Report

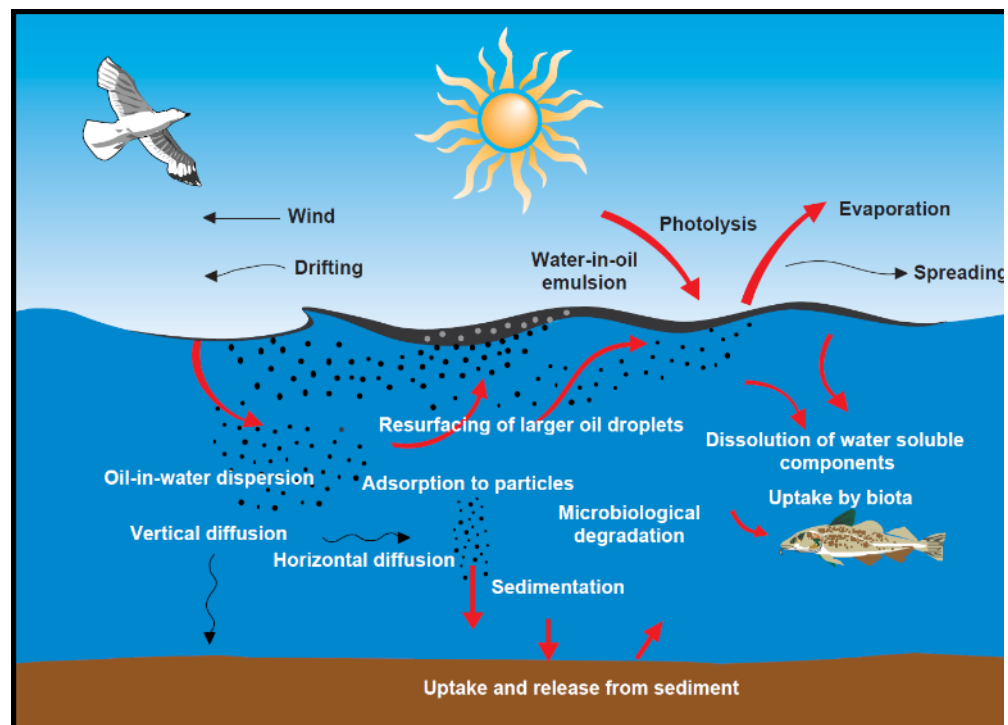## Kvitebjørn condensate – Weathering properties and behaviour at sea

In relation to oil spill response

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Report

Kvitebjørn condensate – Weathering properties and behaviour at sea

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KEYWORDS:
Weathering properties;
Emulsification;
Oil Weathering Model
(OWM);
Kvitebjørn

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ABSTRACT
A weathering study has been conducted on the Kvitebjørn condensate. This study is based on a small-scale laboratory testing at 13 °C. The SINTEF Oil Weathering Model (OWM) was used to predict the weathering properties of the Kvitebjørn condensate if spilled on the sea surface. The weathering properties were also discussed in relation to oil spill response.

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Table of contents

PROJECT NO.
302004682

REPORT NO.
OC2019 A-097

VERSION
2.0

4 of 56

1 Executive summary

Spilled oils undergo changes when weathered on the sea surface. These changes affect oil behaviour and consequently oil spill countermeasures. Oil weathering varies over time and with different environmental conditions. Based on input from the experimental weathering data of the oil, the SINTEF Oil Weathering Model (OWM) is used to predict the properties of oil as it weathered over time. The lifetime of an oil spill at sea depends on the oil's composition, the release conditions (e.g. on the surface, underwater) and environmental conditions (temperature, wind, waves). Natural dispersion and evaporation are the main weathering processes that remove an oil spill from the sea surface. Evaporation of the lightest compounds increases the relative amount of wax and asphaltenes and changes the physical properties on the residual oil. This summary gives a brief overview of the main changes predicted for Kvitebjørn 2019 when weathered on the sea surface.

Kvitebjørn 2019 is a light condensate with density of 0.752 g/mL with low contents of asphaltenes (0.01 wt. %), and wax (0.14 wt. %). The pour points are low where the fresh Kvitebjørn 2019 and its residues ranges from - 36 to + 9°C. The condensate also exhibits low viscosity of the fresh oil, and weathered residues are ranging from 1 to 26 mPa.s, measured at 13°C. Based on it physico-chemical properties, it is not expected that Kvitebjørn 2019 will emulsify if spilled at sea or will solidify.

The mass balance shows that the condensate has short lifetime on the sea surface, particularly at high wind speeds (1-2 hours) at 10-15 m/s due to high evaporative loss and natural dispersion/entrainment into the water column. At lower wind speeds (2-5 m/s), the oil/residue may remain for a longer time on the surface.

Spilled oil on the sea surface assumes to reach the ambient water temperature within a short time period. The fire hazard, based on the volatile components from the oil, may be high if the flash point of the oil is below the sea temperature. For Kvitebjørn 2019, the flash point is predicted to exceed the sea temperature within the first 15 minutes at wind speeds (10-15 m/s), and within 0.5-1.5 hours at lower winds speeds (2-5 m/s). However, for larger release rates, the time for the flash point to exceed the sea temperature can be extended. Moreover, some storage tanks in vessels engaged in oil recovery operations may not be classified to carry liquids with flash points lower than 60 °C. Kvitebjørn 2019 reaches this limit (60 °C) in 3.5-6 hours after a spill at calm wind speed (2 m/s) at summer and winter conditions, and more rapidly at higher wind speeds.

Mechanical recovery is assumed not to be an appropriate response method due to very low viscosities that pronounce high risk for boom leakage for low viscous oils (lower than 1000 mPa.s). In addition, low oil film thickness (<0.1 mm) is also too low for effective confinement in a boom.

It was not performed dispersibility testing on Kvitebjørn 2019. The oil is expected to have a rapid and vast spreading on the sea surface and produce thin oil films within short time. Use of dispersants for film thicknesses < 0.1 mm are not considered to be optimal and efficient.

Mechanical dispersion by use of high-capacity water flushing can be an option for thin oil films < 0.2-0.3 mm and for low viscous oil/residues such as Kvitebjørn 2019. Such condition is expected to be the case after few hours from a batch surface release, and immediately after a subsurface release.

Monitoring and remote sensing will in any case be important in an oil spill operation and can be evaluated as a sufficient and practical response option, particularly in increasing wind speeds (> 5m/s) for Kvitebjørn 2019.

2 Introduction

New oil types (from heavy crude oil to light crude oils and condensates) are continuously coming into production worldwide. Due to large variations in different crude oils' physical and chemical properties, their behaviour and fate may vary greatly if spilled at sea. For example, the "Braer" accident at the Shetlands (1993) and the "Sea Empress" accident in Wales (1996) have demonstrated how different the fate and behaviour of the crude oils can be when spilled on the sea surface. For that reason, obtaining comprehensive knowledge about the expected behaviour of spilled oil at sea is of great importance. Moreover, the "Deepwater Horizon" incident in the Gulf of Mexico (2010) clearly showed how the efficacy of the different response techniques changed as the oil weathered and emulsified on the sea surface over a long period. These past experiences shape the knowledge base and the subsequent refinement of future operative strategies in terms of where, when and how the mitigation methods should operate during a response operation. Appendix A describes the general physical and chemical properties and weathering processes of crude oils spilled on the sea surface.

SINTEF Ocean, Dept. of Environment and New Recourses has performed a weathering study on Kvitebjørn condensate (2019) based on a request from Equinor. The weathering study was conducted at 13 °C. The obtained laboratory data were used to predict the weathering properties of the oil by use of the SINTEF Oil Weathering Model (OWM).

