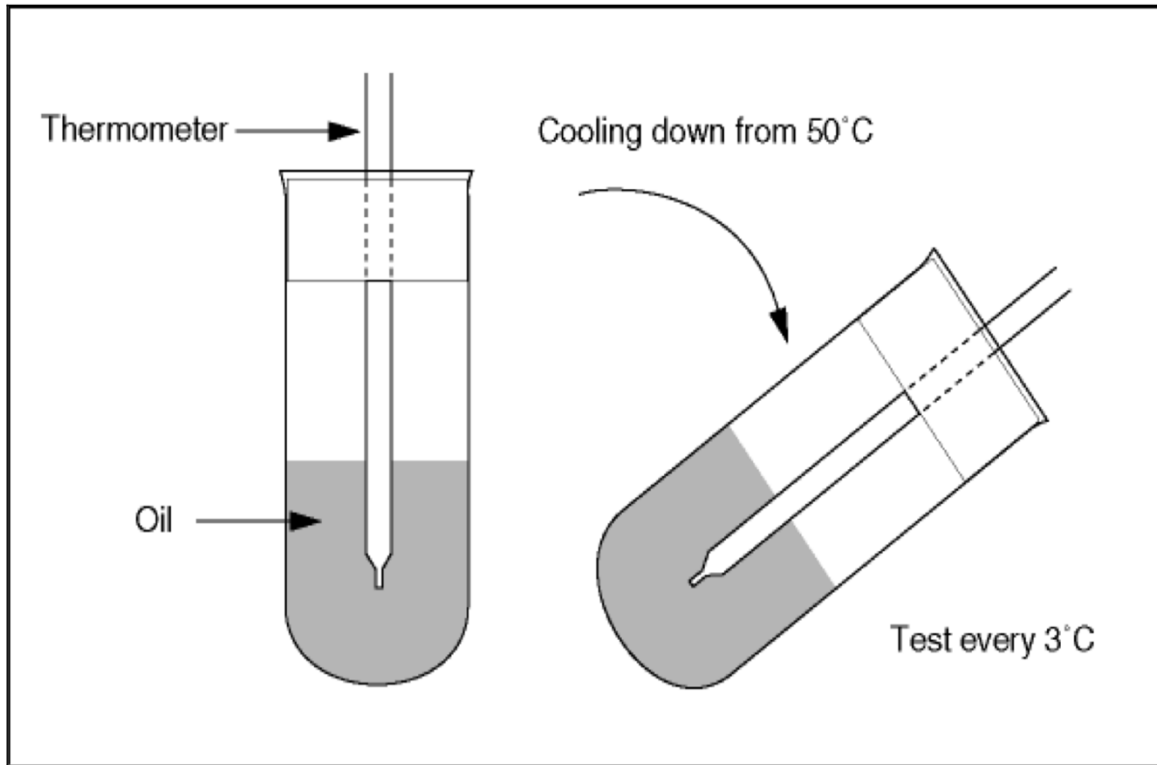
Figure 2-6: Demonstration of procedure for pour point determination. Reprinted with permission from Brandvik, P. J., & Daling, P. S. (2015a). Crude oil composition, properties, and laboratory methods to characterize crude oils [Lecture compendium KJ3050].

The ASDM D97 procedure yields an error margin of minimum ±3 °C, the same interval at which the oil is being tested. It should also be noted that the determination of the pour point is done purely by observation.

2.3.2 Density

Density is the mass of a substance per unit of volume (Merriam-Webster, 2022). For crude oils, the density usually varies from 0.780–0.99 kg/L (Brandvik & Daling, 2015a). The density varies based on whether the crude consists primarily of heavy- or lightweight molecular components. Although the density affects different aspects of a subsea release, one of the more critical properties in this thesis is that oil density affects the rising time of the oil droplets in seawater. A high density often results in a slower rising time.

Density is often measured in kg/L or by API gravity, which is mainly used in American literature. The formula for converting specific gravity to °API gravity is given in Equation 2-1.

$$°API = \frac{141.5}{Specific\ gravity} - 131.5$$

Specific gravity is the density of the crude oil at 15.5 °C divided by the density of distilled water at the same temperature.

A way to measure density is by ASTM method D4052-15 (Sørheim et al., 2012). In this method, 1–2 ml of oil is introduced into an oscillating test tube. The oil mass causes a change in the frequency of the oscillation compared to a control, which is measured. Using the change in frequency and some calibration numbers, one can calculate the density or API gravity using Equation 2-2:

$$density\ in\ g/mL\ at\ t = d_w + K_1(T_s^2 - T_w^2)$$

Here d_w is the density of water, K_1 is the instrument constant for density, T_w is the observed period of a cell containing water, and T_s is the observed period of the cell containing the sample (ASTM-international, 2016).

2.3.3 Viscosity

The viscosity of a liquid is its resistance to flow or inner friction and is measured in cP for oil. The viscosity for crude oils varies from 3–2,000 cP at 13 °C. Viscosity is affected by the chemical composition of the oil, where oils with a high ratio of lightweight molecular components often have a lower viscosity than oils with a low ratio (Brandvik & Daling, 2015a).

The viscosity of a petroleum product can be identified through different procedures. One of the more common methods is ASDM D445. This procedure determines the kinetic viscosity by measuring the time a specified amount of liquid needs to go through a capillary viscometer using only gravity as a force. The kinetic viscosity can then be transformed into dynamic

viscosity by multiplying the dynamic viscosity with the liquid's density (ASTM-international, 2021).

2.3.4 Buoyancy

The glossary of meteorology defines buoyancy as "That property of an object that enables it to float on the surface of a liquid, or ascend through and remain freely suspended in a compressible fluid such as the atmosphere." (Doswell III & Markowski, 2004; Glickman & Zenk, 2000) Applied to subsea releases, the buoyancy is the upwards force making the oil droplets travel through the water column and float at the surface. The driving force for buoyancy in a subsea release is a density difference (Olsen & Skjetne, 2015). Based on Archimedes' principle, the buoyancy force is given in Equation 2-3. It should be noted that the displacement of liquid in the ocean is not possible to measure but can be calculated in the laboratory.

$$F_b = V\rho g$$ *Equation 2-3*

Here F_b is the force of buoyancy, V is volume displaced liquid, ρ is density and g is the acceleration of gravity (Doshi, 2006)

A buoyant plume can be created during a subsea release, where a continuous release of buoyant fluid creates a rising force away from the source. (Cushman-Roisin, 2019). The driving force will then be the buoyant flux (B) given in Equation 2-4.

$$B = g\frac{\Delta\rho}{\rho_a}Q$$ *Equation 2-4*

Here g is the acceleration of gravity, $\Delta\rho$ is the density of oil and gas subtracted by the density of water. ρ_a is the density of water and Q is the total exit volume flow (Johansen et al., 2013; Papanicolaou & List, 1988)

2.4 Oil weathering

When released into the environment, oil changes its composition and physical properties based on different processes. This change affects both the oil's environmental impact and the

optimal clean-up procedure. This section discusses evaporation, dispersion, emulsion, and photooxidation. The different weathering processes are drawn in Figure 2-7, with the importance based on time exposed to nature in Figure 2-8.
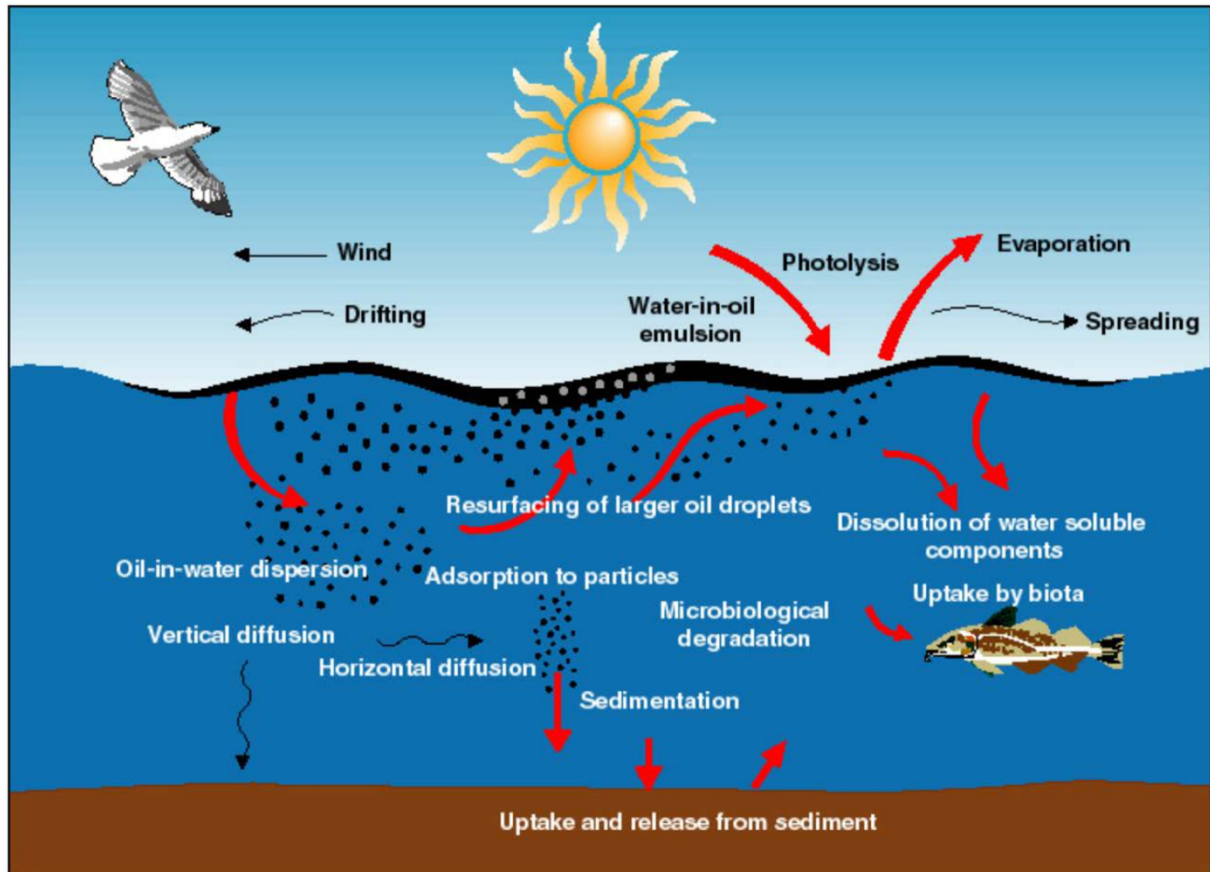
Figure 2-7: Drawing of different weathering processes oil is subjected to when released into the environment. Reprinted with permission from Brandvik, P. J., & Daling, P. S. (2015b). Weathering of oil spills at sea and use of numerical oil weathering models [Lecture compendium KJ3050].
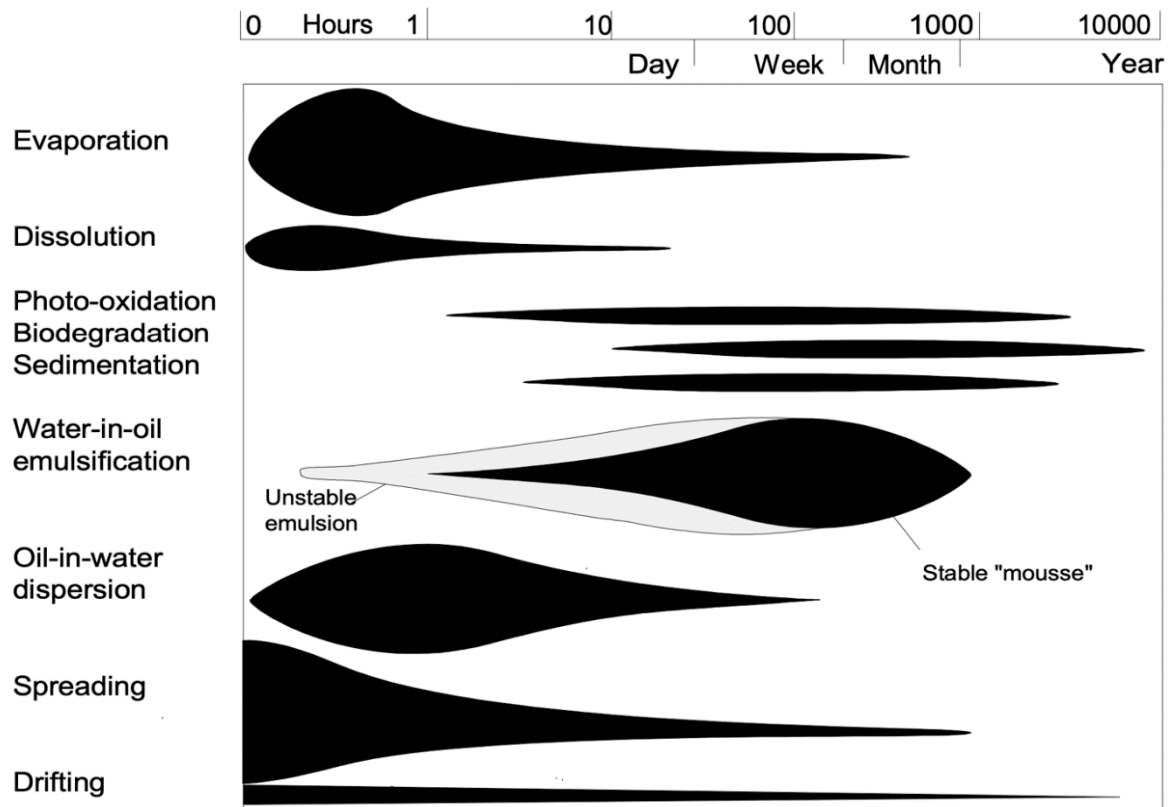
Figure 2-8: Shows when the different weathering processes predominate during an oil spill at sea. Reprinted with permission from Brandvik, P. J., & Daling, P. S. (2015b). Weathering of oil spills at sea and use of numerical oil weathering models [Lecture compendium KJ3050].

2.4.1 Evaporation process

Evaporation occurs when components from the oil transfer to the gas phase and escape from the slick. It happens primarily with the light components in the oil, as these are the ones with a low enough boiling point to convert to the gas phase with the help of sunlight or a high sea temperature. (Fingas, 2015)

The evaporation rate depends on the following factors: the proportion of light components in the oil, wind speed, sea temperature, and oil film thickness (Brandvik & Daling, 2015b). Due to the multicomponent nature of oil, another important regulator is the diffusion rate. The components that can evaporate during the current conditions need to diffuse through the heavier components in the slick to the surface before evaporating. (Fingas, 2015)

Evaporation rated as one of the faster weathering methods, and occurs mostly during the first hours of the oil spill but continues as long as components are light enough.

2.4.2 Emulsification process

Emulsification happens when water droplets are trapped in the oil film, changing the film's properties. The emulsification rate of different crude oils varies significantly. There is a correlation between the degree of emulsification and the oil's viscosity. Furthermore, wax, resin, and asphaltene content are essential in the emulsion process, as they make an interfacial film between the oil and water droplets. This interfacial film stabilizes the emulsion, increasing the maximum water uptake. (Brandvik & Daling, 2015b)

2.4.3 Oil in water dispersion

Dispersion and emulsification are competing weathering processes. The dispersion process is not entirely known, but the ocean breaks up the oil slick, and tiny droplets are formed and trapped in the water column. As an oil droplet with a diameter of less than 100 μm has a rising velocity of less than 1–2 m/hr, which is less than what the natural turbulence in the water column is assumed to be, it is presumed that a droplet of that size will never resurface (Brandvik & Daling, 2015b).

2.4.4 Photooxidation

Sunlight itself is a vital energy source, and by having sunlight on the oil slick for a period, oxidation of some components occurs. Typically, oxidization makes components oxidize into resins and asphaltenes. Oxidation usually makes the compounds more polar, stabilizing water in oil emulsions. (Brandvik & Daling, 2015b)

2.5 Oil spill clean-up methods

When petroleum enters the water, it might be essential to clean it up. Depending on the oil's properties and the weather conditions, a single method or a combination of various clean-up methods might be used to minimize the release's environmental impact. In some cases, the best response is no response. The oil might evaporate and disperse so quickly that human intervention is unnecessary. Therefore, it is crucial to know the oil's behavior before an accidental release.

The different coastal environments may also need special protection. If oil is released close to a fish-hatching habitat, dispersion might make a more negative impact on the environment than keeping the oil on the surface. Therefore, having information about a release point's environment is crucial for planning the best clean-up procedure.

This section presents the most common clean-up methods used today: dispersants, booming, and skimmers. The no-response response method has been described at the beginning of this

section and is not described further here. Section 2.4 oil weathering shows what would happen in a no clean-up response. Numerous instruments and chemicals are used in oil-spill contingency plans around the world. As most instruments differ depending on the manufacturer and country, and most specific, instrument- or chemical-build up are often company secrets, this thesis presents a generalization of each method.

2.5.1 Dispersant application

Dispersants are artificial soap-like structures that help the oil disperse into the water column by breaking the oil slick into smaller droplets. Dispersants usually contain one hydrophobic and one hydrophilic part. The aim is to have the hydrophobic part connect to the oil and the hydrophilic part connect to the water. As polar compounds dissolve in polar solvents and vice versa, the dispersant can surround the oil droplets and disperse in the water. (Brandvik & Daling, 2015c)

The hydrophobic part of dispersants is usually long alkane chains, while the hydrophilic part is polar groups such as carboxy, amino. Surfactants are often composed of the same structures used in the cosmetic or food industry, as those structures have low toxicity and high biodegradation(Brandvik & Daling, 2015c; Prince, 2015). However, an evaluation of the pros and cons for each specific release needs to be performed, as the dispersants and oil in the water column can harm ecosystems, which sometimes is more devastating than letting the oil weather naturally.
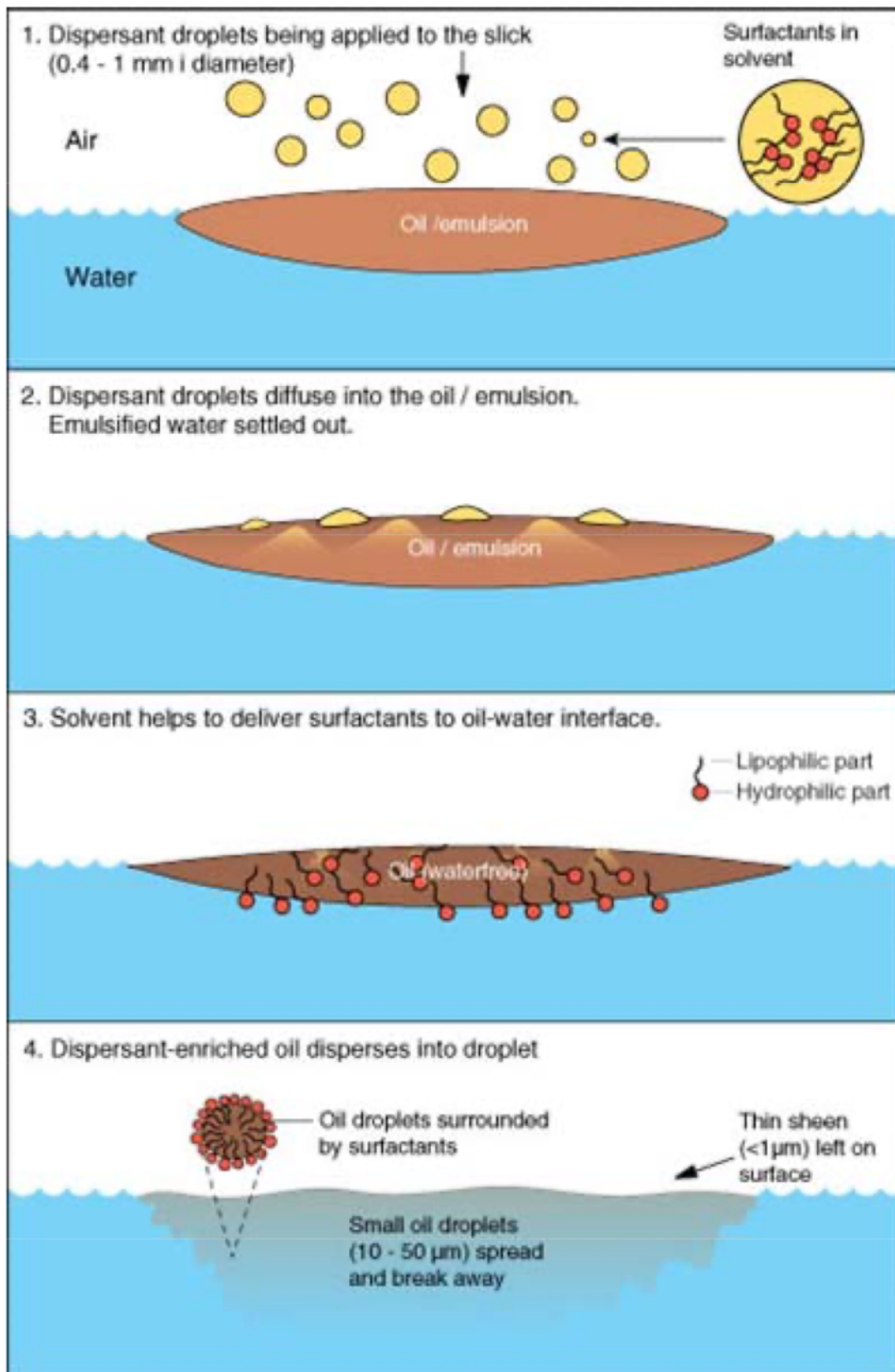
Figure 2-9: Drawing of the process of dispersion, where (1) shows the oil application, (2) shows the dispersant sinking into the oil slick,(3) shows how the different parts of the dispersant help sort the oil slick, and (4) shows how the dispersant creates tiny droplets that can break away from the slick and enter into the water column. Reprinted with permission from Brandvik, P. J., & Daling, P. S. (2015c). What are oil spill dispersants and how are they used? [Lecture compendium KJ3050].

Dispersants work by being sprayed onto the oil slick, either by air (plane or helicopter) or by sea (boat). When atop the slick, they penetrate the top layer and create smaller droplets that become trapped in the water column. For a visual representation of how the dispersants work, see Figure 2-9.

Because the dispersants penetrate the oil from above, the oil cannot be too viscous, as this can make the dispersants "roll off" the slick instead of penetrating it. Different crude oils vary in dispersibility at the same viscosities, but a rule of thumb is that about half of the dispersant effect is gone at 1,000 cp, and most are non-dispersible at 6,000 cp (Brandvik & Daling, 2015c).

Historically, the toxicity of dispersants has been a concern regarding their use. However, modern dispersants have as high toxicity as the shampoo used on birds during oil spill clean-up, and the necessary concentrations create only minimal adverse effects (Prince, 2015). Even though dispersed droplets still have a toxicological impact, which can be of great concern, it is often considered less harmful than keeping the oil at the water's surface.

2.5.2 Boom collection

Booming is a mechanical way to clean up oil spills. Essentially, it involves a large tube floating on top of the water. The tube contains the oil, keeping it from spreading any further. The booms can either be connected to the shore to stop oil from entering a small passage of water or connect to boats that drive around collecting oil. A typical boom contains a flotation device, a skirt, and ballast (Wong & Barin, 2003). See Figure 2-10 for a boom skimmer in use.
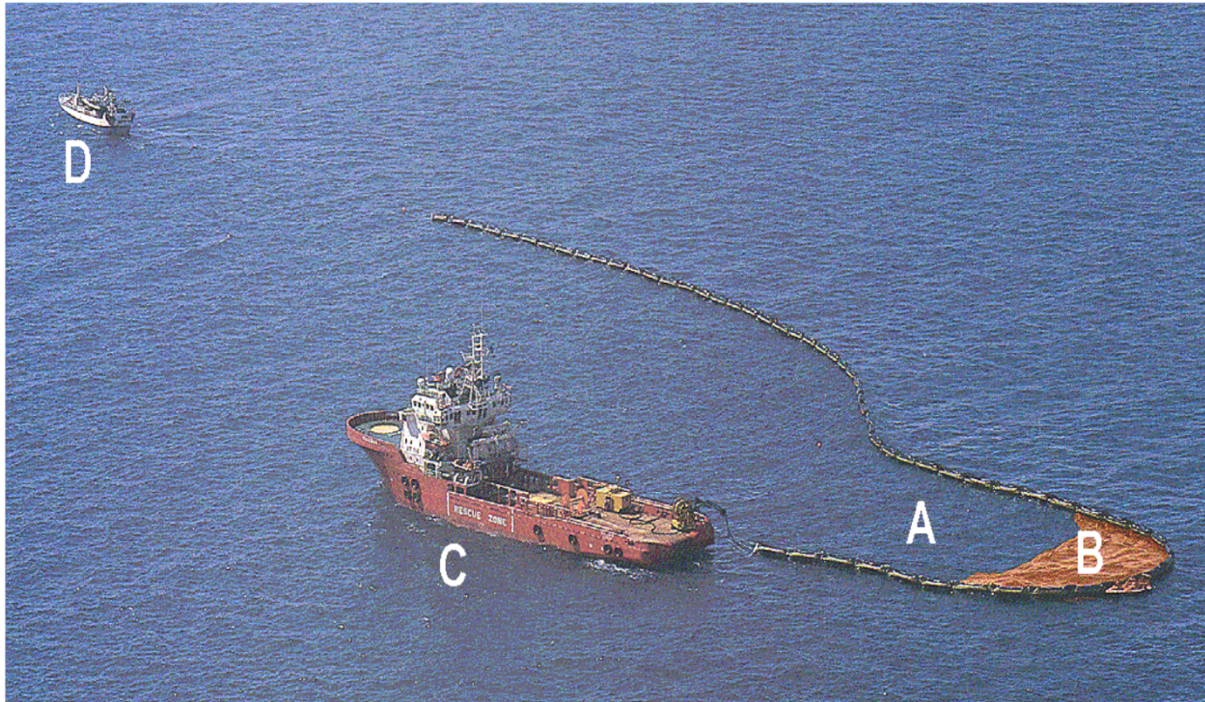
Figure 2-10: Booms in use in open water. A shows the boom, B the skimmer, C the main vessel, and D the asserting vessel. Reposted with permission from Brandvik, P. J. (2020). Oil Spill Contingency methods [Lecture presentation KJ3050].

The boom may fail under certain conditions. The boom failure most interesting for this thesis is critical accumulation, which happens when the oil viscosity exceeds 3,000 cs (ca 2,400 cp; (Delvigne, 1989). Critical accumulation happens when a critical velocity is reached to contain the oil at the leading edge of the boom. From there, the oil is swept under the boom at a critical accumulation point (Fingas, 2012).

2.5.3 Skimmer collection

Skimmers are a mechanical method of collecting oil. By using various materials, the oil separates from the water. Depending on the oil, skimmer, and weather conditions, different water-to-oil ratios can be collected.(Brandvik, 2020) According to the EPA, there are three types of skimmers: weir, oleophilic, and suction (Environmental Protection Agency, 2021).

Weir skimmers make an enclosure that floats on the water. As the brim of the enclosure is just above the surface, the oil floats over the brim and enters the enclosure. From the enclosure, the oil can be pumped into different barrels. However, weir skimmers are prone to become clogged by various debris. It has further been shown that a viscosity higher than 15,000–20,000 mPa•s reduces the skimmer's effect (Leirvik et al., 2001). See Figure 2-11 for a visual representation of the principles of a weir skimmer, and Figure 2-12 for a weir skimmer in use.
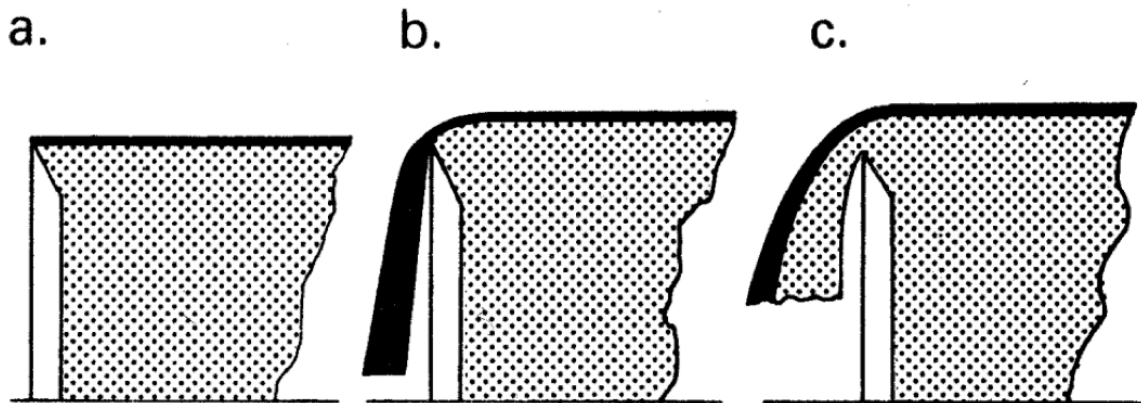
Figure 2-11: The principle of a weir skimmer, where (a) is too light of a barrier so that no liquid flows into the basin; (b) shows a perfect barrier, where only the oil is let into the basin; and (c) shows too heavy of a barrier, where both water and oil are let into the basin. Reposted with permission from Brandvik, P. J. (2020). Oil Spill Contingency methods [Lecture presentation KJ3050]

Figure 2-12: Example of a weir skimmer in use. Reposted with permission from Brandvik, P. J. (2020). Oil Spill Contingency methods [Lecture presentation KJ3050]

Oleophilic skimmers make the oil stick to oleophilic materials such as disks, belts, or ropes, separating it from the water. The material can then be squeezed or scraped into a recovery tank and reused. (Brandvik, 2020) See Figure 2-13 for a fox tail oleophilic skimmer in use.

Figure 2-13: Example of an oleophilic skimmer: a Foxtail rope skimmer being tested in a SINTEF laboratory. Reposted with permission from Brandvik, P. J. (2020). Oil Spill Contingency methods [Lecture presentation KJ3050]

A suction skimmer works like a vacuum to suck up the oil from the water's surface. The oil can then be stored in a tank. This skimmer needs a thick layer of oil and semi-calm weather to be effective, as the vacuum will suck up anything. However, the vacuums are prone to get clogged by various debris (Environmental Protection Agency, 2021). See Figure 2-14 for a picture of a suction skimmer.

Figure 2-14: An example of a suction skimmer in use. Reposted with permission from Brandvik, P. J. (2020). Oil Spill Contingency methods [Lecture presentation KJ3050](Brandvik, 2020)

2.5.4 *In situ* burning

In situ burning is an oil spill clean-up method where the oil is set on fire to evaporate and burn most of the spill. It is one of the oldest oil response methods, and have been used for land-spills for as long as land-spills have existed. There is however, little documentation of the first *in situ* burnings. (Fingas, 2011) In depth research on the technique in water started around 1980 wich is quite recently compared to other clean up methods.(Buist et al., 1999; Fingas, 2011) The technique removes the surface oil relatively rapidly and effectively, but toxic smoke might be released from the burnout, and a heavy residue remains (Faksness et al., 2022). See Figure 2-15 for a visual representation of an in situ burning

Figure 2-15: Example of in situ burning being tested in the Arctic. Reposted with permission from Brandvik, P. J. (2020). Oil Spill Contingency methods [Lecture presentation KJ3050]

The properties that determine the effectiveness of burning oil have not yet been understood (van Gelderen et al., 2021). *In situ* burning has been used on large clean-up sites with high efficiency. The burning of the oil in Exxon Valdes reported losing 98–99% of the weight using *in situ* burning (Allen, 1990; van Gelderen et al., 2021).

For *in-situ* burning to work properly, fuel, oxygen, and a source of ignition are needed. Furthermore, the slick thickness must be 2–3 mm and emulsification of the slick low (less than 20–30% water). A thin slick thickness or a high water percentage makes the burning slick lose heat to the water and extinguish itself (Bullock et al., 2019).

Van Gelderen et al. state that the evaporation order of the oil's components is the most crucial part of determining how well an oil will burn. There is conflicting research on whether the volatile component burns first and then if the less volatile components evaporate or if all the oil burns. It seems like newer research leans toward the volatile compounds burning first. In that case, the fire needs to generate more and more heat for the less volatile components to

burn. Afterward, it extinguishes itself when the heat emitted from the less volatile components is insufficient to make the next component burn (van Gelderen et al., 2021).

2.5.5 High wax recovery procedure

Few of the above clean-up methods have been proven effective in the laboratory for high-wax oil. For this reason, Norne's field had to close for 35 days in 1998 to discover effective ways to clean up wax-rich oils (Moldestad, 2006). Over the past 24 years, the development has advanced significantly, and both mechanical and chemical methods have been found to be effective. It should be noted that chemical recovery procedures described here work to lower the wax formation so that clean-up crews can utilize the clean-up methods that were described previously.

Chemical recovery utilizes wax inhibitors. *Wax inhibitors* is an umbrella term for "various ways to prevent the effect of wax-formation." Wax inhibitors can be pour point depressants, as described in section 2.2, thermal wax inhibitors, dispersants, or surfactants (Ruwoldt et al., 2017; Ruwoldt et al., 2019). The chemical reactions of the wax inhibitors are unknown, but their effectiveness is well-documented. Although the effect of wax inhibitors is powerful in pipelines, adding it after a release, such as with dispersants, seems ineffective (Sørheim et al., 2012).

Development of mechanical recovery for high-viscosity oil has also been researched. For example, high-viscosity skimmers are well-developed, where belt skimmers and other skimmers exploiting the wax-interaction within the slick have proven effective. These skimmers lift the oil from the water. From there, the skimmer feeds the oil into a valve (Hvidbak & Mosevej).

The weir and drum skimmers can also be helpful in high-viscosity oil recovery. Creating a vortex and mechanically breaking the wax crystals can lower the oil's viscosity and help recover the oil (Sabbar et al., 2021).

2.6 Current oil detection methods

2.6.1 Oil spill detectors

A blowout usually releases enough oil to be easily detected by the eyes. However, minor releases and leaks might require other detection methods to find them. Radar and other tools are essential to detect those types of oil spills (Lu et al., 2020). For a visual representation of how an oil spill looks using radar detection see Figure 2-16.

Figure 2-16: Example of an oil spill observed by radar. Reposted from Oil spill detection by satellite remote sensing. Remote sensing of environment, 95(1), 1-13. By *Brekke, C., & Solberg, A. H*, 2005, Copyright 2004 by Elseviser Inc. Reprinted with permission

Oil spill detection methods can be classified as either passive or active. Passive detection often uses a visual or an infrared camera to sense the oil. The problem with passive detection is that oil does not differ much from water in the visual spectrum. Furthermore, detection is dependent on the weather. Too much sun, clouds, or darkness confuses the detectors. Infrared detection also has a high error rate, as it often confuses seaweed and other marine matters for oil. However, passive detection is inexpensive. A UV camera can also be useful for tracking oil sheens and is considered suitable for determining slick thickness. Nonetheless, these cameras also mistake oil for other marine debris (Fingas & Brown, 2018).

Satellite radars are one of the main spill detectors for offshore oil spills (Fingas & Brown, 2014). The satellite works independently of the weather, but clutter is still a major factor. Twenty percent of classified oil spills are later found to be false positives; however, several different algorithms have been proposed to improve accuracy (Liu et al., 2010). In the algorithm, slick source, shape, size, dimensions, texture, damping, and gradients are used to

determine if there is a spill or not (Espedal & Johannessen, 2000). It should be noted that the algorithm has a sense of self-learning as well, so the exact parameters vary depending on the algorithm.

2.6.2 Fluorescein tracing

In addition to using different methods to detect oil spills, fluorescein has been added as a tracer to different oil reservoirs. Fluorescein as a tracer is proven effective for both oil spill behavior research and findings of well reservoirs. (Aparecida de Melo et al., 2001; French-McCay et al., 2007)

Fluorescein is shown in Figure 2-17. It is a tracer that will emit green light when exposed to blue light and are active even in small amounts. Its´ light is visible to the naked eye in even small amounts and is considered non-toxic to the environment (Pataveepaisit & Srisuriyachai, 2020).
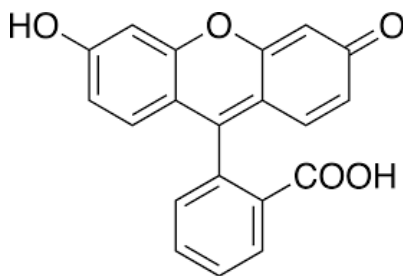
Figure 2-17: Drawing of the fluorescein molecule.

2.7 Subsea releases

Due to the big variations in releases and oils, it is important to classify a release as accurately as possible, both during the release, to have a correct response, and before a release to have correct predictions. Therefore, every release is classified and characterized into one of the many divisions of releases. In this section, the different variables that decide the spill's behavior will be described.

The place of the release is one of the fundamental differences between spills; therefore, it is important to classify the place correctly. Due to this thesis' focus being on subsea releases, surface releases are only mentioned in the introduction of this section. There is also a division between a subsea blowout and a leakage. As this thesis primarily looks at subsea blowouts, it will be focused on blowouts if not specified otherwise. However, many of the droplet mechanics of a blowout will be similar if looking into a leakage.

An oil release is usually divided into two categories based on how the spill happens. If the oil is released above the sea's surface, it is called a surface release, while if the oil is released below the sea surface, it is called a subsea release. The nature of those two releases are fundamentally different, as a subsea release must travel through the water layers before reaching the surface; therefore, it has different spreading behaviors.(Brandvik & Johansen, 2020) It should be noted that once the oil reaches the surface, the same weathering processes occur for subsea and surface releases. Thus, only time intervals and slick formation are different for subsea versus surface releases. A typical surface release results from boat failures, such as collisions, strandings, or controlled releases(Board & Council, 2003; ITOPF, 2021). Subsea releases are usually due to well or pipe failures (Olsen & Skjetne, 2015). Since subsea releases typically involve releasing from a more significant supply of oil, they tend to last longer. In contrast, surface releases are often more momentary releases.

A subsea release is a release that happens under the sea surface. It is usually divided into deep-sea and medium-depth release, as the plume's behavior varies in those categories. The division is based on whether the release reaches the surface immediately or bends horizontally in the water column to become an underwater plume. Usually, the division between a deep-sea release and a medium-depth release is 500 m(Brandvik & Johansen, 2020). However, the gas-liquid ratio also plays a significant role in how the release is characterized.

A subsea release is classified as "all gas or oil leaks under the sea's surface." Scientists divide subsea release into different categories based on the amount of oil or gas leaked and the release point of the oil. A seep happens when oil is released from the seabed. Seeps can happen naturally or be anthropogenic. A leak is when oil is released due to faulty equipment or infrastructure. A rupture is a primary or complete break of a gas line, while a blowout is the loss of barrier control in a well. The different categories can further be divided based on the rate at which the oil is released if needed.(Olsen & Skjetne, 2015).

2.7.1 Droplet formation

The oil droplet size distribution (DSD) is one of the most significant determinants of the plume in a single-phase oil plume (Boufadel et al., 2020). The most active degradation and a coalition of the droplets in a subsea release occur during the first few meters of the release point, probably because this is the area releasing the most energy (Li et al., 2017).

The droplet formation process was first described by Hinze. Hinze concluded that the interfacial tension between the oil droplets and the water face would create the droplets we

experience in a turbulent jet stream (Hinze, 1955). This has been expanded but is still used to describe droplet formation today (Boufadel et al., 2020).

Researchers today are still trying to find a suitable mathematical expression to calculate and simulate the DSD. Many researchers have investigated dead oil (purely liquid oil), and now they are trying to simulate live oil (gas and other things being released together with oil).

One way to calculate the predicted droplet size is by using a diagram containing the Reynolds number (Re) and the Ohnesorge number (Oh; Masutani & Adams, 2001; Tang & Masutani, 2003). The Reynolds number is the ratio of inert forces to viscous forces and is given in Equation 2-5 (Rehm et al., 2008; Reynolds, 1883).

$$N_{Re} = \frac{pvd}{\mu}$$

Equation 2-5

Here p is density, v is velocity, d is the diameter, and μ is viscosity.

Ohnesorge number is the ratio of internal viscosity dissipation to surface tension energy. It is used to account for the liquid viscosity in the droplet formation (Li, 2008). The formula for the Ohnesorge number is given in Equation 2-6 (McKinley & Renardy, 2011; Ohnesorge, 1936).

$$Oh = \frac{\sqrt{We}}{Re}$$

Equation 2-6

Here We is the Webster number, which is given in Equation 2-7.

$$We = \frac{pv^2l}{\gamma}$$

Equation 2-7

Here, p is density, v is velocity, l is the length (typically the droplet diameter), and γ is surface tension (Rapp, 2017).