Kvitebjørn

- Kvitebjørn er et gass/kondensatfelt i Tampen-området i nordlige delen av Nordsjøen (blokk 34/11), 15 km sørøst for Gullfaks

- Oppdaget i 1994 – Plan for utbygging og drift (PUD) 2000

- Produksjonsstart i 2004

- Reservoar: 4000 m

- Vanndyp:190 m

- Boring er utfordrende på Kvitebjørn på grunn av lavt reservoartrykk. Feltet produseres med trykkavlastning - økt gassutvinning.

- Gass og kondensat transporteres i rør til hhv. Kollsnes og Mongstad

- Kondensat transportens via Kvitebjørn Oil Pipeline, som er tilknyttet Troll Oil Pipeline II til Mongstad

- Operatør: Equinor Energy (39,5%), Petoro (30%), Spirit Energy (19%), AS Norske Shell (6,5%), Total E&P Norge (5%)

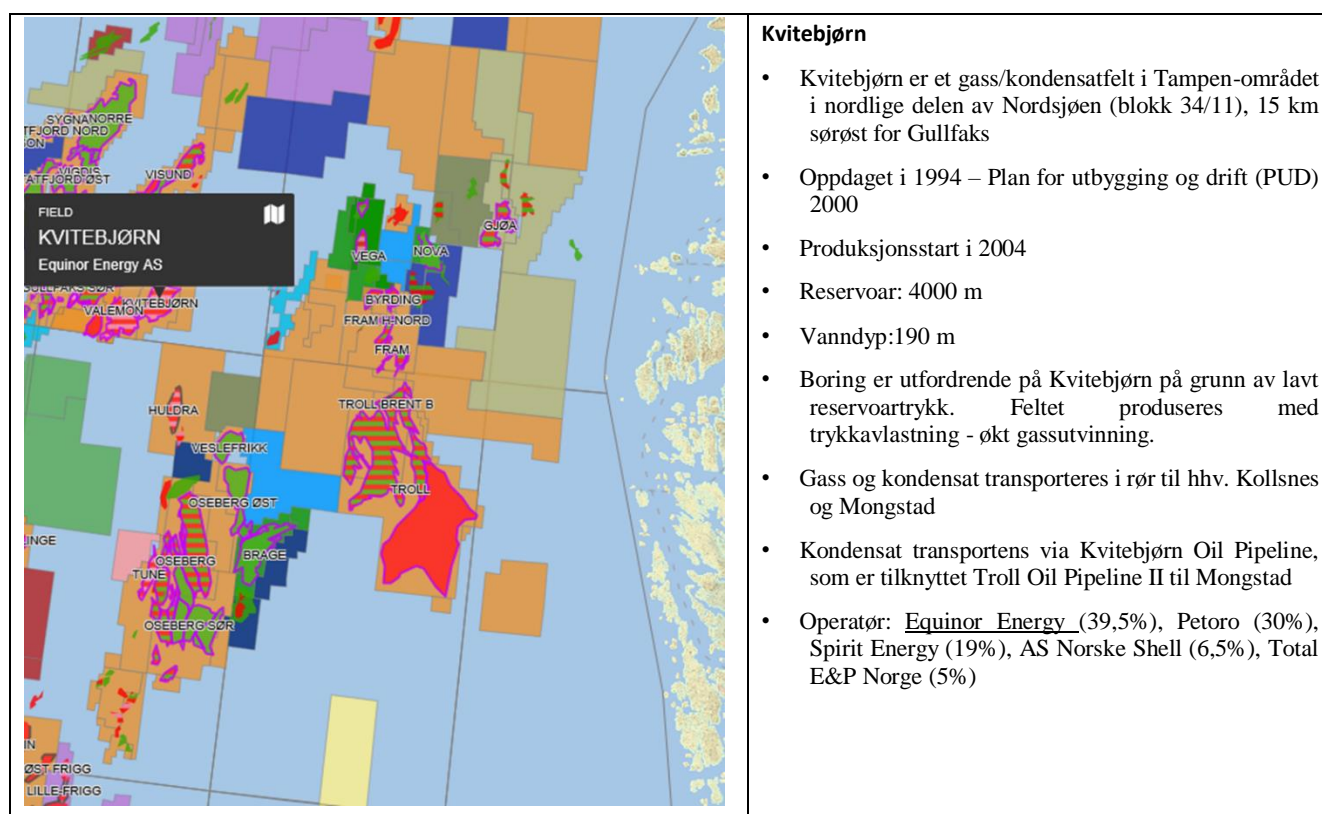*Figure 2-1: https://www.norskpetroleum.no/fakta/felt/kvitebjorn/*

3 Small-scale laboratory testing results

The methodology of small-scale testing is described in Appendix B. Physicochemical parameters and weathering properties of the Kvitebjørn condensate (2019) were compared with similar data of other Norwegian oils as listed in Table 3-1 (Kvitebjørn 2009, Kristin 2006, and Sleipner 1993). The oils in comparison (light crude oil and condensate) were selected in agreement with Equinor. Kvitebjørn was previously tested for its weathering properties in 2009, given as Kvitebjørn 2009, whilst the Kvitebjørn condensate from this current study is presented as Kvitebjørn 2019, for simplicity.

Table 3-1   Oils compared with Kvitebjørn 2019*

Oil	SINTEF ID	Report no	Reference
Kvitebjørn 2009	2009-0239	A 13743	Sørheim og Altin, 2009
Kristin 2006	2006-0256	A 06221	Leirvik, 2006
Sleipner 1993	-	93.126	Almås, 1993

*Kvitebjørn 2019 was given the SINTEF ID 2019-1059

3.1 Chemical composition and physical properties

The chemical composition of the hydrocarbon profile of n-alkanes (nC_5-nC_{36}) of Kvitebjørn 2019 is shown in Figure 3-1. The wax and asphaltene contents are given in Table 3-2, and the physical properties are given Table 3-3. Appendix D shows the composition of OSCAR groups derived from the chemical characterization of the fresh crude oil based on GC-MS analysis and the boiling point fraction.

Gas chromatographic flame ionization detector (GC-FID) characterization

The hydrocarbon profile of Kvitebjørn 2019 was analysed by use of gas chromatography (GC) coupled with Flame Ionization detector (FID). Figure 3-1 illustrates the GC-FID output (i.e. gas chromatogram) of the fresh oil of Kvitebjørn 2019 and its corresponding evaporated residues at three different degree of evaporative loss of volatiles at 150, 200 and 200℃+ (see Appendix B.2). The loss of low molecular weight (volatiles) compounds (shown towards the left of the chromatogram) at the three temperatures mimics that of natural weathering (evaporative loss at sea) and provides support for the artificial evaporation of the crude oil by use of distillation (topping) in the laboratory.

The gas chromatograms show the n-alkanes as systematic narrow peaks. The first peaks in the chromatogram represent components with the lowest boiling points. Some of the more complex components, such as resins and naphthenes, are shown as a broad and poorly defined bump below the sharp peaks and are often described as the "Unresolved Complex Mixture" (UCM). Heavier compounds such as asphaltenes ($> nC_{40}$) are not possible to analyze with this technique.

Kvitebjørn 2019 has a high degree of light paraffins (n-alkanes) in the range of nC_5-nC_{15} and reflects an insignificant content of wax $> nC_{20}$. For comparison (see Figure 3-2), the chromatogram for Kvitebjørn 2009 also show a high content of light compounds but exhibits a higher content of the heavier n-alkanes from nC_{20}-nC_{30} and indicates therefore a higher content of wax compounds. Kvitebjørn 2009 was at that time classified as a light crude oils, similar as Kristin 2006.