The DSD will be a probability function with a normal distribution. The variance and mean define a normal distribution to give a bell curve function, which will be needed to get a correct DSD distribution as well. It is only necessary to find the mean and variation. The DSD prediction has been further developed to predict the droplet size based on Webster and Ohnesorge's numbers to make a normal distribution (Li et al., 2017).

This calculation shows that the droplet velocity, droplet diameter created by the hole size, surface tension, density, and viscosity are the contributing factors to the droplet sizes in a subsea blowout. A big blowout leads to a wide range of droplet sizes due to the normal distribution of the droplets.

2.7.2 Plume behavior

"A plume is a body of fluid-driven by the buoyancy (density between the fluids)" (Boufadel et al., 2020). A plume is usually a collection of gas, oil droplets, or both released from an outlet in a subsea release, creating a solid force traveling upwards. Plumes operate differently depending on whether they are one component—either oil or gas—or a combination of both (Socolofsky et al., 2011).

During a subsea blow out, the release will start off as a forced plume, which is defined as a release that have a difference in density to the water, and are dependent on momentum, buoyancy and mass.(Morton, 1959) The release will behave in a jetlike or plumelike manner depending on its initial volume flux, momentum flux and buoyancy flux.(Papanicolaou & List, 1988)

In a medium-depth subsea release, the oil and gas travel straight up and unravel at the top. It will therefore only have jet behavior, which is driven by a pressure drop from a orifice (List, 1982) In this situation, all the gas and oil does not have time to dissolve in the ocean, and a separate phase of gas may continue up into the atmosphere (Leifer et al., 2006).

In contrast, in a deep-sea release, most of the gas and oil is entrapped and dissolved in the seawater column or condensed into a liquid phase. This will create a plume, which is driven by the buoyancy alone. (Morton et al., 1956) For example, this happened in the Deepwater Horizon blowout (Gros et al., 2017). All forced plumes will convert to a plume if given

enough space and time, but it is possible for the jet to reach the surface before converting to a plume, which is what happens during medium-depth release. (Morton, 1959).

2.7.2.1 Multiphase plume

Two forces decide the fate of a multiphase plume in a subsea release: current and stratification. Stratification is a separation of the oil and gas droplets by buoyancy and, therefore, size. The oil and gas droplets become trapped at different places in the water column where the local turbulence matches the buoyancy of the droplet. The current is the local seawater current, gently trapping and bending the plume.(Socolofsky et al., 2011) See Figure 2-18 for a visual representation of the different plumes one can get.

A pure current plume usually traps ambient fluids such as seawater, creating a plume traveling with the present water current. Usually, the most buoyant gas and oil droplets separate from the plume, either by stratification or ambient currents, and travel to the surface.

The separation of the seawater plume and the buoyant gas and oil droplets in a stratification-dominant situation stops at a height (h_p) where the natural buoyancy can no longer lift the entrapped seawater. Consequently, a downward plume consisting of seawater and dispersed hydrocarbons is created. In a situation where droplet, plume separation is current-dominated, the separation happens at a height (h_s) where the plume is getting trapped by the seawater current, causing the plume to curve more steeply than the oil droplets. The plume behaves as a single phase with a stratification if $h_p > h_s$ and behaves as a single phase with current domination if $h_s > h_p$ (Socolofsky & Adams, 2002; Socolofsky et al., 2011).
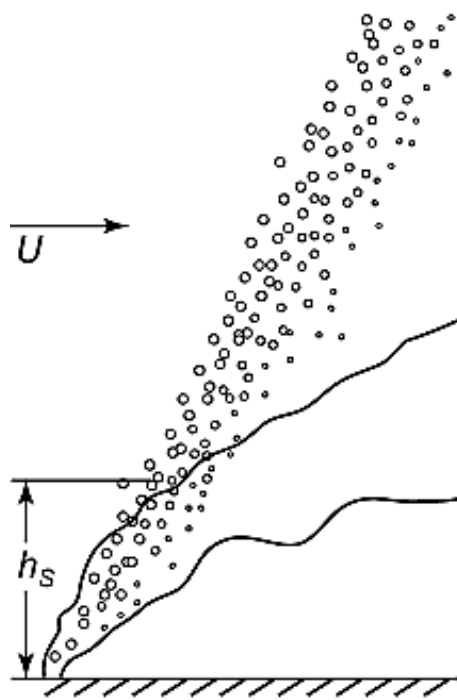
a.) Pure Current
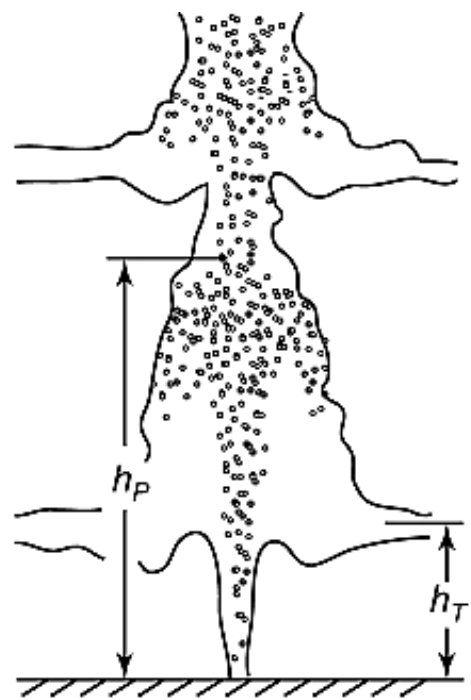
b.) Pure Stratification

Elevation View
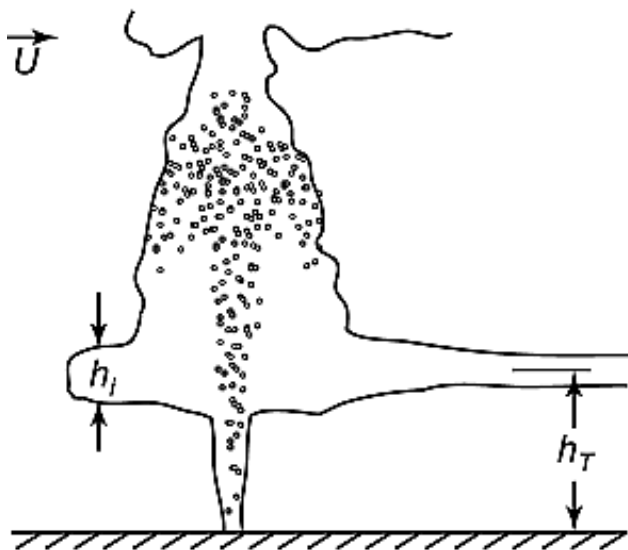
Plan View
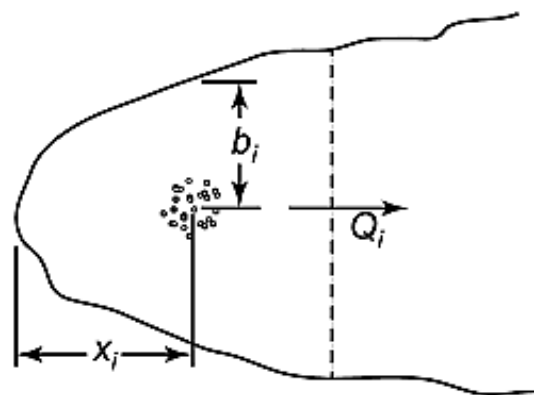
c.) Stratification Dominant in Weak Current

Figure 2-18: Drawing of plume after a blowout whit a.) Pure current b.) pure stratification and c.) Stratification dominating plumes in a weak current. The circles represent oil or gas droplets, curved lines represent edges of entrained seawater and hydrocarbon plume. Reposted from Socolofsky, S. A., Adams, E. E., & Sherwood, C. R. (2011). Formation dynamics of subsurface hydrocarbon intrusions following the Deepwater Horizon blowout. Geophysical Research Letters, 38(9).

2.8 OSCAR

Different simulation programs have been developed in response to learning how the oil travels, behaves, and affects the area around a spill. In SINTEF, OSCAR has been produced to simulate oil spills. OSCAR is a 3D numerical model of the chemo-physical behavior of spilled oil. It can be used to simulate different response methods and to see how the oil behaves physically (Reed et al., 1995). See Figure 2-19 for a drawing of the outputs one can get using OSCAR.

Based on a user's needs, OSCAR can simulate a spill using actual weather and current data and an oil whose parameters have been documented in the laboratory. A simulation allows scientists to see how the oil will spread and which regions will be affected. Scientists can also see how the oil will behave based on mass balance, emulsion, viscosity, and other parameters discussed earlier in this thesis. OSCAR can also simulate different response methods to see which one will be most effective, both in general and when there are special circumstances. One example of a special circumstance is when one specific area, such as a nearby nature reserve, needs to be protected.

The simulations can happen stochastically to predict how the oil will behave when released or by using known data as if a release were happening at a certain time on a particular date.
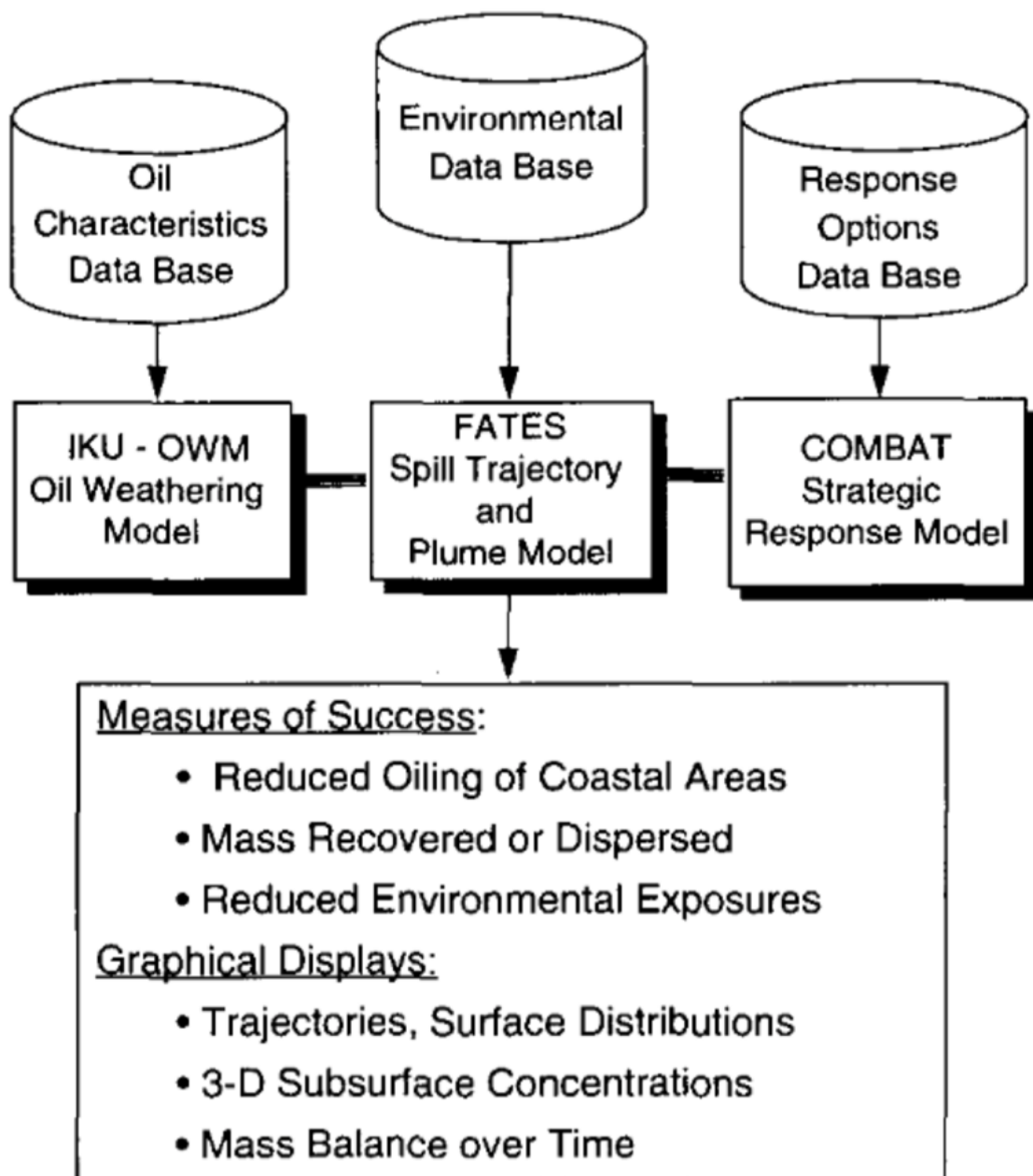
Figure 2-19: Schematic drawing of inputs and outputs of OSCAR (Reed et al., 1995). Reposted from: Quantitative analysis of alternate oil spill response strategies using OSCAR. Spill Science & Technology Bulletin, 2(1), 67-74 by Reed, M., Aamo, O. M., & Daling, P. S. 1995, Copyright by Elsevier Science Ltd. Reposted with permission

For this thesis, the numerical weathering model, OSCAR, has been used to investigate realistic time frames of an oil spill and mimic the behavior of a spill. OSCAR was developed at SINTEF in 1990 and has been continually updated since then. OSCAR uses laboratory data from different weathering studies done at SINTEF to predict how an oil spill will behave. Specifically, OSCAR uses metrological and geographical information and statistical modeling.

2.9 Stokes' law

"Stokes' law is a mathematical equation that expresses the drag force resisting the fall of a small spherical particle through a fluid medium" (Gregersen, 2021). Equation 2-8 solves for the velocity of the particle:

$$v = \frac{2}{9} * \frac{(d_1 - d_2)}{\eta} * gr^2$$

Equation 2-8

where d_1 is the density of the sphere (kg/m^3), d_2 is the density of the fluid (kg/m^3), η is the viscosity of the fluid ($\frac{kg}{m*s}$), g is the acceleration of gravity ($\frac{m}{s^2}$), and r is the radius of the sphere (m).

It should be noted that Stokes' law does not consider any turbulence created by the sphere (Gregersen, 2021). As there is usually a plume in addition to oil, there are probably some deviations from the number found in the simulation versus real-life releases.

Drag force and maximum droplet diameter should also be considered for calculating the correct rise time. However, in the experiments carried out for this thesis, the maximum droplet size was 1.5 mm, which is so tiny that it does not override the maximum droplet diameter. Although an error is to be expected due to drag force and turbulence in the water column, it should be negligible due to small droplet size, and Stokes' law should be adequate to calculate the rise time for different droplet sizes in the modeled subsea release.

3. Method development

The inverted cone has never been used in experiments with a high pour point oil nor for observation of surface activity. This resulted in new problems that had to be solved in the best way possible. This section presents the most significant problems and how they were solved during the experiments.

3.1 Injection system improvements

The first significant problem arose while testing the highest pour point oil in this experiment, Duva, on the inverted cone. During the injection of Duva, the oil came out as a long worm, see Figure A.1-1 and A.1-2. As presented in Section 2.7 The droplet formation is based on, among other factors, viscosity, and release energy. As the force was insufficient compared to the viscosity of Duva, droplets were not created, and we got a worm instead. Since the first pump setup was a bypass injection system, we tried to shorten the injection time as much as possible to make the worm become a droplet but failed.

3.1.1 Heating the injection system

The problem was believed to be that the oil was too viscous to become droplets when injecting. As heat makes the oil less viscous, a way to heat the oil throughout the injection was needed. A decision was made to focus on the column from the pump to the three-way valve. Due to the injection syringe being connected to the pump and the syringe having more than one injection of oil, it seemed complicated and unnecessary to try heating that part of the injection system. With help from SINTEF's engineers, the choice was narrowed down to two possibilities: an electric heating element or an opposite-flowing hot water stream outside the column. The water stream was chosen because it would provide more control over the heat. The water could not heat the column above its own temperature. Since the water stream gave better control of the injection temperature in the experiment, the water stream was preferable with consideration for Health, safety, and environment (HSE). If oil gets overheated in a limited area, there is a risk of an explosion, and having a heating element that might err to heat too much seemed unnecessary when we had other solutions. It should be noted that the water stream had a water leakage risk, but as the inverted cone also had this risk, precautions for leakage had already been implemented. See Figure 3-1 for a drawing of the pump inlet, with corresponding names.
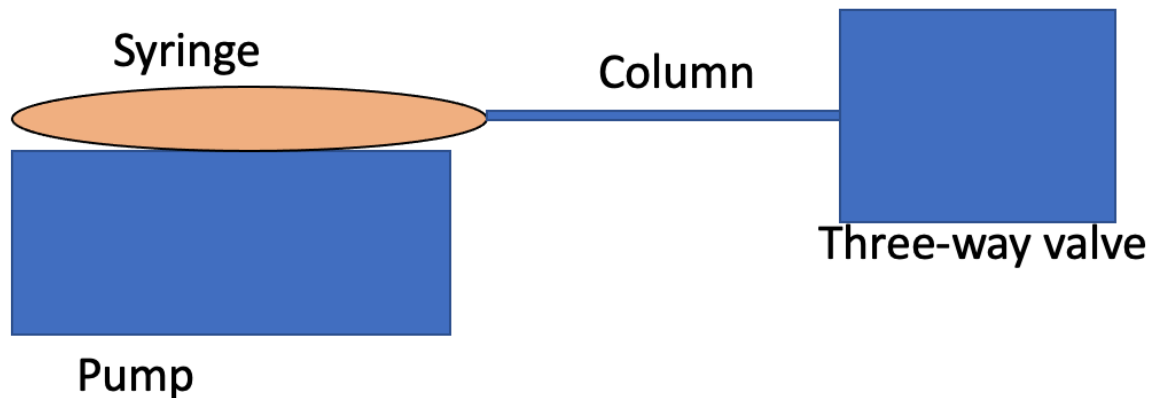
Figure 3-1: Drawing of the injection system of the inverted cone with the corresponding names.

3.1.2 Changing the injection system

The original setup was adjusted so that the syringe was heated from the pump to the three-way valve by having a warm water column surrounding the syringe run water in the opposite direction. When the test was performed, the oil solidified and made the worm as the valve was still cold. The metallic valve could not be surrounded and externally heated because it was exposed to cold water in the basin. Furthermore, the injection column was already being surrounded by the electronics for injection control outside the basin. Another solution was needed. A decision was made to change the bypass system to a two-injection system in addition to heating the column. Instead of having the oil go to waste or injection, there were two injection sites—one from the pump and one from a hot water source. It was now possible for the injection valve to be internally heated with hot water for a couple of seconds before injecting the oil. The disadvantage of this system was an increase in the amount of oil that needed to be injected each time, as there was no bypass flow of oil, making it possible to inject only a few droplets. Without the bypass flow, the oil takes more time to get to the valve head; therefore, there is variation when the oil reaches the basin.

Furthermore, if the valve were open for oil injection, oil would travel into the column. The same problem was present with the pump being turned off. The hot water injection made a different current and affected the oil droplets, so the water injection into the valve could not

remain. A method was found to solve both the non-intended injection and hot water stream, but the injection became a process that needed some skill.

3.1.3 Final process used to inject the oil

The process became as follows: First, heat the water by having the water flow on but have the injection valve set to oil injection. Then, switch the injection valve to water injection for a few seconds. Afterward, turn off the water flow while still having the injection valve set to water. Then, switch the injection to the oil valve and turn on the oil pump until oil droplets are seen. Finally, turn off the oil pump and switch the injection valve to water injection (without turning the water on).

It should be noted that this process should be possible to automate. However, the previous automated-injection was based on time and pump-speed. It proved difficult to automate as the start placement of oil stream in column varied, probably due to the water stream washing some of the oil away. As the manual injection was quite streamlined and did not need to happen often, this process was not optimized further. I would consider having a transparent injection valve to observe the oil if further optimization is desired. By giving the operator more time to react, it would be possible to release less oil into the basin. Less oil would make the rest of the experiment easier to complete due to reducing the interference of other oil droplets, there would also be a reduction of oil waste.