7 of 56

PROJECT NO.
302004682

REPORT NO.
OC2019 A-097

VERSION
2.0

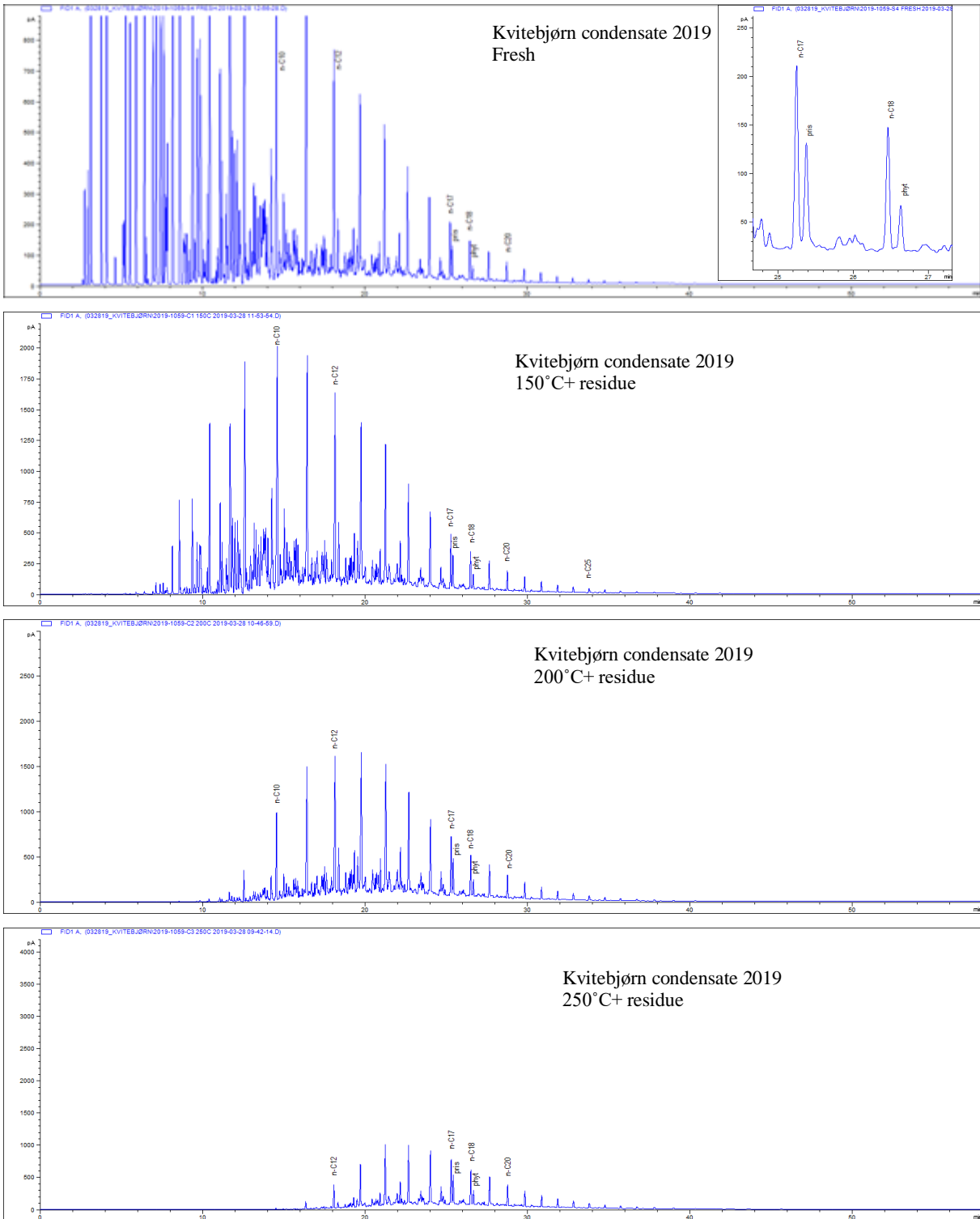*Figure 3-1: GC-FID chromatograms of fresh sample and evaporated residues of Kvitebjørn 2019, normalised on nC20*
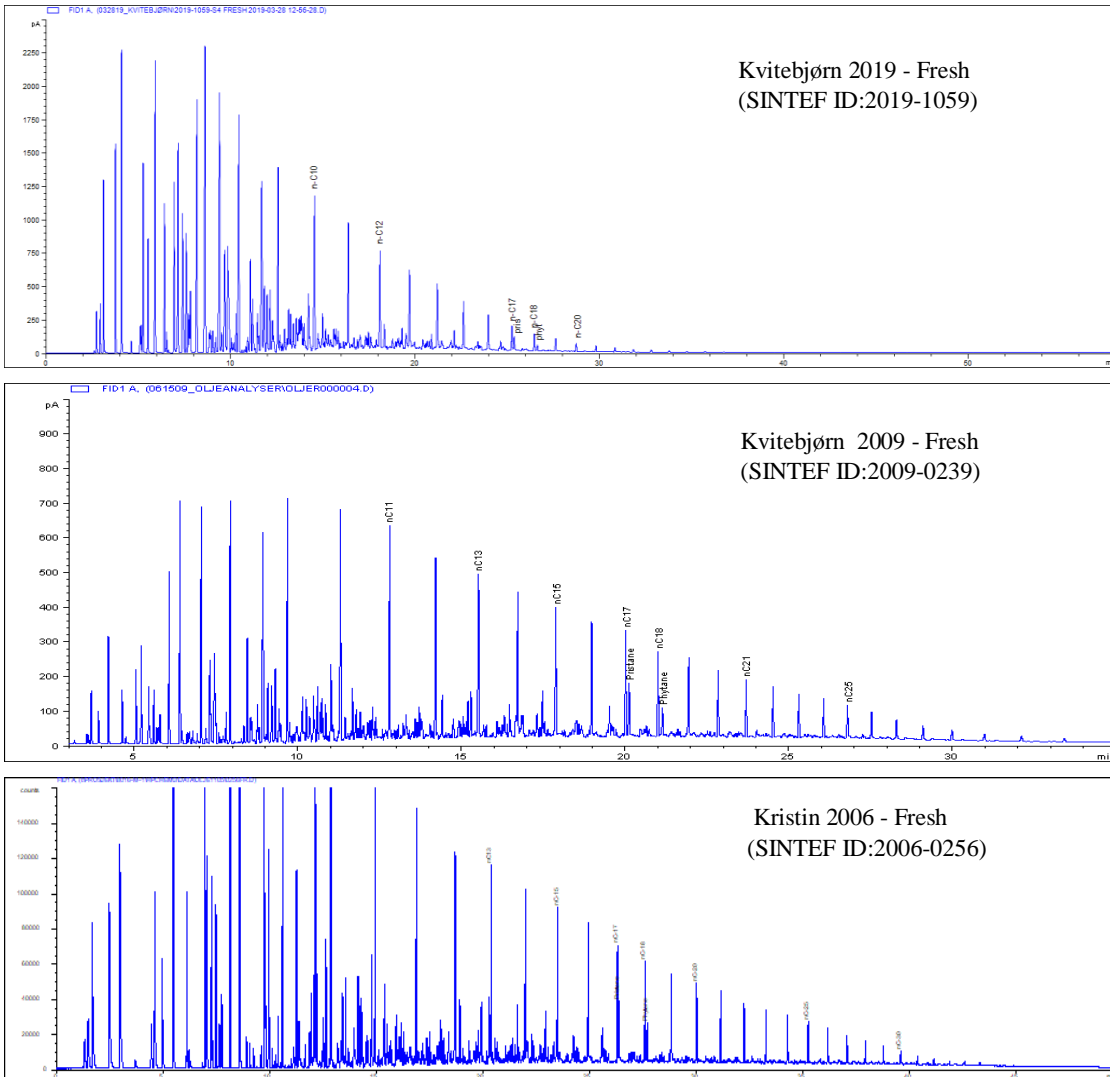
Figure 3-2   ***GC-FID chromatograms for fresh oils of Kvitebjørn (2019) and Kvitebjørn (2009). The retention time differs between the chromatograms due to different temperature programs (relative comparison). A chromatogram of Sleipner from 1993 was not obtained for this comparison***

Asphaltene and wax content for the fresh and weathered residues

The contents of asphaltene and wax for the fresh oil and weathered residues of Kvitebjørn 2019 and the other oils for comparison are given in Table 3-2. The fresh oil of Kvitebjørn 2019 has low contents of wax (0.14 wt.%) and asphaltene (<0.01 wt.%) compared to Kvitebjørn 2009. Kvitebjørn 2019 is currently more comparable with the light condensate Sleipner 1993. Kvitebjørn 2009 and Kristin 2006 exhibits the highest content of wax among these oils with similar concentrations.