3.1.4 Changing the syringe

Without the bypass system, a new problem arose. It became more challenging to control the droplet size and almost impossible to get droplets that were small enough for our experiment. At this stage of the experiment, a decision was made to have three droplet sizes, where the smallest was about 500 µm and the largest 1,500 µm. The smallest droplet detected using the current system was around 2,000 µm. Therefore, the syringe was changed from 20 mL to 100 mL to make it possible to have a higher release velocity. This helped somewhat but was not sufficient to get the smallest droplets. Therefore, more intrusive ways were considered to get small enough droplets. The injection valve was disconnected, and the injection nozzle was adjusted from around 0.5 mm to 0.1 mm. The smaller nozzle size and increased velocity contributed to the formation of smaller droplets. This combination made it possible for small droplets to form and be controlled. For a schematic drawing of the final injection system, see Figure 3-2.
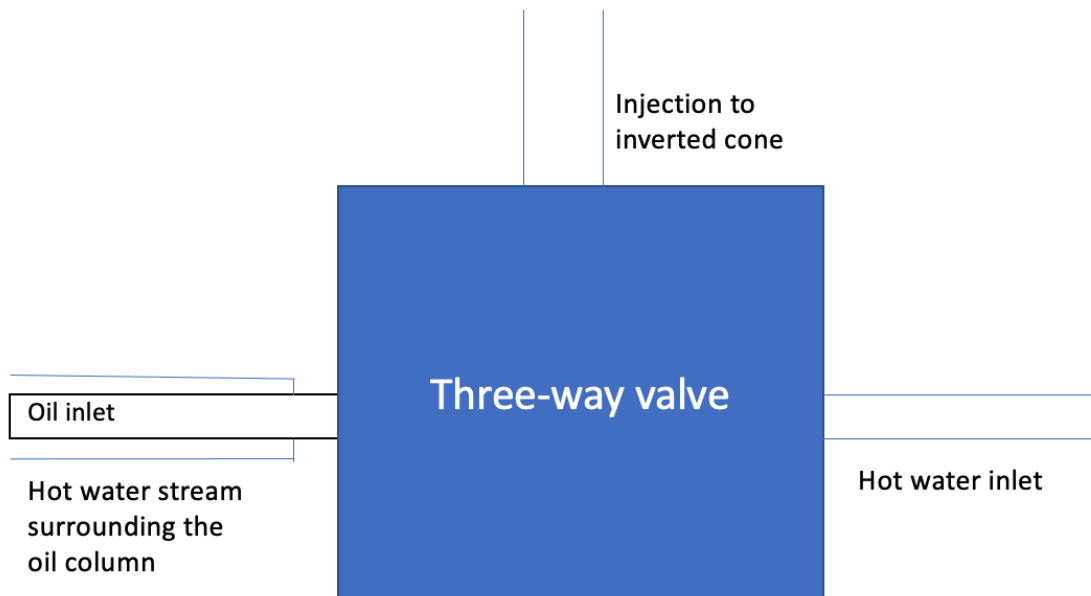
Figure 3-2: Schematic drawing of the pump inlet.

3.2 Oil droplets sticking to walls

The stickiness of the high pour point oils created problems because the oil stuck to the walls. At first, this problem only ruined the aesthetics at the bottom of the instrument, which did not matter. However, the oil sticking made the instrument's materials more oleophilic, making more of the oil stick after each injection run and causing a considerable number of droplets to accumulate. Time was lost when the droplet connected to the wall during a long run yielding no results. Which was especially concerning for the experiments that used hours per run. Numerous solutions were discussed, from coating the instrument in oleophobic substances to adding something in the water to make the water more attracted to the plexiglass. However, there was no data on any previous experiment using similar techniques nor the deviation that might result. Instead, the basin was washed with dish soap (Zalo) when the buildup became significant. Hot water was also discussed as a possibility. However, hot water creates the danger of cracking the plexiglass. The soap also added a bit of an oleophilic characterization to the plexiglass, which hot water could not do.

The washing process added a bit of risk, as the bottom part of the machine needed to be disassembled to clean the instrument. Some fragile parts could and did break when the machine was disassembled. If this experiment were to be replicated, one idea might be to find an easier way to clean the machine. However, at the time, there was no better solution.

The oil sticking created another problem as well. Sometimes the oil would stick to the surface of the photo zone. This made it difficult for the program in MATLAB to identify the oil droplets and determine the correct size of the droplets. The discrepancy was solved the same way as the oil sticking to the walls. Regarding this topic, it should be noted that MATLAB has the ability to write a program to regulate the current so that a droplet stays in the photo zone. However, the higher pour point droplets were challenging to regulate, and the program used in this experiment often lost the droplet. This was especially evident during long-run times. The experiment was easier to control manually, as updating the program would take too much time.

3.3 Detection of droplets

After making sure the droplets were released and captured in the photo zone, we needed to find a way to see the droplets on top of the basin. The best way to get our results was by having cameras catch the droplet behavior when the droplets reached the surface and use human observation to conclude whether the droplet solidified.

3.3.1 Camera placements

The measurement from the top of the cone to the ceiling was only a few centimeters, and it was impossible to place a camera over the inverted cone. Consideration was briefly given to moving the inverted cone to a room with a higher ceiling. However, this solution would have taken a lot of time and effort. Additionally, the present room was temperature controlled. Therefore, a decision was made to stay in the same room. Instead, a circular hole was cut over the waterline, making it possible to place a camera inside the basin and connect it to the ceiling. The camera could be as high as possible over the waterline to catch as much water's surface possible. However, as the droplets are a maximum of 1.5 mm in diameter, it was hard to catch them using only the GoPro lens. An attempt to add a macro lens (10x) to the GoPro was made, but only a small fraction of the water basin was caught. Not observing the whole basin made some of the experiments invalid due to not catching the droplets on film. Nonetheless, it became possible to observe the droplets.

In an attempt to develop this method further, the overflow of water was turned off, and the water level sunk until it was entirely in the picture. It was now possible to see both the droplets and surface. However, the walls did sweat some oil, resulting in a film on top of the water. Since the film prevented any droplets from liquefying, the experiment was invalid. A different attempt was made using an SLR camera under the basin to take the pictures instead,

as this camera has a higher zoom magnification and wide-lens capability. However, the droplets were not visible no matter the zoom magnification. There were also many problems with the curvature and cleanliness of the plexiglass to take clear pictures through it. As the droplets reached the surface at the same place most of the time, a decision was made to keep the macro lens with a GoPro and use an overflow of water so that the droplets could be seen and the experiment would be valid. See figure 3-3 for a visual representation of the camera placement. The SLR camera was discarded for the time being, as it seemed like it would create too much effort without yielding corresponding results. Because the GoPro did not film the whole water's surface, some runs had to be discarded as the droplet was not caught on camera and thus not tracked by the program. It is strongly recommended to have a high ceiling.
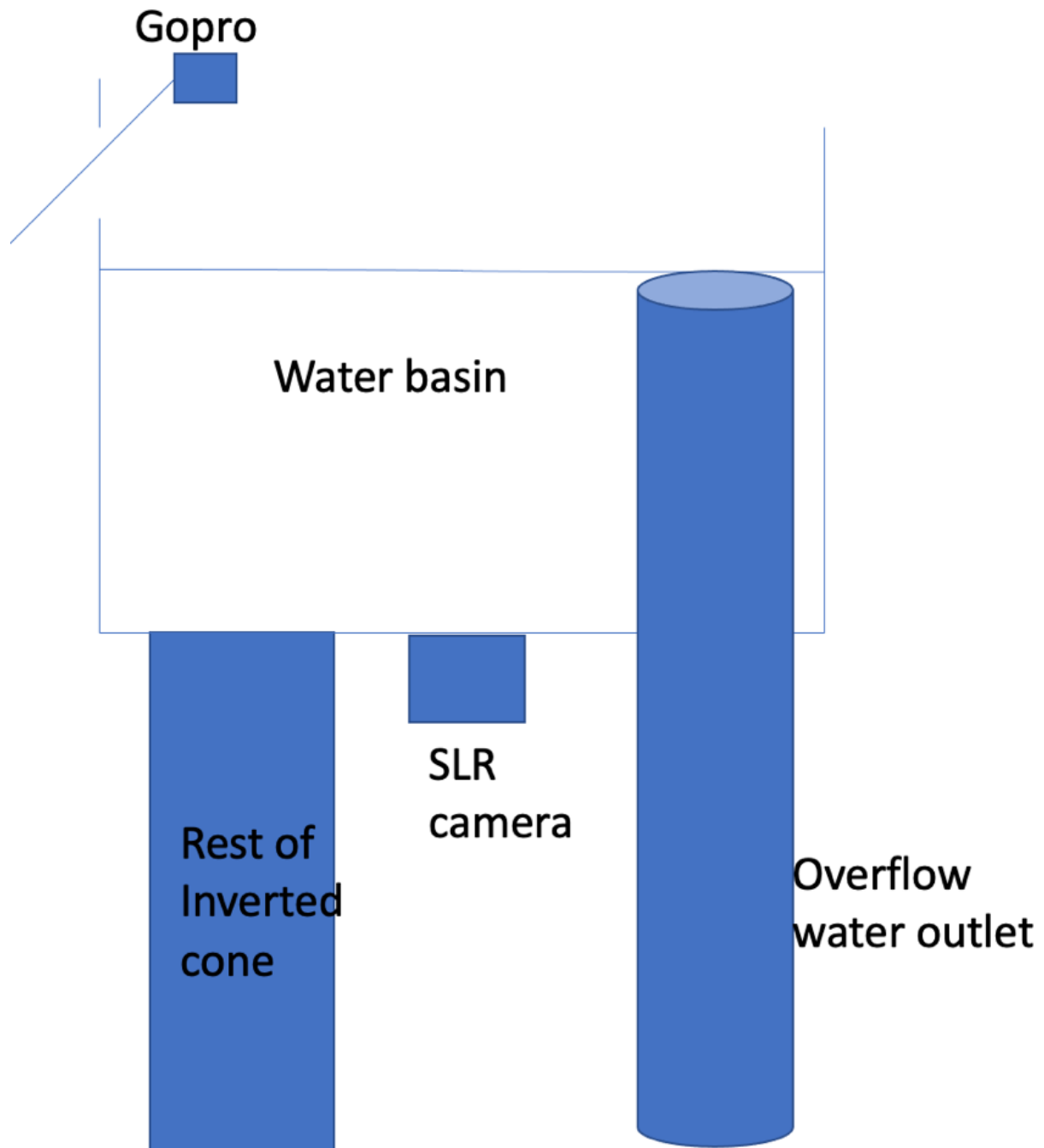
Figure 3-3: Drawing of where the cameras were placed in relation to the rest of the water basin.

3.3.2 Fluorescein addition to the method

After concluding that the low pour point oil liquefied and the high pour point oil solidified, it was hypothesized that there was a gradient of liquification for the rest of the experiment. This part of the experiment, where the droplet did not immediately liquefy nor solidify have been called the medium stage in this thesis. Furthering this research required quantifying this medium stage. It was hypothesized that the oil in the middle stage would have a solidified middle, while the rest of the oil becomes liquefied and spread over a large area, like a fried

egg. An overview of the whole area was needed to quantify this. Furthermore, some instrument was necessary to see the thin slick of oil. So as not to change the chemical composition of the oil, placing a UV-light source at the top of the tank to make the oil light up was discussed. However, because the laboratory technician needed to be in the room when the UV light was on, as many HSE measures needed to be taken, and there was a time restriction, this idea was discarded.

As presented in section 2.6.2 fluorescein is being considered as a good tracer in petroleum well research. It was therefore discussed to use in our experiment as well. It seems like fluorescein is usually added to the water in a small concentration, as done by Pataveepaisit & Srisuriyachai (Pataveepaisit & Srisuriyachai, 2020). However, due to the water in the experiment being continuously changed, a lot of fluorescein would be needed, which seemed wasteful. It was concluded that something had to make the oil droplets light up instead. Looking at the fluorescein compound, it seemed plausible that the compound would be solvable in oil as well, due to being a large aromatic compound, with some polar groups such as the carboxyl and ether group.

To not saturate the system, it was decided to start with a small concentration of 0.01g fluorescein/L oil. During laboratory testing, the fluorescein concentration was concluded to be too low to see a lone droplet popping in the photos. It did however seem like the fluorescein did light up the oil and did not seep into the water. The concentration was determined by testing in the laboratory by pipetting one oil droplet with increasing fluorescein concentration in a beaker glass of saltwater and checking with blue light to see if the green was visible. It was determined that a 0.2g/L concentration gave appropriate results and was used for the rest of the experiment.

Thus, 0.5 g of fluorescein was added to a 250 ml flask of Norne oil, which was heated to 50 °C until it became liquefied (approximately 30 min). The flask was then heated to 30 °C while stirring with a magnet for 4 hr to let the fluorescein dissolve.

Afterward, the flask was cooled overnight at room temperature. The following day, a standard homogenization procedure was performed.

It should be noted that later, it was observed that the fluorescein did not penetrate a high concentration of oil. Moreover, a solidified droplet would still be observed as a black dot.

3.3.3 Using an SLR camera to catch the fluorescein droplets

This addition of fluorescein made it possible for the SLR camera to be placed under the tank and take photos, in which the oil was sufficiently visible. There was some trouble seeing the light emitted by the fluorescein when taking a video, so the SLR camera had to be switched to RAW photos to have enough exposure time for the lens to capture the light adequately. The main disadvantage of switching from video to photo was not being able to film the complete process. It was a bit coincidental when the picture was taken, as the time between each photo was around half a second, and the oil went through a lot of change between each photo. It therefore also seemed like the quantified results became more coincidental than factual. Furthermore, it was still challenging to observe the 1 mm and 0.5 mm droplets in the SLR. As preliminary tests had shown no variation in the results based on droplet size in both pp 30 and pp 3, it was decided to simplify the procedure and not use 0.5- and 1-mm droplets for the rest of the experiment. Based on the setup for this thesis, it would probably not be possible to draw conclusions on droplets smaller than 1,500 µm. Knowing how difficult it is to interpret the 1.5 mm droplets, one would probably need more robust equipment, as recommended in the conclusion of this section, to get results other than "solidified" or "not solidified" for droplets having less than 1.5 mm diameter.

It was discovered that the walls that had oil with fluorescein covering them sweated, which could give false positives or a positive error by sweating and contributing oil to the area calculations of a result. When demolition (the droplets parted into two or more smaller droplets) of some of the droplets was observed, the hypothesis of the fried egg behavior was concluded to be wrong. It was therefore concluded to discontinue the area calculations. Demolition had been observed in a previous study, where the demolition led to complete liquefication after a few minutes(Zhao et al., 2022). Unfortunately, it was not possible to further test this theory, as the droplet only spends approximately 30 sec in the basin before being flushed out by the overflow. As stated previously, this overflow could not be turned off due to the sweating and the creation of oil film.

3.4 Conclusion method development

The inverted cone and the method used in this experiment performed well and gave good results in determining whether the droplets solidified. However, it is unclear how to check this theory for the second hypothesis. All the components that created obstacles were solved individually but did not work well as a combination for the middle phase oils. The inverted cone might not be the best instrument for further testing. If this experiment were recreated,

one suggestion is to use a cone with a larger basin to have the droplet at the surface for a longer time. This solution might also solve the problem of the oil film, as it would take longer to form. However, a larger basin might make it more difficult for the cameras to see the droplets, but a multi-camera solution might work. One recommendation is to use UV instead of fluorescein to see if it makes it easier for the cameras to catch the light emitted. If it were possible to redesign the inverted cone, a recommendation is to make it possible to clean the top basin between each run. Regular cleaning would help reduce the false positives, and it might decrease the creation of oil film. However, the simplest solution may just be placing the setup in a room with a higher ceiling, making it possible to use some Zalo and a brush for cleaning. Another potential solution that was not tried is cleaning the basin with magnets. A cleaning brush equipped with a magnet on the inside and a magnet to drag it around on the outside of the basin could be used to clean the walls. The hole for the overhead camera could be used to insert the cleaner, and one would be able to drag it to all the places in the top basin. However, a problem could occur if the cleaner were lost inside of the basin, as there is no way to reach the bottom, only using a hand. Furthermore, it is hard to move a magnet around corners.

Furthermore, frequent clean-up would create extra work for the laboratory technician, especially since the basin becomes dirty between each session. Less cleaning than after nearly every run would probably not be sufficient to eliminate the problems described. In conclusion, the main problem is the time of the droplets in the basin. However, this main problem might not be solvable with the inverted cone setup.

4. Experiment and set up:

In this section, the final version of the experiment is presented. As most of the laboratory work was done with a focus on the inverted cone, this section starts by going into how the inverted cone works and how it has been used previously. Then, how the oils were chosen for this experiment is investigated. OSCAR was used to decide a few of the experimental parameters. The parameters put into OSCAR are also presented. Finally, time underwater and droplet size distribution are presented.

4.1 Inverted cone setup:

As the inverted cone is an instrument with a specific purpose, it has not been used widely in research. Therefore, the makeup and premises of the instrument are not commonly known. This section starts by describing previous research that has used the inverted cone and looking into how the inverted cone works. This section ends by presenting the different procedures used in this experiment to make it possible to recreate.

4.1.1 Previous use of the inverted cone

The inverted cone is an instrument developed by Maini & Bishnoi (Maini & Bishnoi, 1981) and has further been utilized and developed by other researchers to investigate gas bubbles (Masutani & Adams, 2001). The inverted cone was first only used in gas research and has later been transformed for use on oil droplets and dispersant research. SINTEF developed the setup used in this experiment based on ideas from the University of Hawaii (Davies et al., 2019).

4.1.2 Description of the inverted cone

Figure 4-1 shows a schematic drawing of the inverted cone. A stream of oil is pumped out at the bottom of the cone into the water. Due to the droplet having a lower density than water, the droplet flows upwards. An outlet (flow regulator) is at the bottom of the tank. Gravity causes the water to be transported downwards and out the outlet, creating a downward water current inside the tank. The force of the downward current depends on the volume of water escaping at the bottom of the cone and can therefore be regulated to make the droplet stop rising and stay inside a pre-decided "box." A camera is focused on this box and takes pictures of the droplet every 0.5 sec. After a decided time, the downward current is halted, allowing the droplet to rise to the surface, where it is photographed and observed.
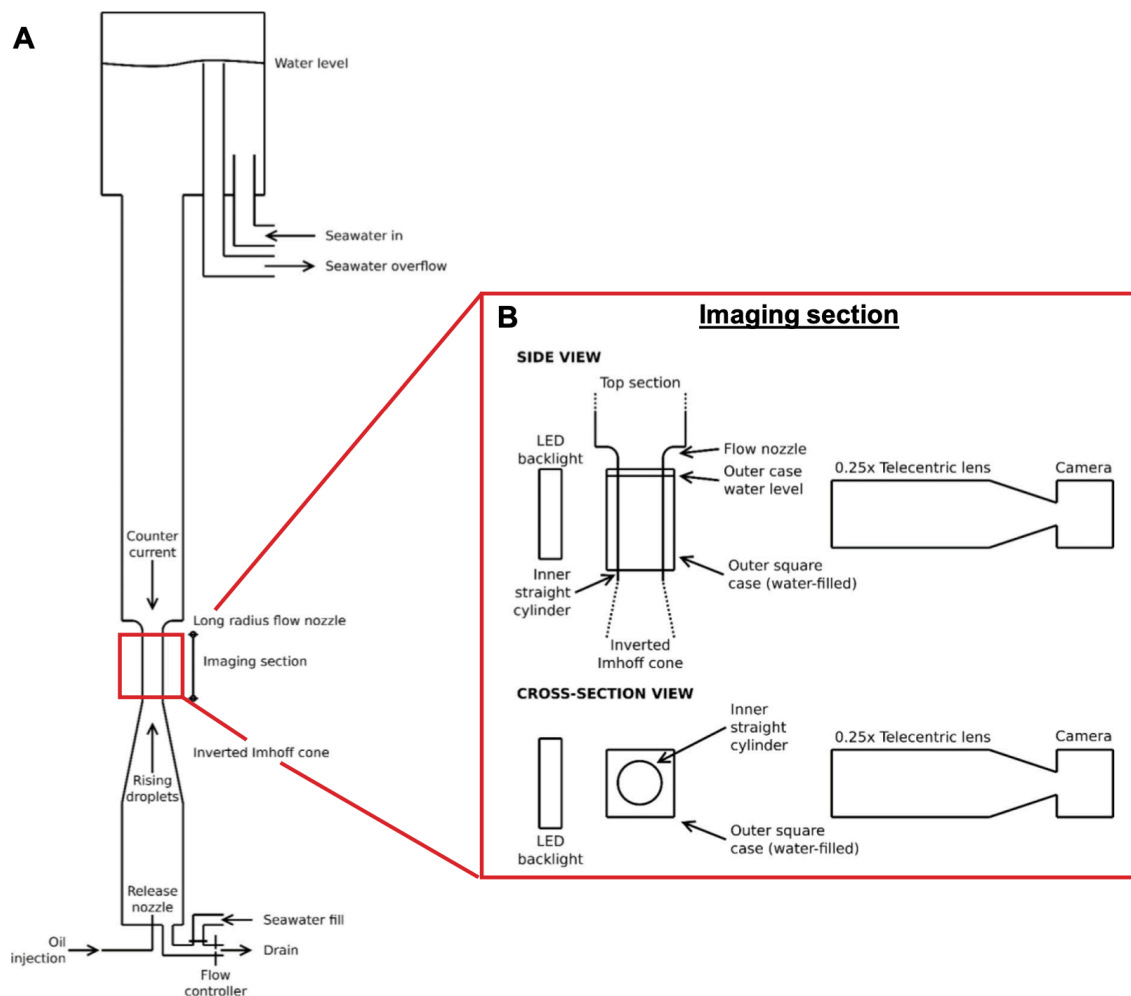
Figure 4-1: Schematic drawing of the inverted cone. Reposted from Shedding from chemically-treated oil droplets rising in seawater. Davies, E. J., Dunnebier, D. A., Johansen, Ø., Masutani, S., Nagamine, I., & Brandvik, P. J, 2019, Marine pollution bulletin, 143, 256-263.

The inverted cone is 3 m high. The observation box is about 1 m above the release point. The cone is acrylic plastic and uses filtered saltwater from 80 m depth in the Trondheim Fjord. The water and the room were kept at 8 °C during this experiment.

From the release point the cone's diameter decreases linearly from 110mm to 25 mm, ending in the photo zone. The photo zone is a cylinder. Behind the cylinder is a strong white light, and in the front is a camera focused on the cylinder. Around the cylinder is a square box filled with water, creating a flat surface to be photographed. The cylinder makes the current different along the walls than in the center. Therefore, the cylinder probably requires more change of the current speed to make it possible to keep the droplet stable in the correct zone. A way to improve this might be to make the photo zone into a cone instead. This makes the droplets of assorted sizes stop in separate places in the photo sone, making it easier to control and get the correct droplet size.

The input valve for the seawater and an overflow tube that empties the basin's surface layer are found in the top basin. The water input is on the top of the instrument while the output is on the bottom. The water is continuously changed and not reused. The top basin is also equipped with a thermometer to monitor the seawater temperature.

A syringe pump inserted the oil into the water. An outer cylinder with water flowing in the opposite direction was connected around the oil-flow cane. In this experiment, the water temperature was 50–60 °C. A three-way valve with two inputs and one output was used for injection. One input was for the oil, and the other was connected to a hot water source that enters the basin and heats the metal in the valve before releasing the oil. The hot water was not on during the low-pour-point experiments. See Figure 3-2 for a schematic drawing of the pump inlet.

The last part of the apparatus is the seawater filler. This is used to fill the tank with seawater from the bottom up.

Blue LEDs were added to the poles next to the basin for fluorescein detection. A GoPro Hero 7 with a macro lens 10x was placed above the water. Beneath the basin was an SLR camera (Cameron) with a wide-frame lens. The GoPro was set to video mode and used to observe whether the droplet liquefied immediately upon reaching the surface. RAW photos with a professional photo editor were used to get the best photos of the droplets lit up by fluorescence.

4.1.3 Homogenization of oil procedure

The oil must be homogenized before injection to make sure the oil sample in the pump represents the actual sample. For all the oils except Oda, the oil was first heated to 50 °C in a water bath for an hour. Afterward, the oil was manually shaken for one minute before being injected into the syringe.

As Oda is an oil with numerous low volatile compounds, it cannot be heated without the risk of high pressure and, therefore, explosion. Therefore, Oda was homogenized at room temperature overnight and then shaken in ventilation and the lid opened in short intervals before being injected into the syringe.

4.1.4 Fluorescein addition procedure

The procedure for adding fluorescein to the oil was as follows: First, the oil was heated in a water bath at 50 °C until completely liquified (after about 30 min, depending on the pour

point of the oil). The sodium salt of fluorescein was then added to a concentration of 0.2 g/L. Afterward, the oil was homogenized, as mentioned in section 4.1.3.

4.1.5 Oil used in the experiment

In this experiment, the oils were sorted by pour point. The pour point is the most accessible variable related to the solidification of an oil. One could look at the wax content as well, as the wax affects the solidification. However, the asphaltene content, for example, affects how much the wax can affect an oil's solidification, and it is not the best way to rate the oils. High- and low-wax oil is often used to classify oil in the petroleum industry and is often interconnected with the oil's pour point.

This experiment only looked at crude oils since a subsea release only entails the release of crude oil.

Oils across a large span of pour points were examined. The oil with the lowest pour point, the Oseberg blend, has a –36 °C pour point. While the oil with the highest pour point, Duva, has a pour point of 30 °C. Because solidification was not expected to occur in the negative range, a jump is made to −3 °C for the next pour point after the Oseberg blend. Because the aim was to figure out what happens between complete solidification and liquefication, most oils have a pour point of 0–12 °C. Above 18 °C, the solidification happens instantly; Duva is the only other oil tested in this range, as it is expected that every oil with a pp above instant solidification will solidify as well. The oils used in this experiment are listed in Table 4-1.

The way to determine all parameters in the table is described in the theory under subsections 2.2 and 2.3.

Table 4-1: Name and chemical properties of the oils used in this experiment.

Name	Pour point	Wax concentration (wt.%)	Asphaltene concentration (wt.%)	Density (g/mL)	Viscosity Fresh oil (mPa.s) 13°C (10s^{-1})	Year sample is from	SINTEF-ID
Oseberg blend	-36	2.3	0.2	0.826	3*	2015	2015-0014
Oda	−3	5.580	0.440	0.820	10	2019	2019-4130
Grosbeak	0	8.100	0.050	0.810	41	2011	2011-0424
Skogul	3	4.400	0.040	0.842	67	2020	2020-4687
Oseberg East	9	4.880	0.450	0.842	163	2012	2012-0333
None 2017	18	5.160	0.050	0.861	541	2017	2017-3365
Duva	30	6.8	0.11	0.868	6,412	2021	2021-4882

* Measured at 40°C

4.2 OSCAR setup

OSCAR has been used for decades to simulate actual oil spill releases and is quite strong in predicting how an oil spill will behave. A decision was made to use simulated oil spill scenarios as a framework for the parameters of this thesis. It was decided to simulate an actual subsea release, using weather and current data from a specific date, and actual coordinates and oils. This makes the release seem as if it happened at the chosen well at that specific time on that particular date. This method provides laboratory data that are compatible with real-life releases and raises the accuracy of the experiment.

For this simulation, a decision was made to use an oil spill with the same conditions but with different GLRs. The simulated oil spill was placed at the exact coordinates that Duva is extracted now, at a depth of 359 m. Because the weathering report of Duva only became public this year (2021), Duva is not in the oil database. Therefore another oil with a high pour point was used instead (Pil, pp27).

The spill was simulated with wind and water currents from 2 February 1990 in 10 °C water. The diameter of the release was set to 15 cm, and the amount of oil released was set to 4,000 tons per day.

The results were used in Stokes' law calculations to find the correct droplet sizes for this experiment.

4.3 Rising times used in the experiment

Based on results from OSCAR and calculations using Stokes' law, a decision was made to use 15 min to 2 hr as the time underwater for the droplets. See Table 4-2 for a complete list of times. It was also decided to use droplet size 1. 5 mm ± 0.1 mm for the entirety of this experiment.

Table 4-2: Rising times used for the droplets in this experiment.

Droplet time underwater (min)
15
30
60
90
120

5. Results

5.1 Results for inverted cone

Oils with varying pour points were exposed to seawater to see how the droplets behave upon reaching the surface. Different underwater times were used to simulate different release depths. Different droplet sizes were also tried for Oda, but due to the droplets being difficult to observe on camera, the other oils were only run using 1.5 mm droplets. The experiment was carried out as described in Sections 3 and 4.

Table 5-1 shows the results of the testing. As presented in section 3.3, studies have concluded that some oil fully spreads after minutes on the surface (Zhao et al., 2022). As this experiment used an overflow of water, the oil was transported to waste in seconds, and "unsure" had to be used regarding whether the oil solidified. The "unsure" answer in Table 5-1 means that the result was indeterminable regarding whether "yes" or "no" was appropriate, primarily due to no deconstruction being observed, while the SLR or Gopro camera gives fluorescein flashes after the droplet exiting the frame, indication a deconstruction. See section 6.1 for further reasoning of this decision. Deconstruction has been considered for this table, so every deconstruction witnessed is put down as "no" and then commented on as "deconstructed."

It was observed that an oil with a pour point less than 0 °C would liquefy immediately in every test in our experiment. Furthermore, an oil with a pour point over 18 °C would solidify in every test.

Table 5-1: Results of all tests done by the inverted cone. "Unsure" means even though the droplets solidified upon reaching the surface, a deconstruction seemed to happen according to the SLR camera.

Name oil	Droplet size (mm)	Time underwater	Solidified?	Comment
Oda	0.5	1 h	No	
Oda	1	2 h	No	
Oda	1.5 mm	2 h	No	
Grosbeak	1.5 mm	15 min	No	Deconstructed
Grosbeak	1.5 mm	30 min	No	
Grosbeak	1.5 mm	1 h	No	
Grosbeak	1,5 mm	1.5 h	Unsure	
Grosbeak	1.5 mm	2 h	Yes	Connected to basin wall, time at surface approx.5 seconds.
Skogul	1.5 mm	15 min	Unsure	
Skogul	1.5 mm	1 h	No	
Skogul	1,5 mm	1.5 h	Unsure	
Skogul	1.5 mm	2 h	No	
Oseberg East	1.5 mm	15 min	Unsure	
Oseberg East	1.5 mm	30 min	No	
Oseberg East	1.5 mm	1 h	No	
Oseberg East	1.5 mm	1.5 h	No	Deconstructed
Oseberg East	1.5 mm	2 h	No	

| None 2017 | 1.5 mm | 0 min | Yes | |
| Duva | 1.5 mm | 0 min | Yes | |

5.2 Results from OSCAR and Stokes law calculations

OSCAR was used to find accurate rising times of oil droplets in a subsea release. The findings show that in a spill with a GLR of 2, the first droplet took 45 min to reach the water surface. In a spill with the same conditions but a GLR of 200, the first droplet took 8 min to reach the surface. In a spill with a GLR of 2,000 under the same conditions, the droplet took 4 min to reach the surface. Refer to Figure 5-1, 5-2 and 5-3 for simulation from OSCAR of the plume when the first droplet reaches the sea surface.
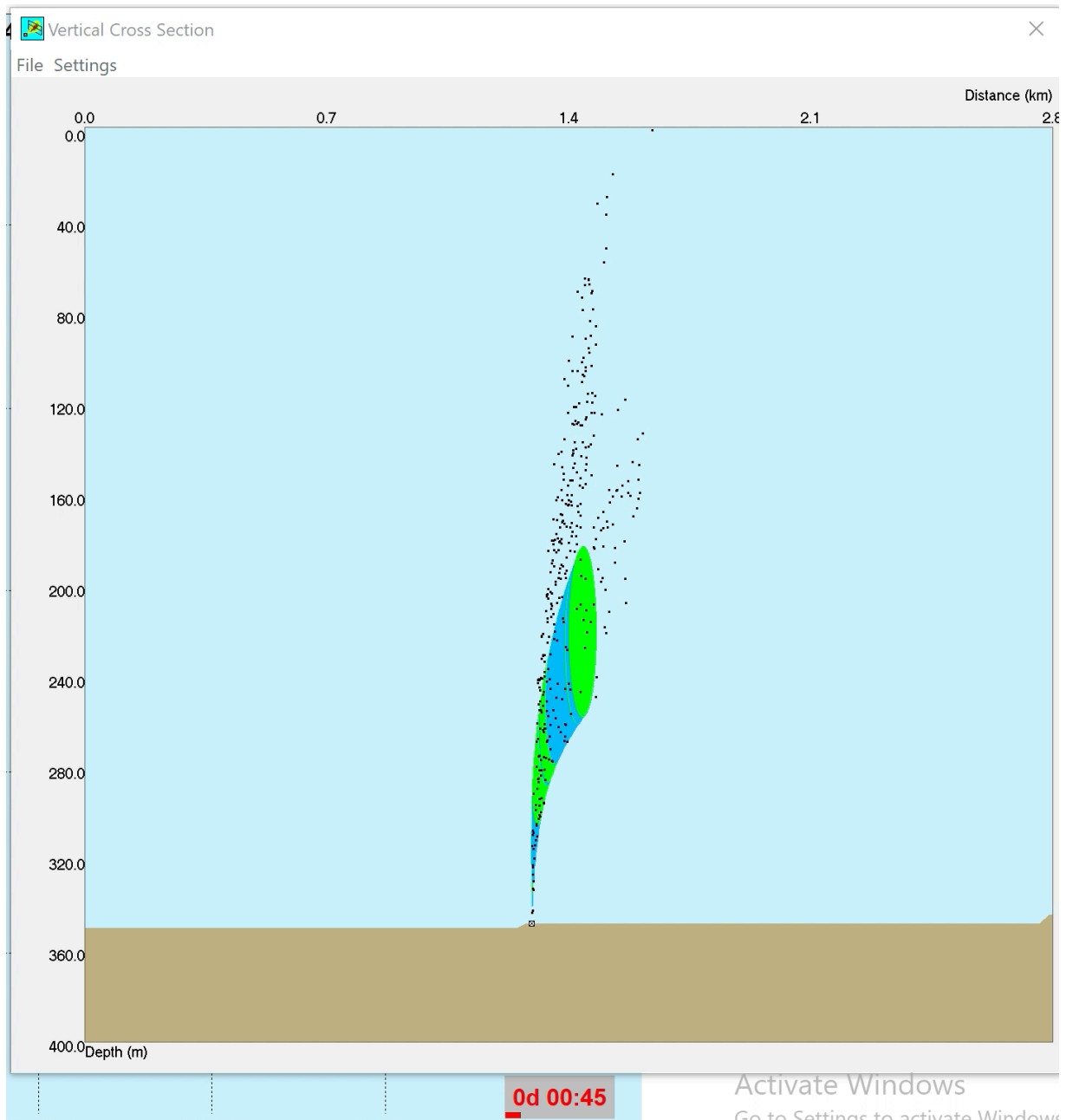
Figure 5-1: Screenshot from OSCAR showing when the oil reached the surface in a release with a gas-liquid ratio of 2. The black dots are the oil droplets, while the blue and green stream is the plume. The number in red at the bottom is the time (day: hour: minute).
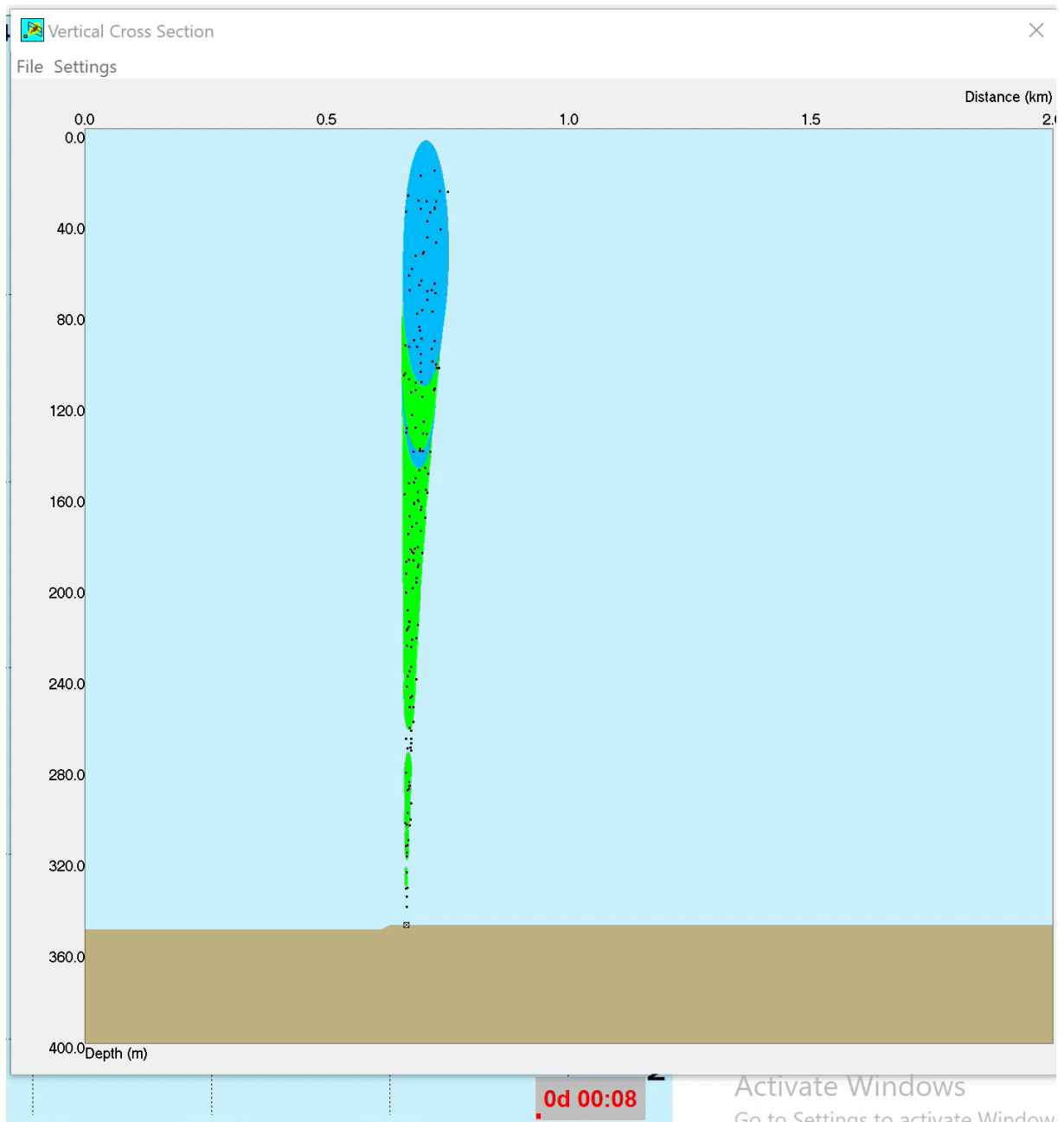
Figure 5-2: Screenshot from OSCAR showing when the oil reached the surface with a gas-liquid ratio of 200. The black dots are the oil droplets, while the blue and green stream is the plume. The number in red at the bottom is the time (day: hour: minute).
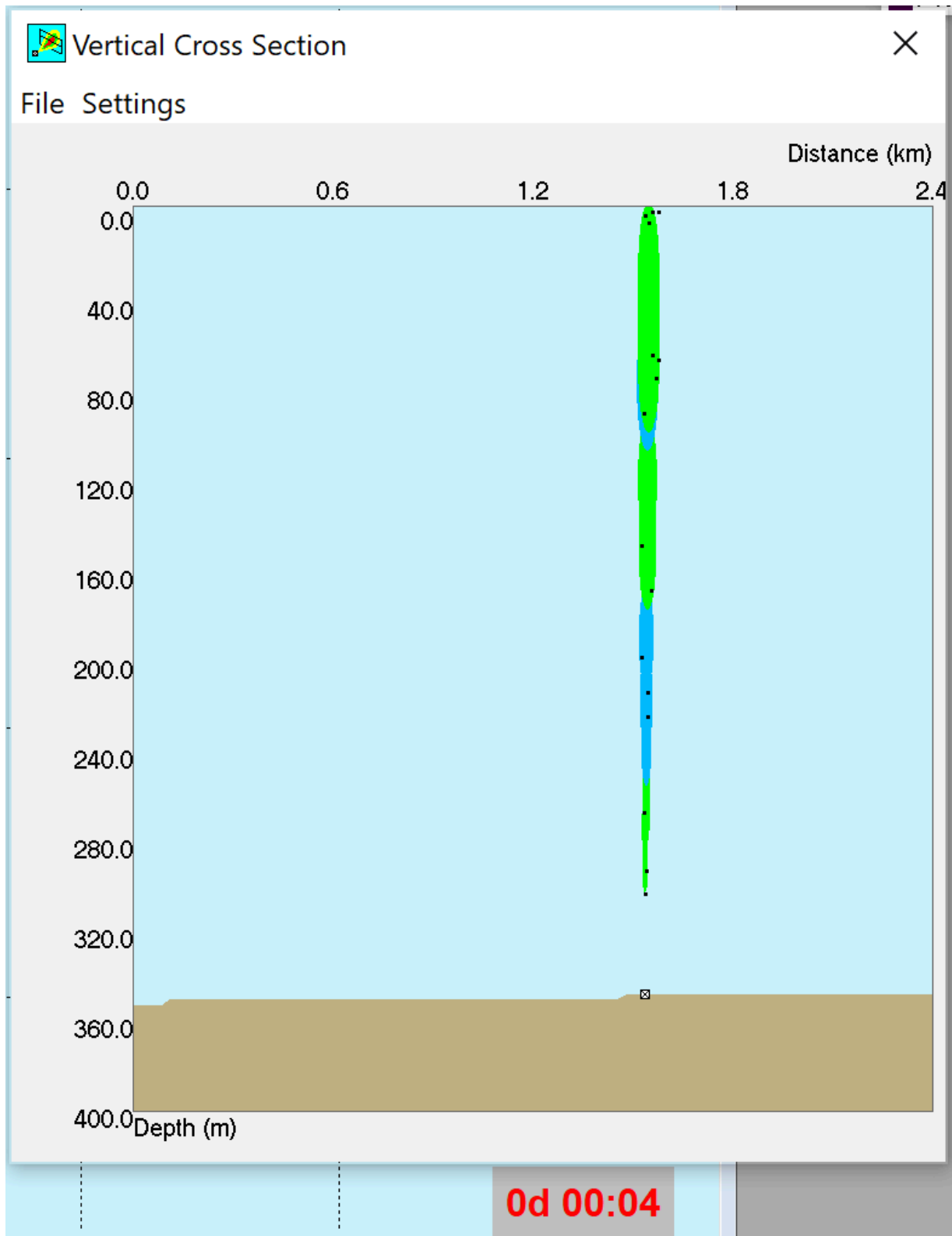
Figure 5-3: Screenshot from OSCAR showing when the oil reached the surface in a subsea release with a gas-liquid ratio of 2,000. The black dots are the oil droplets, while the blue and green stream is the plume. The number in red at the bottom is the time (day: hour: minute).5.3 Results from Stokes' law calculations.