Table 3-2   Asphaltene ("hard") and wax content for different oils in comparison

Oil type	Residue	Asph.* (wt. %)	Wax (wt. %)
Kvitebjørn 2019	Fresh	<0.01	0.14
	150°C+	0.01	0.39
	200°C+	0.02	0.80
	250°C+	0.05	1.91
Kvitebjørn 2009	Fresh	0.07	4.31
	150°C+	0.09	5.63
	200°C+	0.12	7.06
	250°C+	0.15	9.18
Kristin 2006	Fresh	0.04	3.91
	150°C+	0.03	5.58
	200°C+	0.04	6.91
	250°C+	0.05	8.64
Sleipner 1993	Fresh	<0.1	0.85
	150°C+	<0.1	2.1
	200°C+	<0.1	3.5
	250°C+	<0.1	5.3

*n-heptane (nC_7) precipitation

Physical properties for the fresh and weathered residues

The physical properties of Kvitebjørn 2019 in comparison Kvitebjørn 2009, Kristin 2006 and Sleipner 1993 are listed in Table 3-3. The evaporative loss of Kvitebjørn 2019 has significantly increased from 2009 and is now more comparable with the Sleipner 1993 condensate. At the same time, the density of Kvitebjørn 2019 has decreased since 2009. Furthermore, the parameters of pour points and viscosities of the fresh oil and residues are lower for Kvitebjørn 2019 compared with Kvitebjørn 2009. Overall, Kvitebjørn 2019 has from 2009 to 2019 become more a light condensate with similarities like the Sleipner 1993 condensate, whilst Kvitebjørn 2009 has similarities with the light crude oil Kristin 2006.

The true boiling point curves (TBP) of Kvitebjørn 2019, Kvitebjørn 2009, Kristin 2006 and Sleipner 1993 are shown in Figure 3-3. The TBP clearly show the similarities of the light condensate of Kvitebjørn 2019 and Sleipner 1993 and the lighter crude oils of Kvitebjørn 2009 and Kristin 2006.

Table 3-3   *Physical properties of Kvitebjørn 2019, Kvitebjørn 2009, Kristin 2006 and Sleipner 1993*

Oil type	Residue	Evap. (vol. %)	Residue (wt. %)	Density (g/mL)	Flash point (°C)	Pour point (°C)	Visc. (mPa.s) 13°C(10 s⁻¹)
Kvitebjørn 2019	Fresh	0	100	0.752	-	<-36	1
	150°C+	65	37	0.797	33	-24	2
	200°C+	84	18	0.816	72	-6	4
	250°C+	93	7.5	0.835	102	9	26
Kvitebjørn 2009	Fresh	0	100	0.802	<-22	-9	5
	150°C+	25	77	0.827	37	-3	43
	200°C+	41	61	0.841	67	9	300
	250°C+	53	47	0.853	105	24	4090
Kristin 2006	Fresh	0	100	0.794	-	-39	2
	150°C+	33	70	0.831	36	0	26
	200°C+	47	57	0.846	72	12	539
	250°C+	58	45	0.860	114	27	7730
Sleipner 1993	Fresh	0	100	0.745	-	<-30	1*
	150°C+	63	40	0.814	38	-9	2.5*
	200°C+	78	25	0.830	69	3	4*
	250°C+	86	16	0.839	98	12	5*

*-: No data *:Viscosity measured given at shear rate 100s⁻¹*

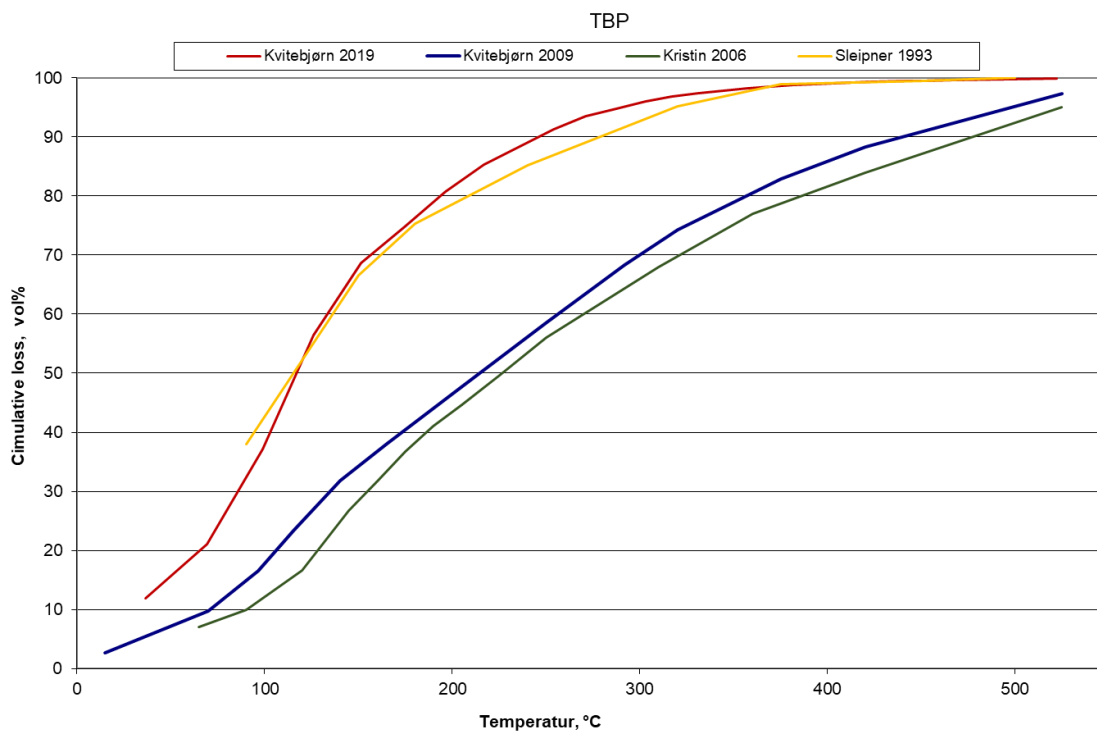*Figure 3-3*   *Distillation curves from SINTEF OWM for Kvitebjørn 2019, Kvitebjørn 2009, Kristin 2006 and Sleipner 1993*

PROJECT NO.
302004682

REPORT NO.
OC2019 A-097

VERSION
2.0

11 of 56

3.2 Emulsifying properties

In general, emulsification is the mixing of seawater droplets into spilled oil at the water's surface (water-in-oil emulsion), forming a weathered oil residue that often tends to be relatively resistant to other weathering processes such as evaporation, and increases the total volume of oil due to the uptake of water into the oil.

Based upon the fact that Kvitebjørn 2019 is a very light condensate with physico-chemical similarities with Sleipner 1993, the testing of emulsifying properties was decided not to be conducted on this oil, assuming non-emulsifying properties. Lack/negligible content of stabilizing components like asphaltenes and very low content of wax also justified this assumption. Moreover, Kvitebjørn 2009 did not produce stable water-in-oil (w/o) emulsions but showed a mixture of oil and water with a certain (low) water uptake based on its physico-chemical properties.

4 Predictions with SINTEF Oil Weathering Model (OWM)

4.1 Description of SINTEF OWM

A systematic stepwise laboratory procedure developed at SINTEF (Daling et al., 1990) was used to isolate and map the various weathering processes that take place when oil is spilled on the sea surface. Laboratory study of Kvitebjørn 2019 was conducted at 13 °C, and the analytical data were further used as input to the SINTEF Oil Weathering Model (OWM) (version 11.0.0). The experimental design for the study is described in Appendix B. The input data to the SINTEF OWM is given in Appendix C.