The rise time of different oil droplet sizes from the same depth as modeled in OSCAR was found using simple Stokes' law. The results showed that a 1,500 μm droplet took 34 min to reach the surface, a 2,300 μm droplet took 15 min to reach the surface, and an 800 μm droplet took 2 hr to reach the surface.

5.3 Results from the addition of fluorescein

It was quickly observed that some oil solidified when it was released, while other oils liquified, unaffected by time spent underwater. A middle phase was also observed, where neither of those conditions happened. It was hypothesized that this middle phase would have a combination of spreading and liquefication, which could be quantified. Fluorescein was added to quantify the spreading of the liquefied parts of the droplet.

The hypothesis of the fried egg, where it was believed that the droplets in the middle phase would partially solidify by having a core of solidified oil and the surrounding oil liquefy and spread out, did not happen. Instead, a more complicated process happened, which this thesis was unable to solve. Due to the quick transport of the oil to waste and problems with false positives, which are presented in section 3.3.3. and discussed in section 6.3, a decision was made not to use any numerical results, as the results would lack support.

6. Discussion

During the past year, the inverted cone has been used to study the behavior of oil droplets during a subsea blowout. This thesis examines droplets having different pour points in a subsea blowout to determine droplet solidification, droplet underwater times, and droplet sizes.

6.1 Presentation of results

It was concluded that a high enough pour point would yield solidified droplets, while a low enough pour point would cause liquefication immediately upon reaching the surface. After more experiments, it was determined that a pour point below −3 °C in 8 °C water would always liquefy immediately upon reaching the surface. Further, a pour point above 15 °C in 8 °C water would always solidify upon reaching the surface. This means an approximately 20 °C window with pour points from -3°C to 15°C exists, where the results are more complex. In this window, it was first hypothesized that there would be a partial spreading and solidification. However, the process was more complicated than that, as it included deconstruction of the droplets. More research is needed to draw any conclusions.

Some parts of the results had to be noted down as inconclusive. It was observed instances where a droplet reached the surface solidified, but after exiting the GoPro frame, fluorescein flashes were observed. As presented in section 3.3 and discussed in 6.3.3, there was a problem with sweating of fluorescein from the basin wall. Therefore, it is not possible to be certain if the fluorescein flashes stem from the droplet being deconstructed or sweating. It was, therefore, decided not to assume a deconstruction if it was not observed. Obvious false positives, where the droplet is still visible by SLR camera, are discarded as false positives and noted as solidified. This might be an error source, as a deconstruction where one fraction remains visible is possible. Based on the observed deconstructions, however, none had visible fractions after deconstruction. It, therefore, seemed improbable that a large portion of visible droplets had gone through deconstruction.

The droplets had different times in frame for the GoPro camera. Due to it being immediate solidification and liquefication that is the objective of this thesis, droplets that did spend more than a couple of seconds solidified in the frame were also noted as solidified. The deconstruction in Zhao et al. could use 10 minutes until liquefication (Zhao et al., 2022); another error source might stem from this decision. There could be variations of when the

droplets start deconstructing. If true, more runs of the solidified droplets with a pour point around the middle phase might give a variety of observed deconstruction and solidification.

An interesting observation happened between Grosbeak and Skogul. Skogul is supposed to have a pour point 3°C higher than Grosbeak. However, while deconstruction was observed at numerous Grosbeak runs, none was observed for Skogul. Instead, Skogul seemed to liquefy quicker than Grosbeak and denser than Oda. It is hard to tell why this happened, the error sources that are presented in 6.3 might be a reason. Grosbeak might also have components that do not make the pour point representative of the solidification point, or maybe the pour point is not a perfect indicator of how the oil will behave in the middle phase. More research is needed to be able to conclude anything.

6.2 The inverted cone

Using the inverted cone for this experiment has provided a unique, precise environment for observing how the droplets behave in an actual subsea release. Using real filtered seawater from 80 m depth in Trondheim Fjord, the droplet conditions underwater are realistic. However, the salinity might differ depending on the release point. Currently, there seems to be no research on how salinity affects the solidification of oil. Therefore, a difference in solidification based on this parameter is possible. However, as the seawater used is from the North Sea, it should be comparable to the salinity in the rest of the North Sea.

A significant contributor to the oil's solidification is probably the sea temperature. In this experiment, 8 °C water was used. Although the water temperature would vary based on location, seawater temperature is never lower than 4 °C, and below 1,000 m, one would expect the temperature to be constant at 4 °C. In furthering this work, changing seawater temperature would be interesting. Different seawater temperatures would probably cause differences in which oils solidify and liquefy. However, 8 °C is a typical seawater temperature during winter months in the North Sea, (Janssen et al., 1999) so the results should be valid for a realistic subsea release. As the whole laboratory was temperature-controlled at 8 °C during testing, there is little to no chance of having a significant error in the water temperature. It is also worth mentioning that the seawater-to-oil ratio during a blowout is so vast that any heat from the well would be cooled the moment it interacts with the seawater. Therefore, the seawater temperature would also be the temperature surrounding the oil droplets during their travel to through the water-column.

As mentioned in the experimental part of this thesis, extra care has been taken to choose representative droplet sizes and underwater periods; there should not be any conflict with real-life scenarios in this part. However, it should be noted that in a subsea release, droplets come out normally distributed, yielding a range of both droplet sizes and time underwater. Nevertheless, it is presumed that a smaller droplet size will solidify in all instances where the bigger droplet solidifies. Since this experiment involves a big droplet size and has a combination of long and short times underwater, most of the droplets in a release oil will be represented by a conclusion of solidification. On the other hand, the inverse is presumed for a liquefied droplet. If a small droplet liquefies it is presumed that larger droplets will liquefy as well. A large droplet will therefore not necessarily represent smaller droplet sizes when the result is a liquefication. For the middle phase studies, a variation in droplet sizes will probably yield different results.

6.3 Error sources

In all likelihood, this experiment accurately depicts an actual subsea blowout. However, more research is needed to better understand the behavior of an oil whose pour point is ± 10 °C of the sea temperature. However, the finding that some oils solidify would probably match closely with an actual release.

6.3.1 Error in pour-point determination

An experiment can only be as accurate as its parameters, and the pour point determination has, as described in section 2.3, a significant error margin of minimum 3 °C. This is not ideal, as the oils chosen does not have as linear correlation of solidification as expected, and therefore conclusions are harder to draw from the experiment. Furthermore, the determined pour point is based on human observation, which probably creates some variance based on who makes the determination. As one is looking for movement of black liquid, making correct observation might be especially hard. Lastly, stirring affects wax formation. Some stirring-related errors might occur since it is necessary to have a thermometer in the oil to ensure the correct temperature and tilt the apparatus to create movement in the oil. It should be noted that if an observational or stirring error occurs, the base of the experiment will make an error of an additional 3 °C.

Due to this thesis primarily looking at the solidification process, and not having quantifiable results, the error from the pour point determination is not determinantal. The conclusion that some oils solidifies is not affected by a correct pour point, as an observation of a solidified

droplet would be the same. It might however affect the phase in-between liquification and solidification, as the oils might not have as linear relationship as shown in Table 4-1. Two oils with a reported 3 °C difference could, in theory, be 6 °C apart if they are on each extreme of the error margin. The inverse could also happen, making a reported 3 °C difference none.

The danger of wrong pour-point determination can be limited by parallel testing, which will dampen the rate of human error. Pour point is primarily used in environmental chemistry to determine when oil solidifies when it is released at sea. Wave turbulence will break up the wax-formation. Therefore, 10–15 °C is usually subtracted to the laboratory pour point when predicting solidification in oil spill response reports. However, it is difficult to say whether the extra precision by parallel testing is necessary. Finding an accurate pour point might not be worth the time and resources. Although an accurate pour point might be nice, the sea conditions would probably make the standard error more than 3 °C from laboratory to sea. Therefore, the extra precision in the laboratory might not be necessary.

6.3.2 Errors with the overflow

One of the errors in this experiment was due to the water overflow. The tank had a constant overflow of water to prevent the water in the water tank from creating an oil film and making the surface impenetrable for the droplets. This created a clean water surface but made it impossible for the droplets to stay in the tank for more than approximately 30 sec before being flushed out with the water. Therefore, it was not possible to conclude anything more than the immediate behavior of the droplet upon reaching the surface.

This was not a significant problem for the droplets that either liquefied or solidified, although it would have been nice to see what happened to the solidified droplets after 30 sec. However, due to the nature of the experiment, it seemed like the process had stopped by the time the droplet reached the surface, and more time in the basin would probably not yield more information on the complete solidification without any interaction with heat, collisions, or other weathering processes. It should be noted that the results are only based on the initial 30 sec, without any weather or wave interactions. Therefore, the process after the initial surfacing is challenging to draw any conclusions on. Refer to section "possible implications for oil spill response," where this topic is discussed in more detail.

The most significant error concerning overflow occurred at the stage between absolute liquefication and absolute solidification. Deconstruction was observed in several simulations. Therefore, it is hypothesized that if given more time, the droplet would be completely

liquefied. (Zhao et al., 2022) Based on this report, the droplet completely liquefies after a few minutes. However, it should be noted that this report was done with emulsions, not crude oil, but that should not make a significant difference, particularly since a similar deconstruction was observed in this thesis experiment as well. This would mean that a longer time in the basin would probably yield different results than what was observed in this experiment, given its short time frame. Additionally, this thesis has given the droplets the "benefit of the doubt," so if a deconstruction took place, the droplets would be assumed to liquefy if given enough time in the basin. This was done based on the observed droplets not having visible parts after a deconstruction. Furthermore, Zhao et al concluding that their deconstructed oils ended liquefied. However, there was no way for this thesis to test if the deconstructed oil ended as completely liquefied, solidified particles not visible to the naked eye, or something else.

6.3.3 Error with the addition of fluorescein

Although the addition of fluorescein did not yield any results that could be reported with certainty, the potential error should be noted here. First, although fluorescein has previously been added without having any reported effects on the oil's behavior, it seems like no study has been done on the oil's solidification process before. Fluorescein might therefore react to the oil and skew the results. During the start of the experiment the oils did not have an addition of fluorescein, and both liquefication and solidification was observed. There should therefore not be any interaction with fluorescein and the solidification process that significantly affects the results. Furthermore, all results reported are with the addition of fluorescein, so any potential error from fluorescein will be of similar effect on all results.

It should also be noted that there was a significant error regarding the location of the fluorescein due to oil sweating from the basin walls giving false positives and positive errors, which rendered area calculations inconclusive.

7. Conclusion

7.1 Conclusion of the inverted cone

In this thesis, the behavior of petroleum droplets during a subsea release has been studied using the inverted cone. It was found that droplets with a high enough pour point did solidify while droplets with a low enough pour point liquefied immediately upon reaching the surface. It was concluded that oils with a pour point of 10 °C degrees above the seawater temperature would solidify independent of the amount of time spent underwater. In comparison, oils with a pour point of 10 °C below seawater temperature would liquefy immediately upon reaching the water surface independent of the time spent underwater. Fluorescein was added to see what happened with the droplets having a pour point around the same temperature as the seawater. Due to deconstruction of the droplets upon reaching the surface, it was not possible to conclude with certainty what happens to those types of oils.

7.2 Conclusion of OSCAR simulation and Stokes' law calculations

OSCAR and Stokes' law calculations were used to accurately calculate time underwater and droplet sizes. Simulating a release as if it happened on the Duva field on 2 February 1990, it took 4–45 min, depending on the gas-liquid ratio, for the first droplet to reach the sea's surface. Therefore, a decision was made to use 15–120 min intervals as the time underwater.

Using Stokes' law to calculate the droplet sizes that use the time interval decided on from the simulation, it was found that the droplet should be between 2,300 μm and 800 μm. A decision was made to use 1,500 μm as the droplet size, which would take 34 min to reach the sea's surface if released on the Duva field 349 m below sea level.

8. Possible implications for oil spill response

The finding that the oil solidifies creates many new questions. This part of the thesis focuses on presenting some of those questions and tries to pose answers based on what is already known. The questions are as follows: (a) How does solidification affect weathering of oil? and (b) How does solidification affect clean-up and detection? It should be noted that the primary goal of this thesis is to examine the behavior of droplets after a subsea blowout, not leakage. Although solidification will probably happen for a leak, due to having a smaller stream of oil, and therefore a smaller surface concentration, it is probable that not all the interactions and clean-up measures are relevant for a leakage.

8.1 The middle phase

After proving that some oils solidify while the others do not, one of the more interesting discoveries is the middle phase. A general rule of many clean-up procedures is that if the oil's viscosity becomes too high, different procedures, such as dispersants, will be rendered ineffective. This often happens when the pour point is 10 °C or less below the sea temperature. In this experiment, a definite liquefication around 10°C below sea temperature was observed. We also had a definitive solidification around 10 °C above sea temperature. In the middle, what happened was indeterminable, but deconstruction was observed for some droplets.

More research is needed to conclude what happens in this pour point mid-range. Previous research done at SINTEF has investigated emulsion droplet spreading, and a similar deconstruction was observed in that study as well (Zhao et al., 2022).

8.2 How does solidification affect the oil when it reaches the surface?

When oil reaches the surface, this research concludes that the oil does not form a film immediately. Instead, it seems like many small, discreet balls of oil come to the surface. What happens afterward has not been determined.

In this thesis and in general, it has been observed that the oil takes the form of numerous small droplets when underwater. Upon reaching the surface, the droplets liquefy and create a liquid layer on top of the water, creating a slick or film if the release is significant enough. Therefore, it can be concluded that the oil droplets that liquify usually find each other and interact when being released from the same place. The interaction between the solidified droplets is a factor when considering how the release behaves. It should be noted that the probability of two liquified droplet hitting each other is larger than two solidified droplets.

A liquefication covers a larger area than the solidified droplets do. Due to the liquefication having a bigger area, the probability of them connecting is also bigger. Although the currents and waves help push the droplets together, the ocean is big, so there is a high probability that some droplets would disappear and never interact again.

If the droplets encounter each other, what happens next will be detrimental, especially to the clean-up procedure. This section will present three possibilities of what might happen after a droplet interaction. It should be noted that this experiment does not have basis to conclude what happens, but the indications of what have been observed in the laboratory is presented.

The first possibility is effectless interaction. Similar to when two golf balls collide, the solid phase is strong enough to not interact. Instead, the droplets are pushed away from each other. From there the droplets can continue their journey as if no interaction had occurred.

The other possibility is that the droplets completely merge to become either a liquid slick or one large solid-state droplet. Even though a complete merge has not been observed in the laboratory, it is the other extreme of the first possibility. This is interesting to consider, especially since it is possible for this to happen with some outside forces such as mechanical recovery or heating of the droplet.

The last possibility this thesis looks at is a hybrid between the two droplets. Sometimes it seems like the droplets connect but keep a solid phase to make a bulky droplet, in which it can be seen where one droplet ends and the other starts. For a visual representation of the three possibilities, see Figure 8-1.
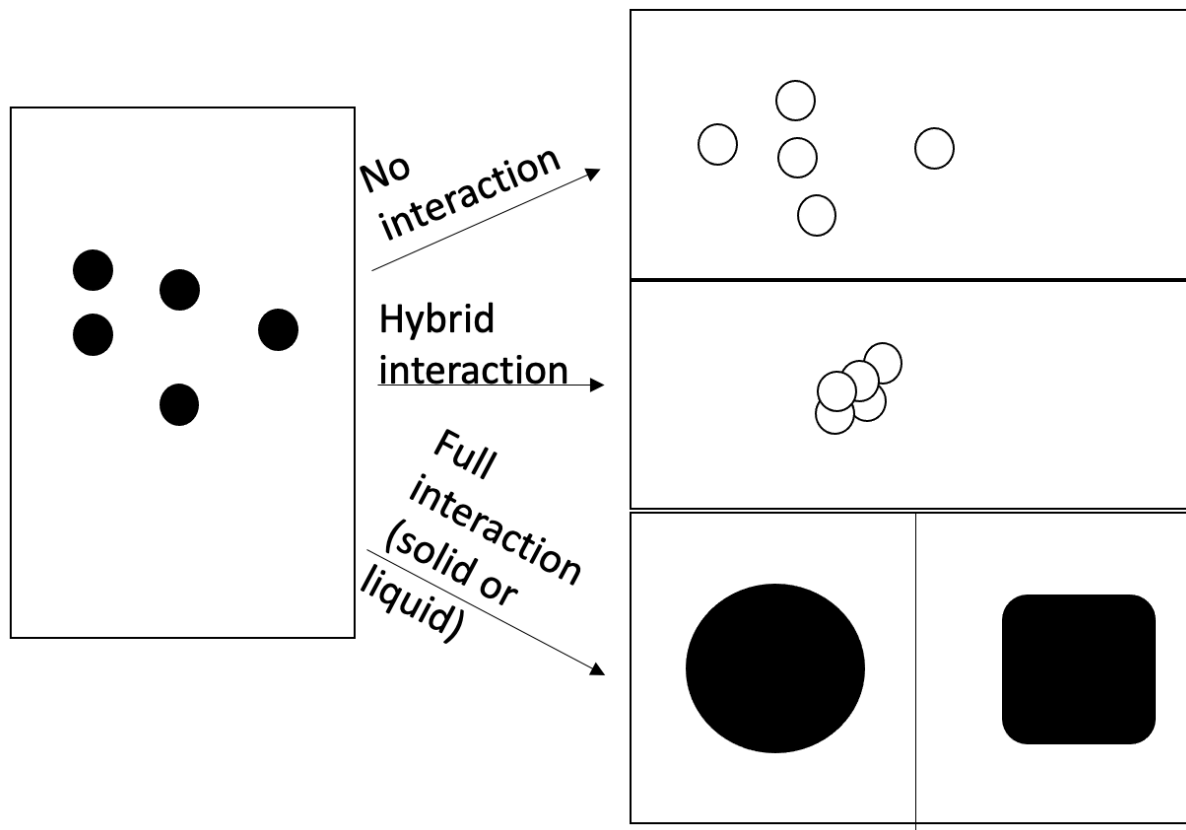
Figure 8-1: Visual representation of the different ways the droplets might interact after a collision.