The SINTEF OWM relates oil properties to a chosen set of conditions (oil/emulsion film thickness, wind speeds and sea temperature) and predicts the change rate of the oil's properties on the sea surface with time. The SINTEF OWM is schematically shown in Figure 4-1. The predictions obtained from the SINTEF OWM are useful tools in the oil spill contingency planning related to the expected behaviour of oil on the sea surface, and to evaluate the time window for operational response strategies in a spill operation. In this report, the presented predictions span a period from 15 minutes to 5 days after an oil spill has occurred. The SINTEF OWM is described in more detail in Johansen (1991), and in the user's guide for the model.
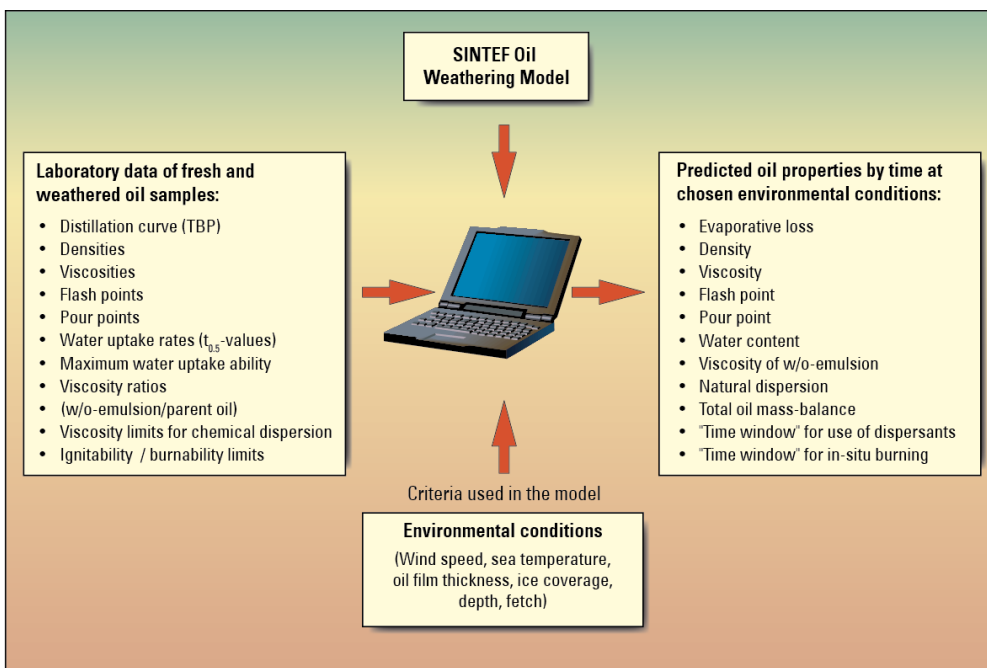

Figure 4-1: Schematic input data to the SINTEF OWM and the predicted output oil properties

Spill scenario

A standard surface release was used as a spill scenario (see section 4.2). The scenario chosen is not oil field specific but selected to give predictions of the expected weathering properties of the oil based on the experimental data and specified terminal oil film thickness. A standardized scenario will also more easily compare results of weathering properties with other oils.

Oil film thickness

Oils are categorized as condensate, emulsifying crude, low emulsifying crude, heavy bunker fuel or refined distillate. The categorization is also based on the experimental results obtained in the laboratory. The terminal

PROJECT NO.
302004682

REPORT NO.
OC2019 A-097

VERSION
2.0

13 of 56

film thicknesses vary among these categories based on experimental (field) experience. Kvitebjørn 2019 is categorized as a condensate with a terminal oil film thicknesses of 0.05 mm.

Seawater temperature

The prevailing weather conditions greatly influence the weathering rate of oil on the sea surface. Due to the location of the oil field, the prediction seawater temperature chosen for Kvitebjørn 2019 was 5 and 15 °C, reflecting winter and summer temperature in the North Sea.

Wind speed

The relationship between the wind speed and significant wave heights used in the prediction charts obtained from the SINTEF OWM are shown in Table 4-1.

Table 4-1: Relationship between wind speed and significant wave height used in the SINTEF OWM

Wind speed [m/s]	Beaufort wind	Wind type	Wave height [m]
2	2	Light breeze	0.1 - 0.3
5	3	Gentle to moderate breeze	0.5 - 0.8
10	5	Fresh breeze	1.5 - 2.5
15	6 – 7	Strong breeze	3 - 4

4.2 Predictions of Kvitebjørn 2019 weathering properties

Input to the OWM

Oil type:	Condensate
Geographical area:	North Sea
Terminal oil film thickness:	0.05
Release rate:	1.33 metric tonnes for 15 min, a total of 20 metric tonnes
Seawater temperature:	5 and 15 °C
Wind speed:	2 m/s, 5 m/s, 10 m/s and 15 m/s

Predicted properties

- Evaporative loss
- Viscosity
- Flash point
- Pour point
- Mass balance

The input data in OWM are based on the crude assay data for the fresh oil (distillation curve, wax, asph, density, viscosity and pour point), in addition to the generated weathering data for the evaporated residues.The predictions are based on 5 days weathering independently if there is not predicted any remining oil within shorter time. The predictions are shown to indicate the weathering properties in cases there are patches or oil left on the surface up to 5 days.

How to use the prediction charts: an example

If the oil has drifted on the sea surface, the following prediction charts could be used to determine the weathering properties of the oil/emulsion. Table 4-2 gives an example for the following scenario:

- Drifting time: 2 hours
- Seawater temperature: 15 °C
- Wind speed: 2, 5 and 10 m/s

Table 4-2   ***Example of weathering properties for Kvitebjørn 2019 obtained from the OWM predictions after 2 hours of weathering at 2, 5 and 10 m/s wind speed***

Weathering property	2 hours 15 ˚C 2 m/s	2 hours 15 ˚C 5 m/s	2 hours 15 ˚C 10 m/s
Evaporation, wt. %	67	77	85
Flash point, °C	41	62	81
Pour Point, °C	-12	-7	-4
Viscosity, mPa.s *	5	6	7
Mass balance / Oil on surface wt.%	33	20	0.5