A hybrid interaction was observed numerous times during the experiment using the inverted cone. The droplets also stuck to the walls and each other numerous times throughout testing. It should be noted that other factors such as weathering might render this observation wrong in an actual release. Furthermore, the rate and probabilities of collision might create variation in the time until coalition, and the interaction might differ based on the time after release. However, further research is needed to be able to draw any conclusions.

8.3 How does solidification affect weathering of the oil?

All weathering research seems to focus on a liquid oil layer on the sea. For mesoscale research of weathering properties at SINTEF, even high pour point oils are being applied as a homogenous liquid layer to the basin by heating the oil to 50 °C before application (Sørheim et al., 2021). However, if the droplets remain as discreet droplets upon surfacing, the weathering of the oil might behave differently than assumed.

8.3.1 Possible effect of solidification on evaporation

A solidified droplet would probably have a slower evaporation rate than a liquid slick. A solidified droplet has a lower surface-area-to-volume rate. As presented in 2.4.1, evaporation rate is dependent on area exposed to the atmosphere, which a solidified droplet will have less

of. Furthermore, the solidified compounds must go through two phase changes instead of one, solid to liquid, and liquid to gas, which requires more energy.

It should be noted that the percentage of volatile components in high-pour-point oils is usually lower than in other oils, as they contain a higher percentage of waxes and other components having low volatility. It has already been shown that evaporation is usually not the most significant contributor to weathering for these oils. For example, Duva's evaporation is not significant until after 4 hr, when 2 wt.% of the oil has evaporated (Sørheim et al., 2021).

8.3.2 Possible effect of solidification on emulsification

A solid or semi-solid façade around the droplet makes it difficult for the water to penetrate it and cause emulsification, and it is therefore probable this is not the most significant contributor to weathering for a solidified droplet. It should be noted that, as presented in section 2.4, the emulsification process is not fully understood. Therefore, there is extra uncertainty about what would happen with a solidified droplet.

8.3.3 Possible effect of solidification on dispersion

As dispersion occurs when water droplets become forever trapped in the water column, the first dispersions will happen during the droplets journey through the water column. The outlet of oil would probably still create a normal distribution of droplet sizes traveling to the surface, both due to the pressure from the release as well as the temperature of the oil in the pipes keeping the oil in a liquid phase. However, the density of the droplets might change due to the solidification, which might affect the DSD based on when the solidification happens. As presented in 2.3 the buoyancy of the droplets primarily is based on the density of an object. Therefore, a change in density will change the volume at which the buoyancy of the droplet is less than the turbulence in the water column and become permanently dispersed. It seems like it is no research on the density difference of solid and liquid oil, and therefore it is hard to say how big this effect might be.

When the oil first reaches the surface, the droplets have to break into smaller droplets to be able to disperse. This will probably be more difficult for the solidified droplets versus the liquefied droplets due to higher surface tension.

A liquid oil with a high-wax content already has a low dispersion rate. For the weathering test of Duva, the dispersion was 2 wt.% after 72 hours (Sørheim et al., 2021). Assuming that the dispersion rate is lower for a solidified droplet; Since the dispersion rate cannot be less than 0

wt.% the change in dispersion rate cannot be more than 2 wt.%, which will not affect the spills total clean-up and environmental concerns to a great degree.

8.4 How does solidification affect the clean-up?

After an oil spill, mechanical and chemical clean-up can be crucial for the environmental. Up until now, it seems like research on the best clean-up methods has been limited to liquified experiments. This might create a challenge if a solidified release happens, and the liquid protocols prove ineffective for cleaning up solidified oil.

8.4.1 Possible effect of solidification for application of dispersants

As presented in section 2.5, the dispersant needs to penetrate the oil to disperse the droplets. If the oil is too viscous, the dispersants glide off the slick instead of interacting with the oil. Therefore, if the droplets are already solidified, the dispersion might not be possible. Presently, high-wax dispersants do not seem to exist, and it might take time to make chemical clean-up methods for solidified droplets.

8.4.2 Possible effect of solidification for collection with booms

One of the questions for effectiveness of booms may be how the droplets spread. A low concentration of oil over a large area would be challenging to collect and might render the booms ineffective. However, this would probably not be the case for big blowouts, where there probably would be high enough concentrations of oil to make booming effective. Another problem with the booms might be the high viscosity of the oil. As presented in section 2.5, a high viscosity might lead to critical accumulation, where the oil is swept under the booms due to a collection at the end of the booms.

Another interesting question is how the droplets would behave when collected and mashed together by the booms. The pure force of the waves and collisions might be enough to make the droplets liquefy or as shown in Figure 8-1, make a hybrid droplet.

8.4.3 Possible effect of solidification on skimmer usage

Skimmers prone to clogging would probably not be the best method for solidified droplets, at least not alone. As presented in section 2.5, viscous oil is prone to clog the skimmers, making them ineffective. During the inverted cone experiment, the droplets had a habit of sticking to the walls, and it usually required forceful cleaning to remove them. Therefore, it is probable that the skimmers would be clogged by the oil if used with high concentrations of solidified oil.

However, both the oleophilic skimmer and the weir skimmer might be helpful for clean-up. As sticking to the wall was experienced during the research, it is not improbable that there are materials that the oil would prefer more than water. Knowing the degree of droplet solidification would be essential for further predictions. For example, would a hard cover form, like tar balls, or would the oil become sticky and move toward liquefication? It seems there has not been any previous skimmer research performed on tar balls, but the hard shell makes it improbable that the oleophilic forces would be strong enough to make them stick. The water temperature and weather would probably be vital for the droplets' degree of stickiness. Hot water, intense sunlight, or both would probably help melt the oil, while cold water and no sunlight would probably aid in solidification. However, more research is needed to conclude whether these assumptions are correct.

The vortex mentioned in section 2.5 "High wax clean-up measures" might be possible to use in the clean-up of solidified droplets. The vortex might be enough to break up the solidified oils since it is strong enough to attract and destroy the wax net in high viscosity oils. It should be mentioned that since the viscosity of a solid is impossible to define, a solidified oil is not directly a high viscosity oil, and might behave different from a high-viscosity oil.

Regarding the wax inhibitors, it has already been concluded that they have little to no effect on the clean-up and weathering of the oil (Sørheim et al., 2012). Therefore, post-release application is probably not the best response method for solidified oil. However, an addition of wax inhibitors pre-release might influence how the oil behave after a release. Due to the wax inhibitors preventing the wax crystal formation, it is be possible that oil containing wax inhibitors might not solidify or solidifies at higher temperature. As the oil in pipeline production probably already has some wax inhibitors added to hinder clogging, wax inhibitors could influence the weathering and clean-up during a release.

8.4.4 Possible effect of solidification on *in situ* burning

In situ burning might be complicated in open water if the droplets are solidified. As a thick oil slick is necessary to be able to sustain the burning. It should be possible to collect the oil using fireproof booms and set fire to it. However, the lack of volatile compounds might make the oils that solidify difficult to set on fire in the first place. Furthermore, a molecule needs extra energy to transform from a solid to a liquid and a liquid to a gas. The extra energy required to go through one extra phase change might be too much making the fire unsustainable.

As emulsion probably would not be an important weathering factor for solidified droplets, the criteria of a low water percentage for possible *in situ burning* would probably not be a problem. Thus, some of the criteria for sustainable *in situ* burning are probably accomplished.

8.5 How can solidification affect the detection of oil spills?

Compared to a thick oil slick, the solidified droplets would not change much in color for the passive detectors. Therefore, the detector might be able to pick up the droplets the same way. The problem could be that the droplets spread too much to be detected. A lone droplet is only around one millimeter in diameter, and if it is alone in the sea, no camera would be able to capture it visually.

For radars, a solidified droplet would probably have a different texture, slick behavior, and spreading pattern than a typical slick. Therefore, it is expected that today's algorithms will not work on these kinds of releases. The algorithm might be easy to fix by regulating the algorithm to include these parameters. However, as it is already struggling with false positives, it is expected that this change would probably still create many false positives, and it seems like researchers are struggling to fix this.

9. Further work

Further work should focus on determining how the oils with a pour point of ± 10 °C the sea temperature behave or what will happen to the solidified droplets after reaching the surface.

If looking into the behavior of the oil with a pour point around the same as sea temperature more camera equipment to simultaneously shoot is recommended. One main problem during this thesis was catching the droplet on video due to the droplet's small size and considerable movement. Keeping the droplet in the basin for a longer time would also be essential to observe the deconstruction of the droplets in their completeness.

It would be interesting to examine how the droplets would behave after reaching the surface. A long-term weathering study with simulated sunlight and waves and an examination of the interaction between droplets' after being released to the surface could accomplish this aim. This information could significantly contribute to the clean-up of released droplets. However, using the inverted cone for either of these studies is not recommended without large changes to the set-up. Since oils with high enough pour points solidify immediately after a droplet is formed, one recommendation is to create the droplets without keeping them submerged and experiment in a weathering tank or typical seawater tank.

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A.1 Pictures from experiment- Solidified worm

Figure A.1-1:Picture from experiment, where Duva oil was released as a worm, instead of droplets.
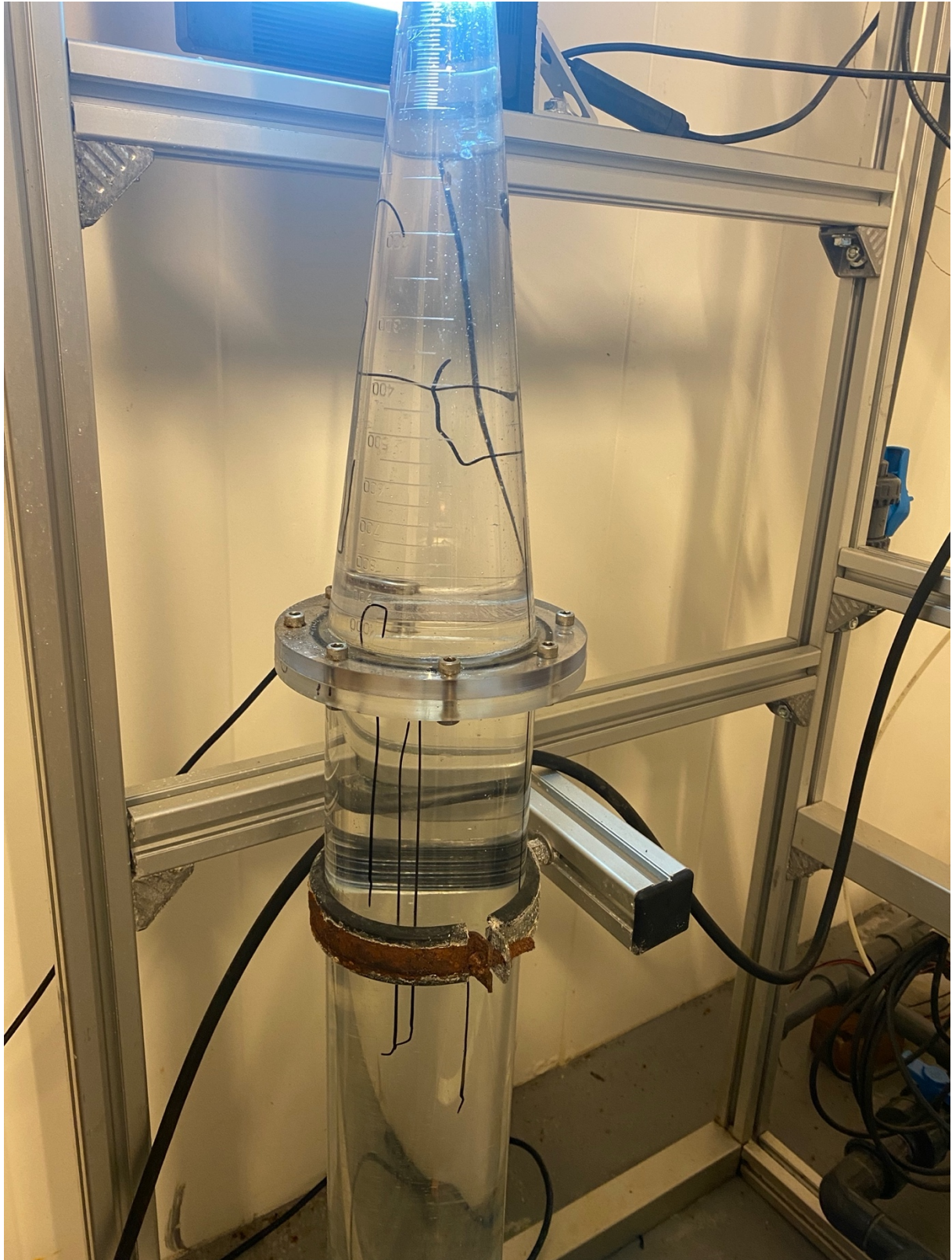
Figure A.1-2: Picture from experiment where duva oil was released as a worm instead of oil droplets.
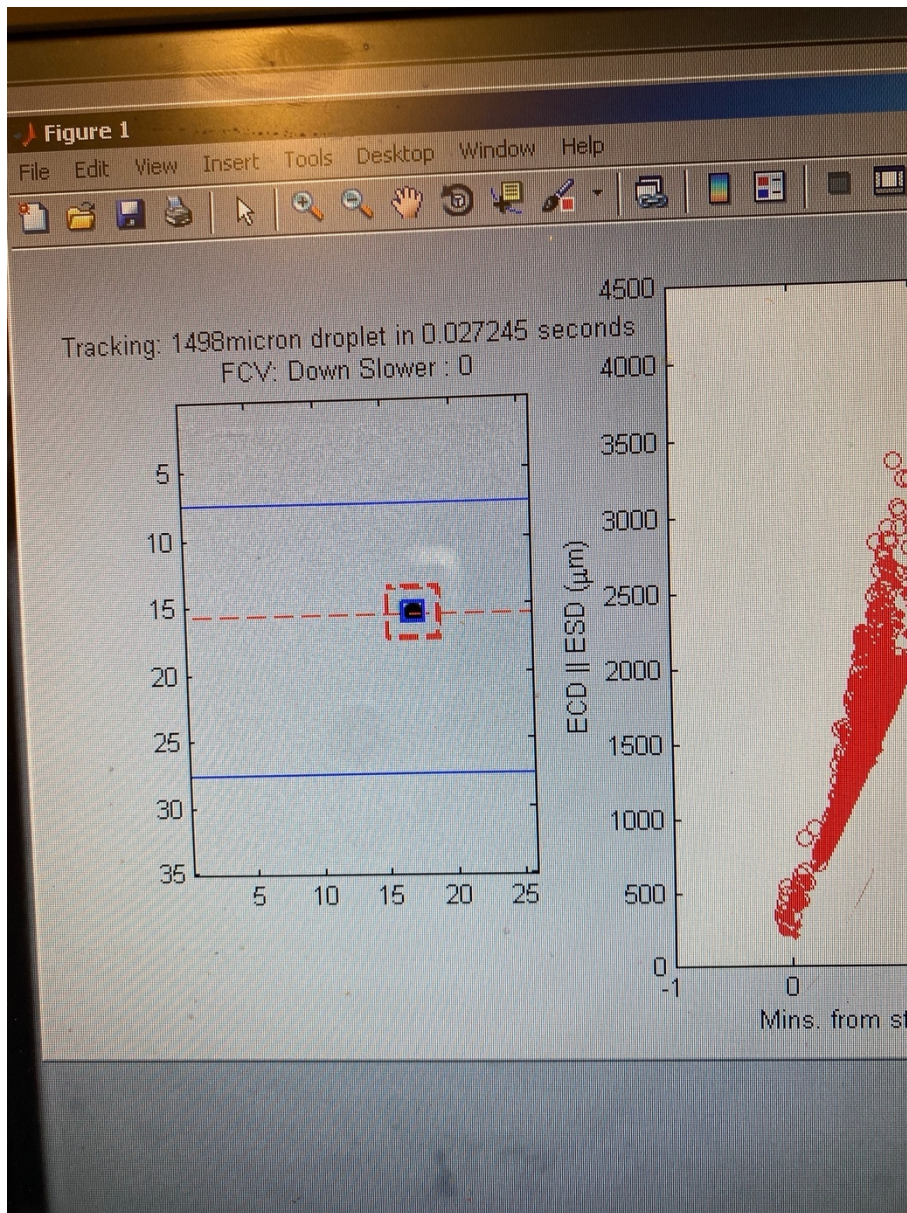
A.2 Pictures from experiment- MATHLAB output

Figure A.2-1: The data screen when MATHLAB is running giving the droplet size and tracking.
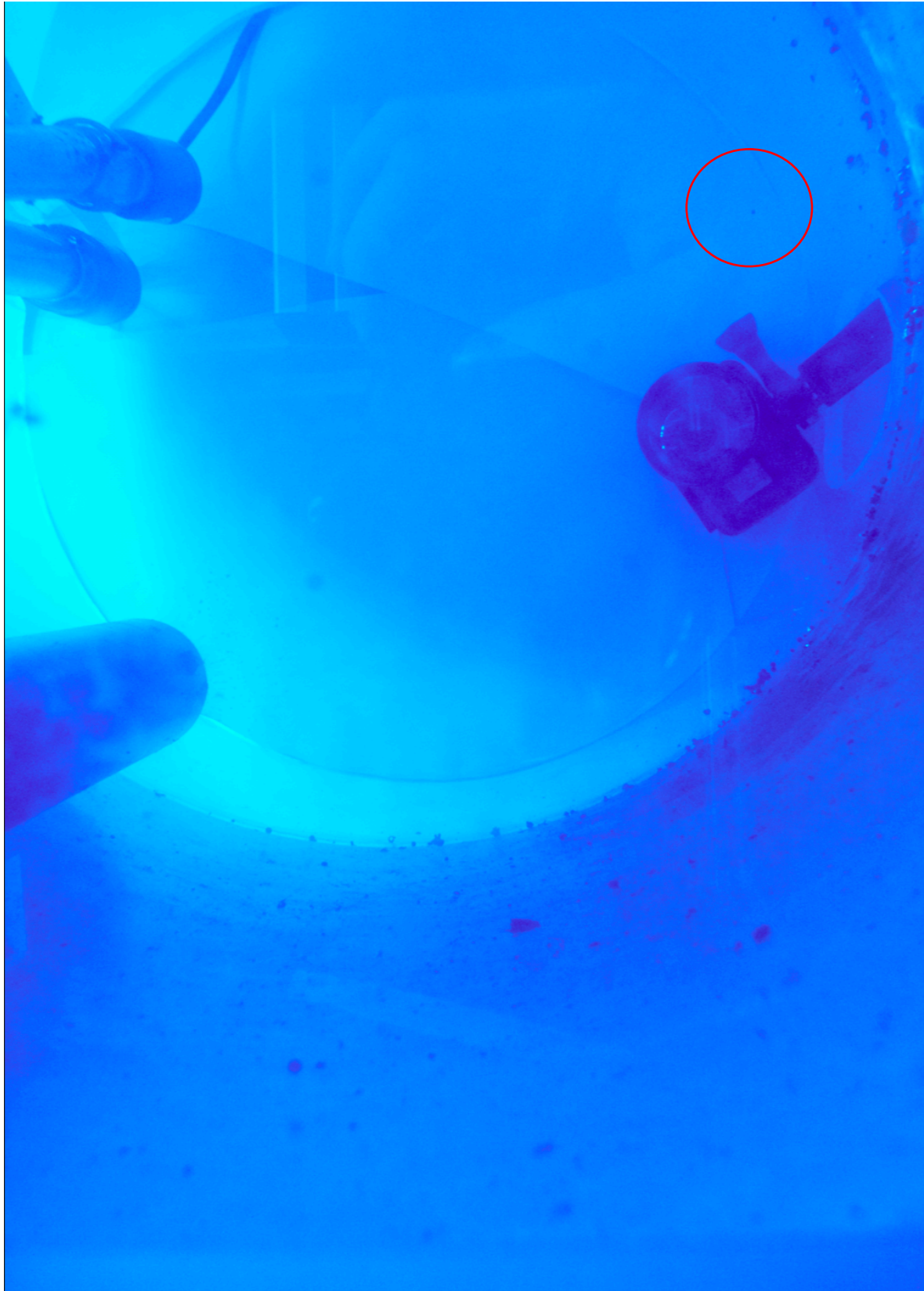
A.3 Pictures from experiment – Fluorescein photos from SLR