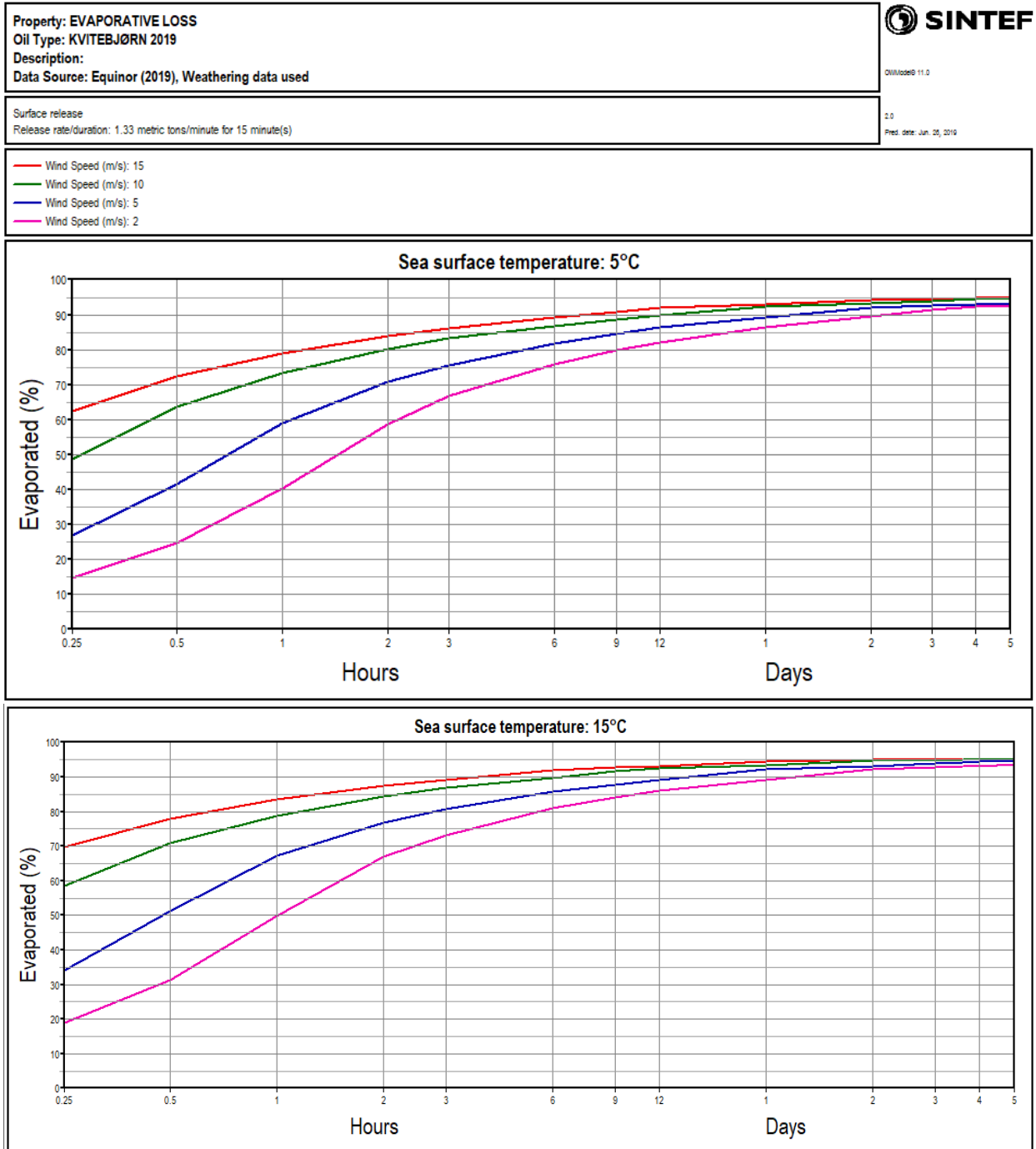**mPa.s = cP (mPa.s: SI-standard / cP: Industrial denotation)*

Figure 4-2 *Evaporative loss of Kvitebjørn 2019 predicted at sea temperatures of 5 and 15 °C*

Property: FLASH POINT FOR WATER-FREE OIL
Oil Type: KVITEBJØRN 2019
Description:
Data Source: Equinor (2019), Weathering data used

SINTEF

OWModel® 11.0

Surface release
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

2.0
Pred. date: Jun. 26, 2019

Wind Speed (m/s): 15 — No fire hazard
Wind Speed (m/s): 10 — Fire hazard in tankage (<60°C
Wind Speed (m/s): 5 — Fire hazard at sea surface (below sea temperature)
Wind Speed (m/s): 2
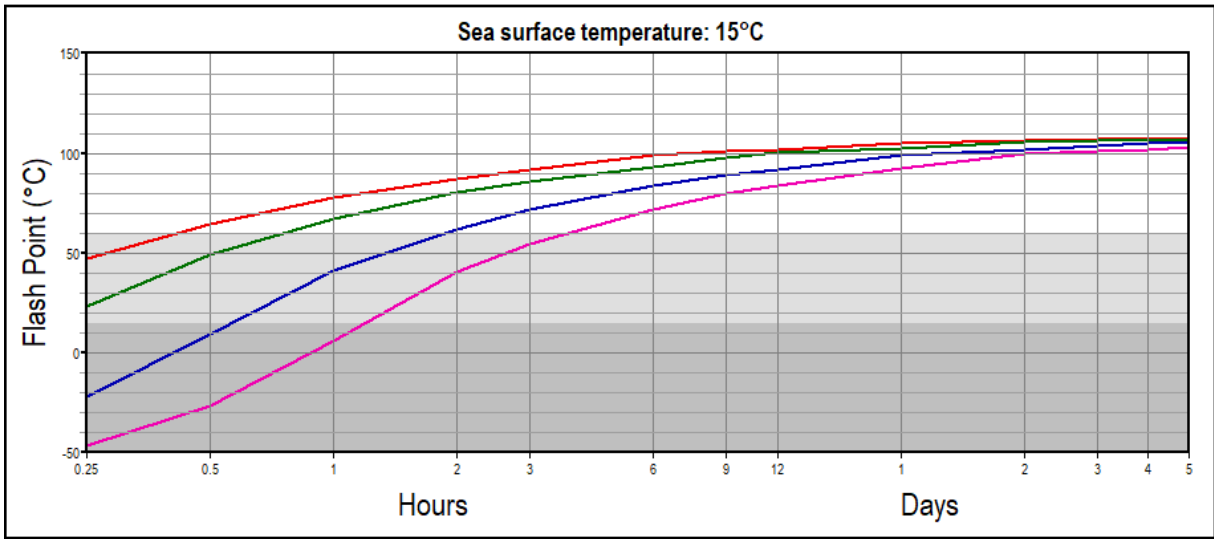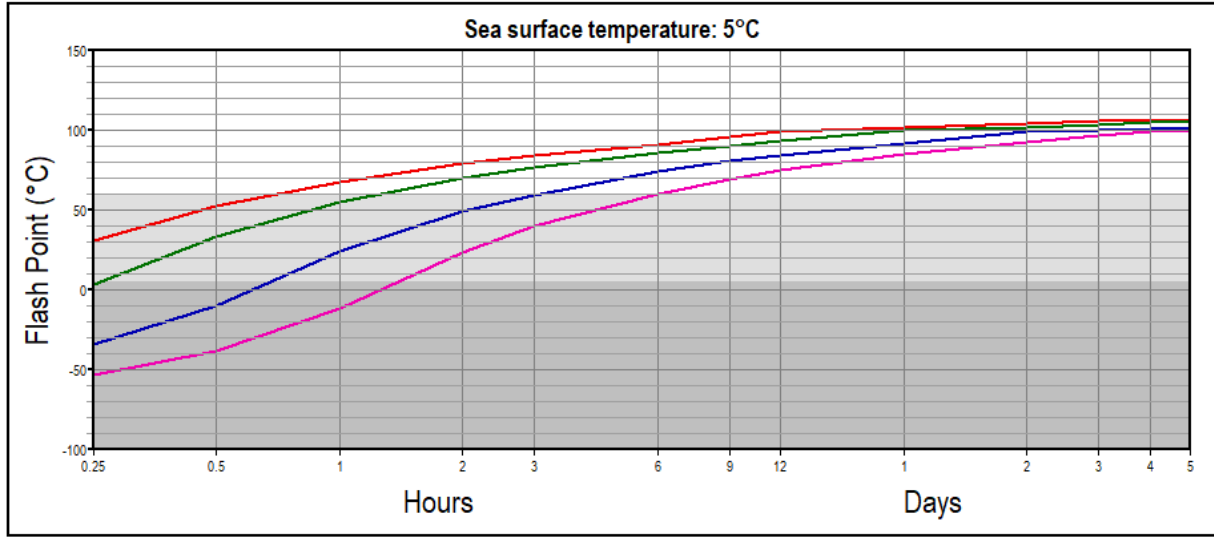
Figure 4-3   Flash point of Kvitebjørn 2019 predicted at sea temperatures of 5 and 15 °C

PROJECT NO.
302004682

REPORT NO.
OC2019 A-097

VERSION
2.0

17 of 56

Property: POUR POINT FOR WATER-FREE OIL
Oil Type: KVITEBJØRN 2019
Description:
Data Source: Equinor (2019), Weathering data used