Figure A.3-1: Picture of droplet from SLR-Camera. 1.5mm droplet of Grosbeak that have been suspended under-water for 2h. Droplet is circled in red. The droplet is found by looking for movement of black droplet in picture sequence.
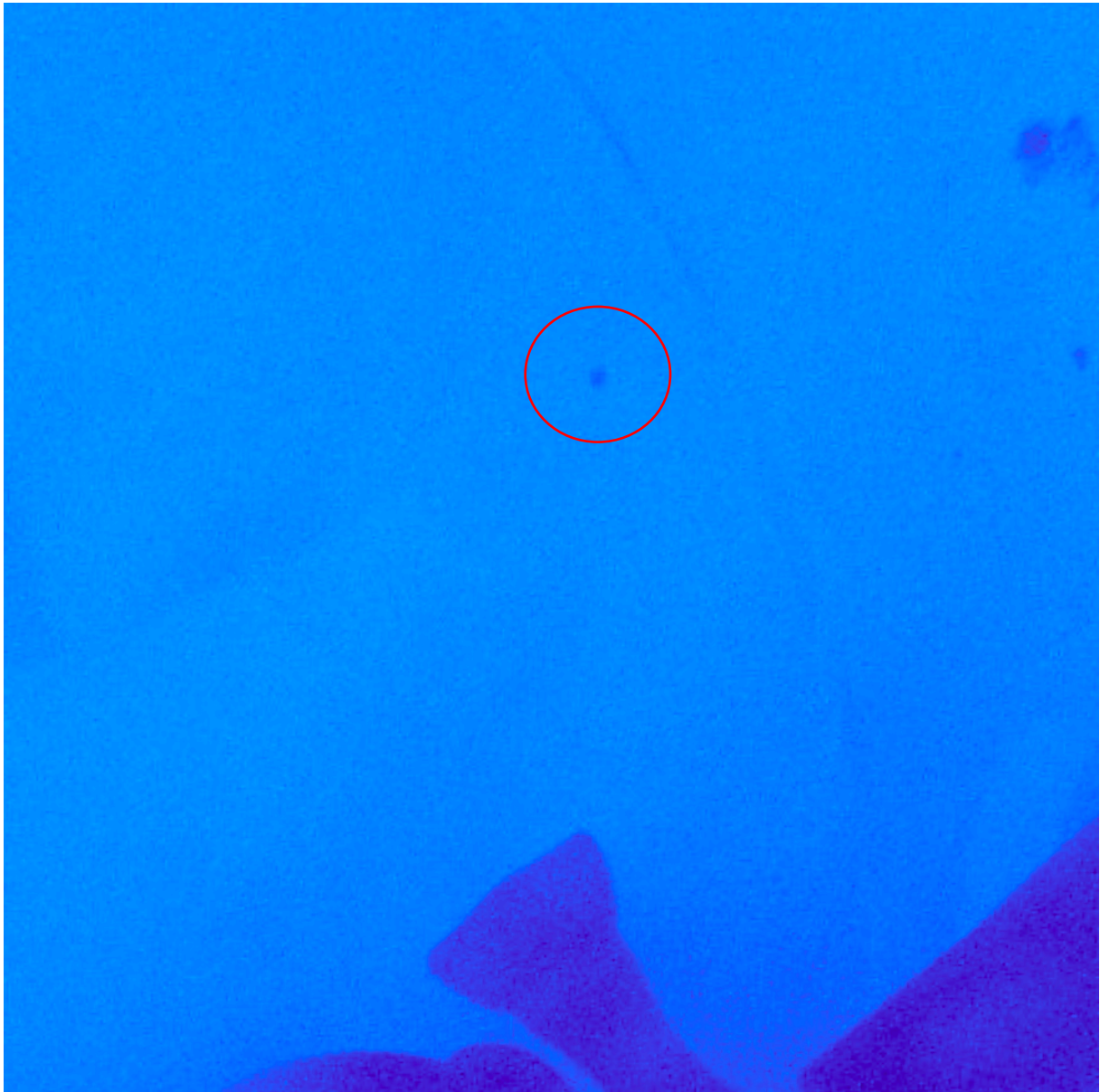
Figure A3-2: Zoomed in picture of droplet from SLR-Camera. 1.5mm droplet of Grosbeak that have been suspended underwater for 2h. The droplet is circled in red. The droplet is found by looking for movement of black droplet in picture sequence.

A.4   Pictures from experiment – Gopro screenshot

Figure A.4-1: Screenshot from video of solidified droplet taken by GoPro. 1.5mm oil droplet of Duva that have been suspended underwater for 0 min. Droplet is circled in red.
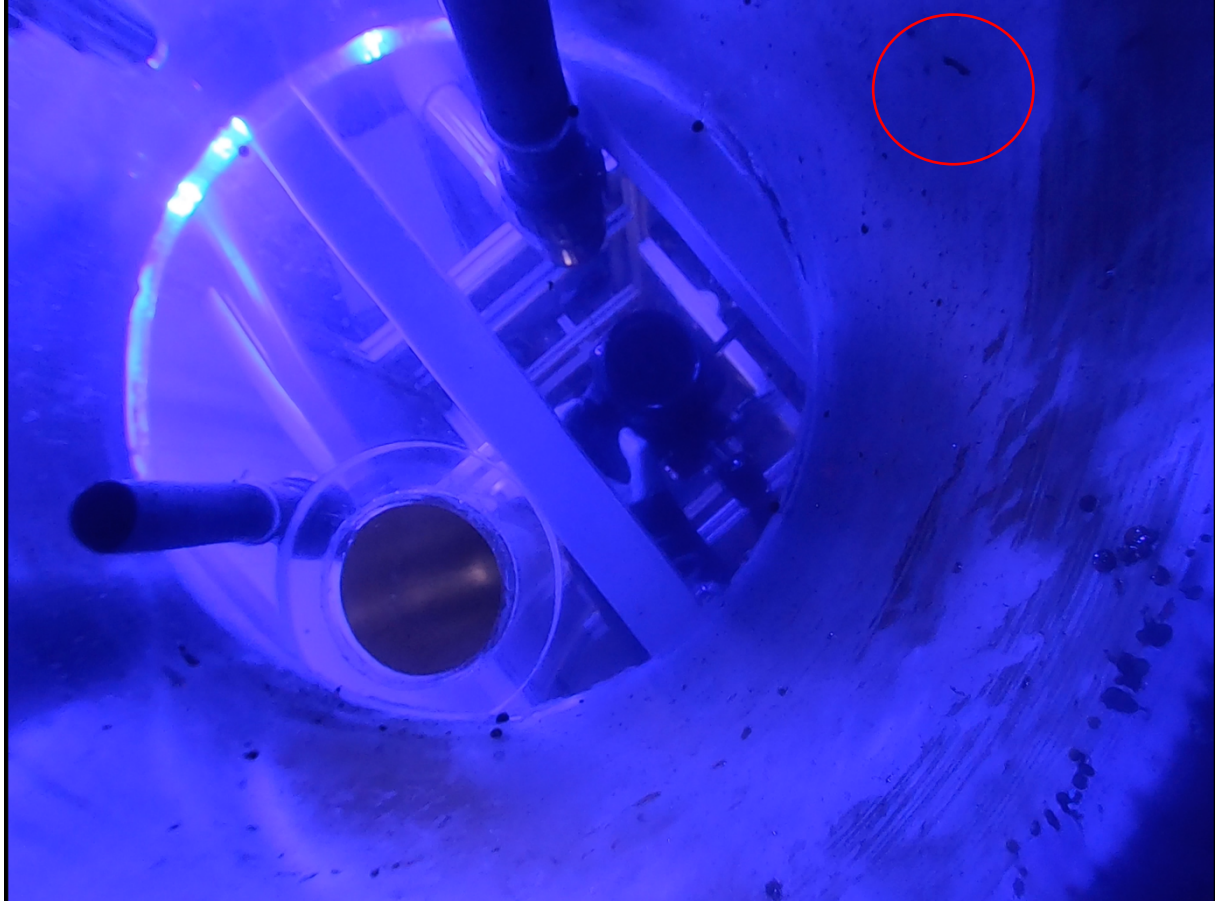
Figure A.4-2: Screenshot from Gopro showing deconstruction of droplet. Droplet being desconstructed are circled in red. Figure A.4-3 is taken less than a second after, where two discreet droplets are seen. Droplet is Oseberg East 1.5mm that have been suspended underwater for 1.5h.
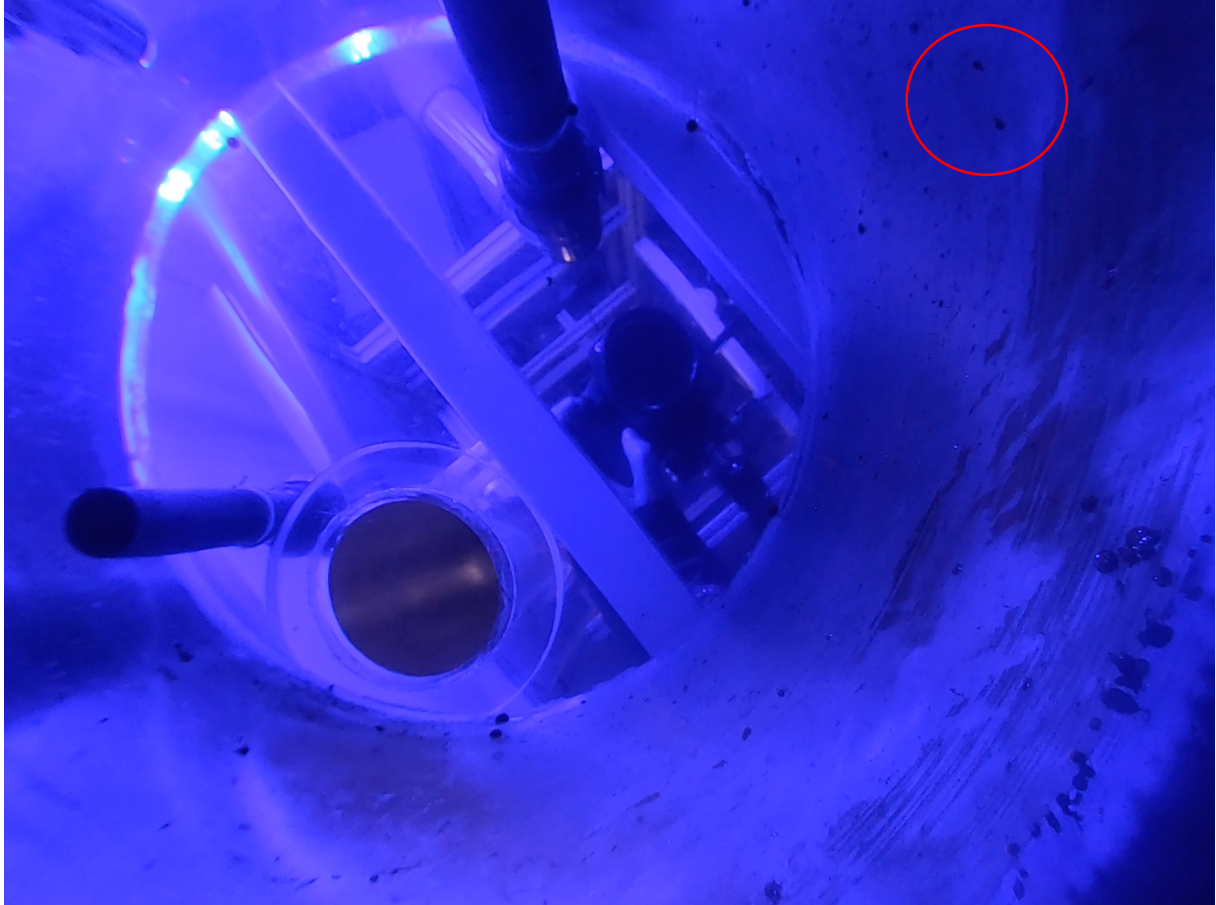
Figure A.4-3: Screenshot from Gopro showing result after a deconstruction of droplet. Here two discreet droplets are seen, highlighted in red. Figure A.4-2 is taken less than a second before, where one droplets are seen. Droplet is Oseberg East 1.5mm that have been suspended underwater for 1.5h.
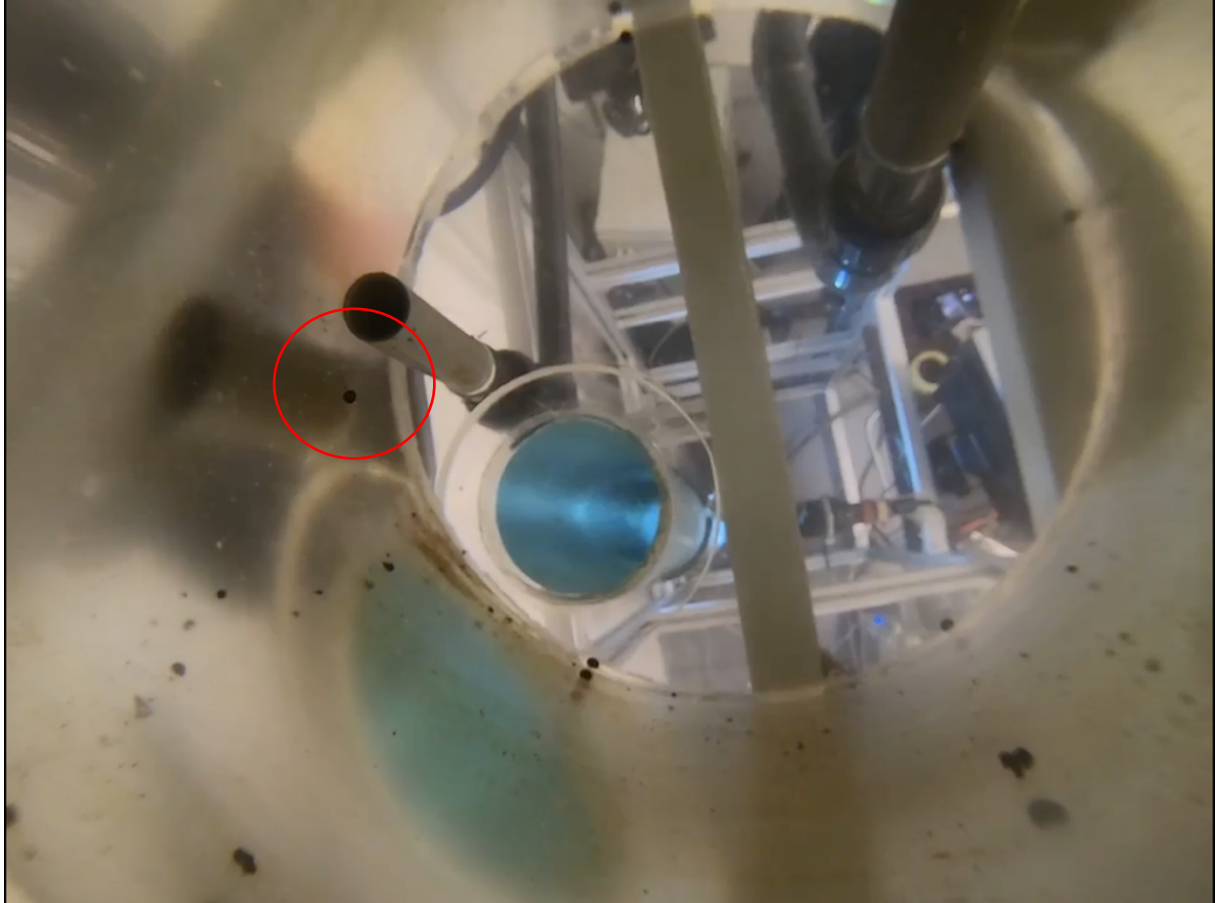
Figure A.4-4: Screenshot from Gopro showing result before liquefication of droplet. The droplet is still submerged, and a whole droplet can be seen. Figure A.4-5 is taken less than a second after, where there is a small discolouring of water instead. Oil used is Oda, droplet size is 1.5mm and the droplet have been submerged for 15 min.
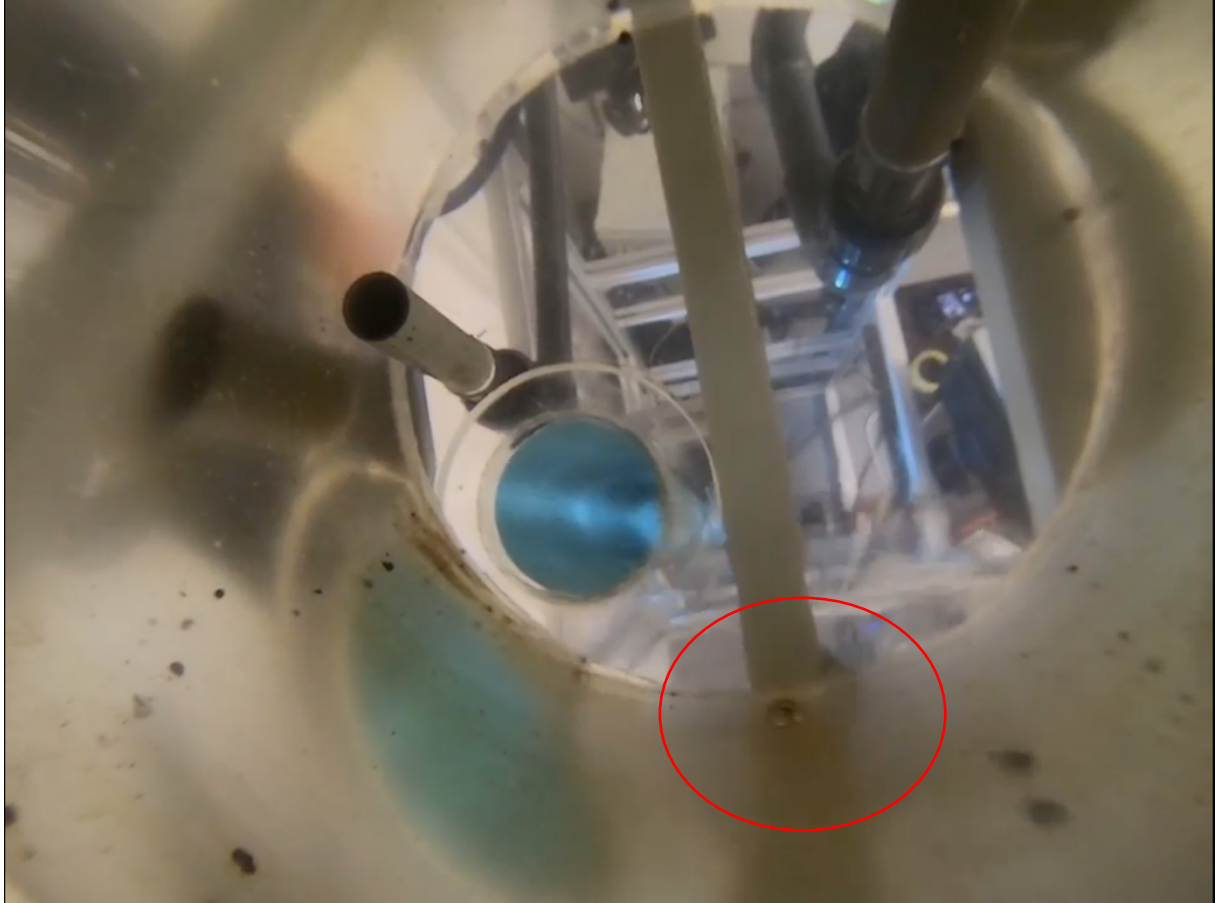
Figure A.4-5: Screenshot from Gopro video showing result after liquefication of droplet. One can see a slight discoloring where the drolet has liquefied. Figure A.4-4 is taken less than a second before where the droplet is still intact. Oil used is Oda, droplet size is 1.5mm and the droplet have been submerged for 15 min.