SINTEF
OWModel® 11.0

Surface release
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

2.0
Pred. date: Jun. 26, 2019

Wind Speed (m/s): 15 — Chemically dispersible
Wind Speed (m/s): 10 — Reduced chemical dispersibility
Wind Speed (m/s): 5 — Poorly / slowly chemically dispersible
Wind Speed (m/s): 2

Sea surface temperature: 5°C

Wind Speed (m/s): 15 — Chemically dispersible
Wind Speed (m/s): 10 — Reduced chemical dispersibility
Wind Speed (m/s): 5 — Poorly / slowly chemically dispersible
Wind Speed (m/s): 2

Sea surface temperature: 15°C

Figure 4-4   Pour point of Kvitebjørn 2019 predicted at sea temperatures of 5 and 15 ℃

PROJECT NO.
302004682

REPORT NO.
OC2019 A-097

VERSION
2.0

18 of 56
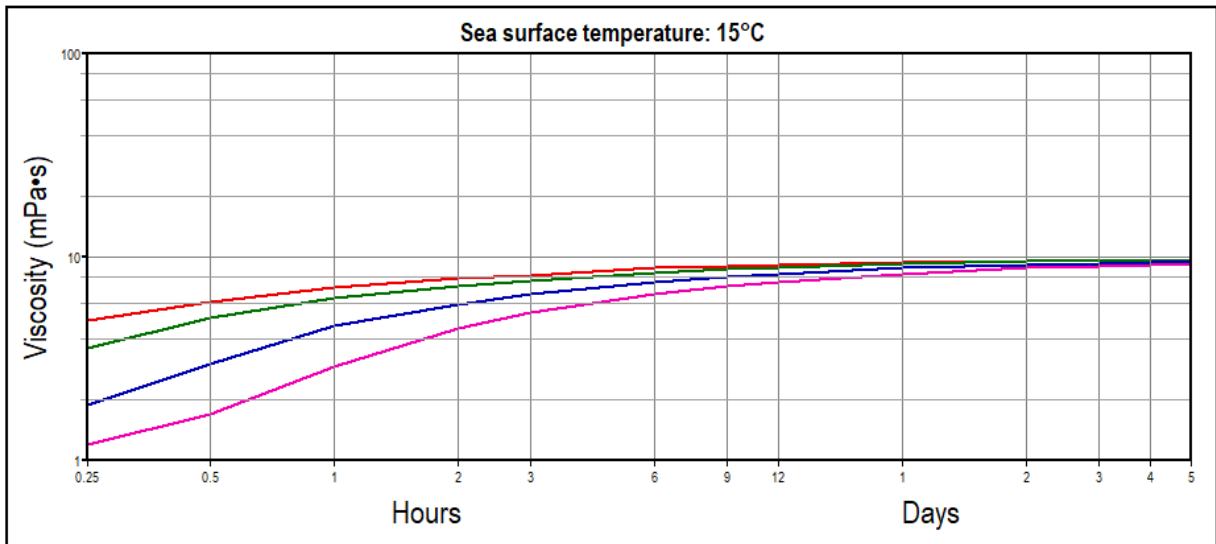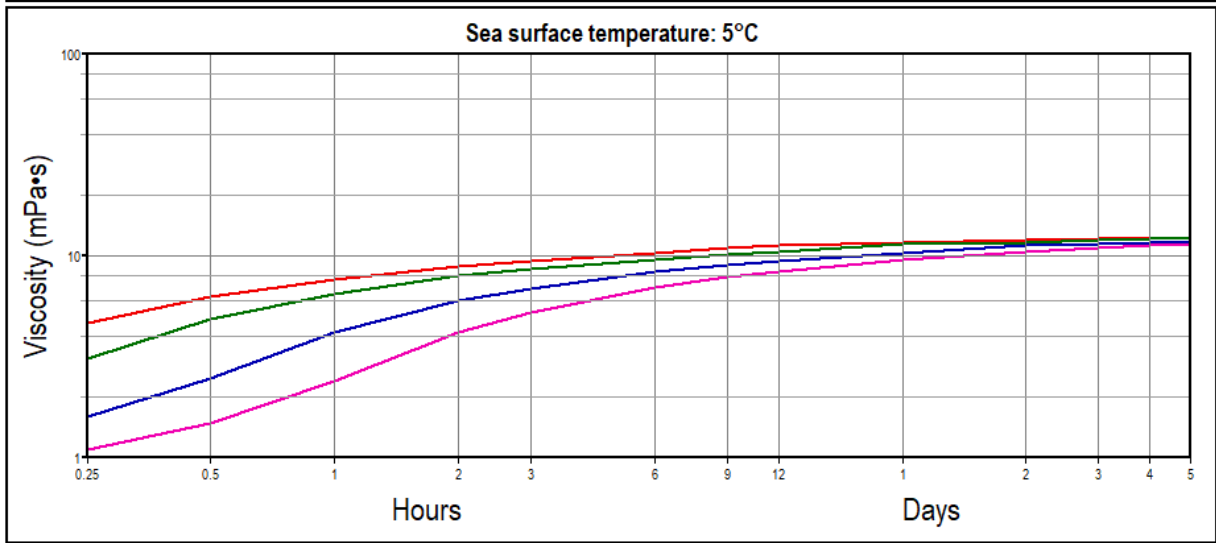
Figure 4-5   Viscosities of Kvitebjørn 2019 predicted at sea temperatures of 5 and 15 °C, shear rate 10 s⁻¹

Figure 4-6   Predicted mass balance of Kvitebjørn 2019 predicted 5 °C, wind speeds of 2 and 5 m/s

Property: MASS BALANCE
Oil Type: KVITEBJØRN 2019
Description:
Data Source: Equinor (2019), Weathering data used

SINTEF

OWModel® 11.0

Surface release
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Jun. 26, 2019

Evaporated
Surface
Naturally dispersed

Temperature: 5°C   Wind speed: 10 m/s

Temperature: 5°C   Wind speed: 15 m/s
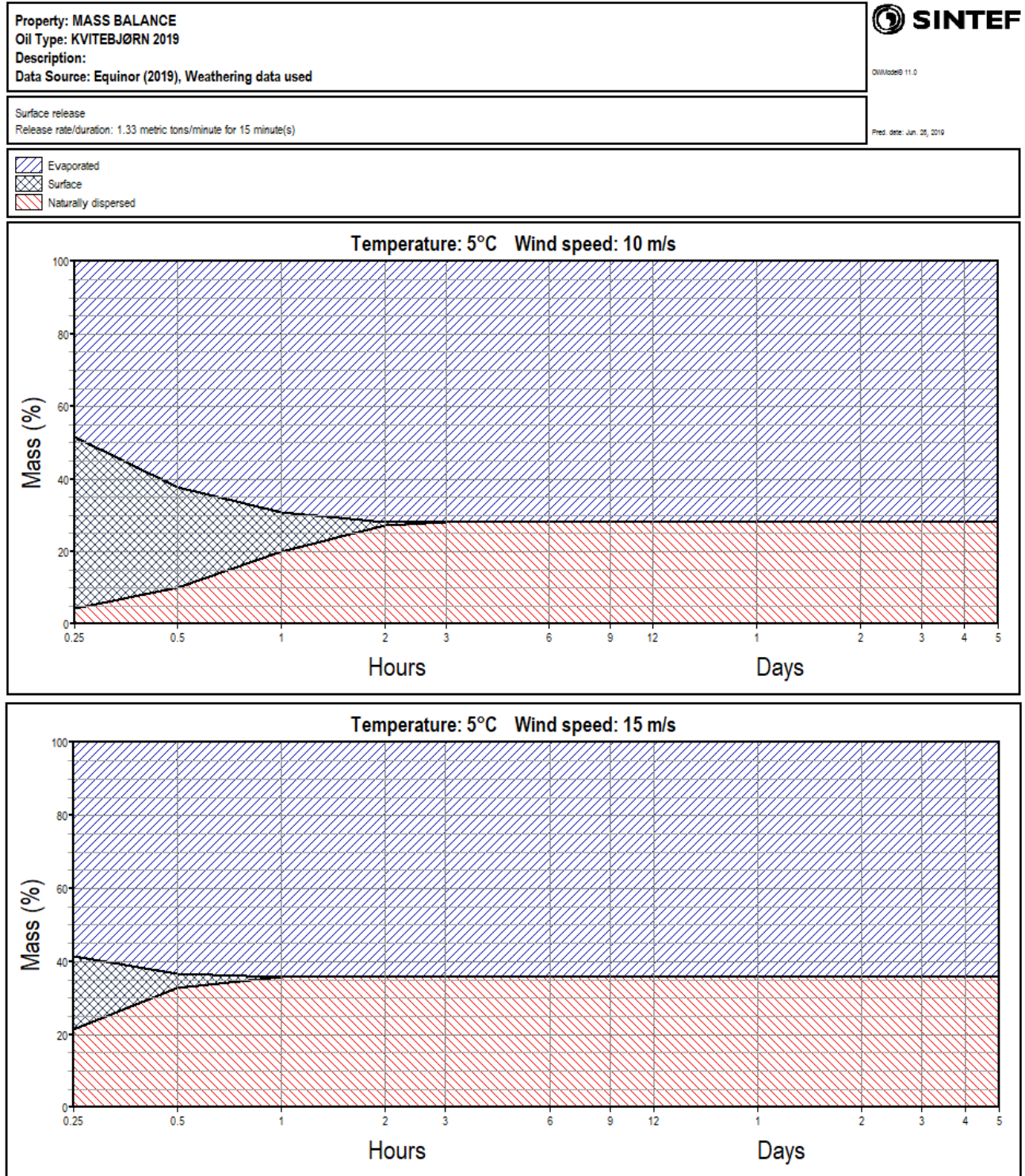
Figure 4-7   Predicted mass balance of Kvitebjørn 2019 predicted 5 °C, wind speeds of 10 and 15 m/s

PROJECT NO.
302004682

REPORT NO.
OC2019 A-097

VERSION
2.0

21 of 56

Property: MASS BALANCE
Oil Type: KVITEBJØRN 2019
Description:
Data Source: Equinor (2019), Weathering data used

SINTEF

OWModel® 11.0

Surface release
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Jun. 26, 2019

- Evaporated
- Surface
- Naturally dispersed

Temperature: 15°C   Wind speed: 2 m/s

Temperature: 15°C   Wind speed: 5 m/s

Figure 4-8   Predicted mass balance of Kvitebjørn 2019 predicted 15 °C, wind speeds of 2 and 5 m/s

PROJECT NO.
302004682

REPORT NO.
OC2019 A-097

VERSION
2.0

22 of 56

![SINTEF]

Property: MASS BALANCE
Oil Type: KVITEBJØRN 2019
Description:
Data Source: Equinor (2019), Weathering data used

SINTEF

OWModel® 11.0

Surface release
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Jun. 26, 2019

```
/// Evaporated
XX Surface
/// Naturally dispersed
```

Temperature: 15°C   Wind speed: 10 m/s

Temperature: 15°C   Wind speed: 15 m/s

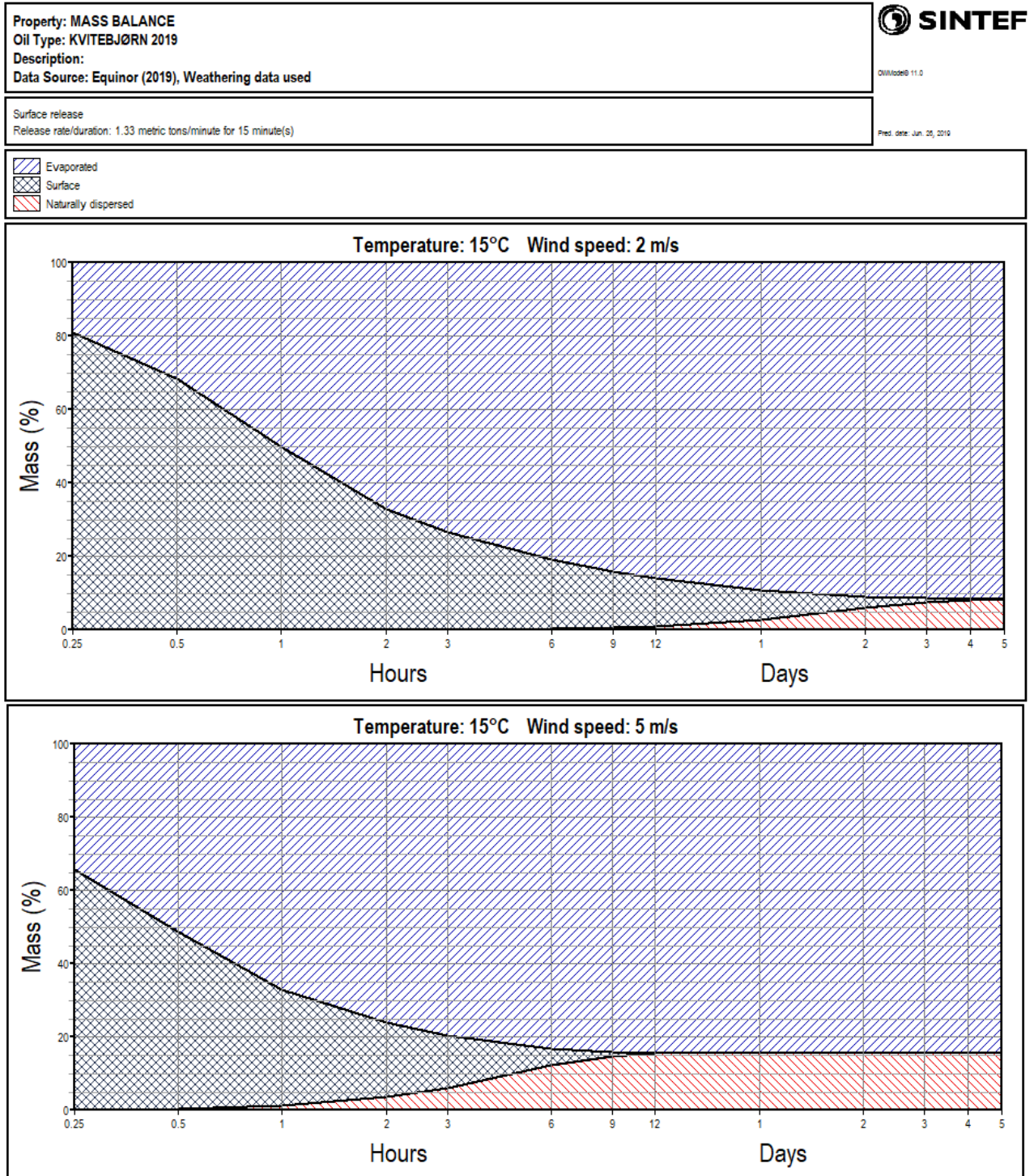*Figure 4-9   Predicted mass balance of Kvitebjørn 2019 predicted 15 ℃, wind speeds of 10 and 15 m/s*

PROJECT NO.
302004682

REPORT NO.
OC2019 A-097

VERSION
2.0

23 of 56

5 Comparison of OWM predictions

Weathering predictions of Kvitebjørn 2019 were compared with predictions Kvitebjørn 2009, Kristin 2006 and Sleipner 1993. The presented comparisons given in the figures below are based on predictions at sea temperature of 15 °C and wind speed of 10 m/s.

5.1 Evaporative loss

Evaporation is one of the natural process that helps removing spilled oil from the sea surface. Kvitebjørn 2019 and Sleipner 1993 show a much higher rate of evaporation compared with Kvitebjørn 2009 and Kristin 2006 (Figure 5-1). The evaporative loss reflects the characteristics of the oils where the light condensate exhibits higher evaporative loss and have lower densities compared with light crude oils.
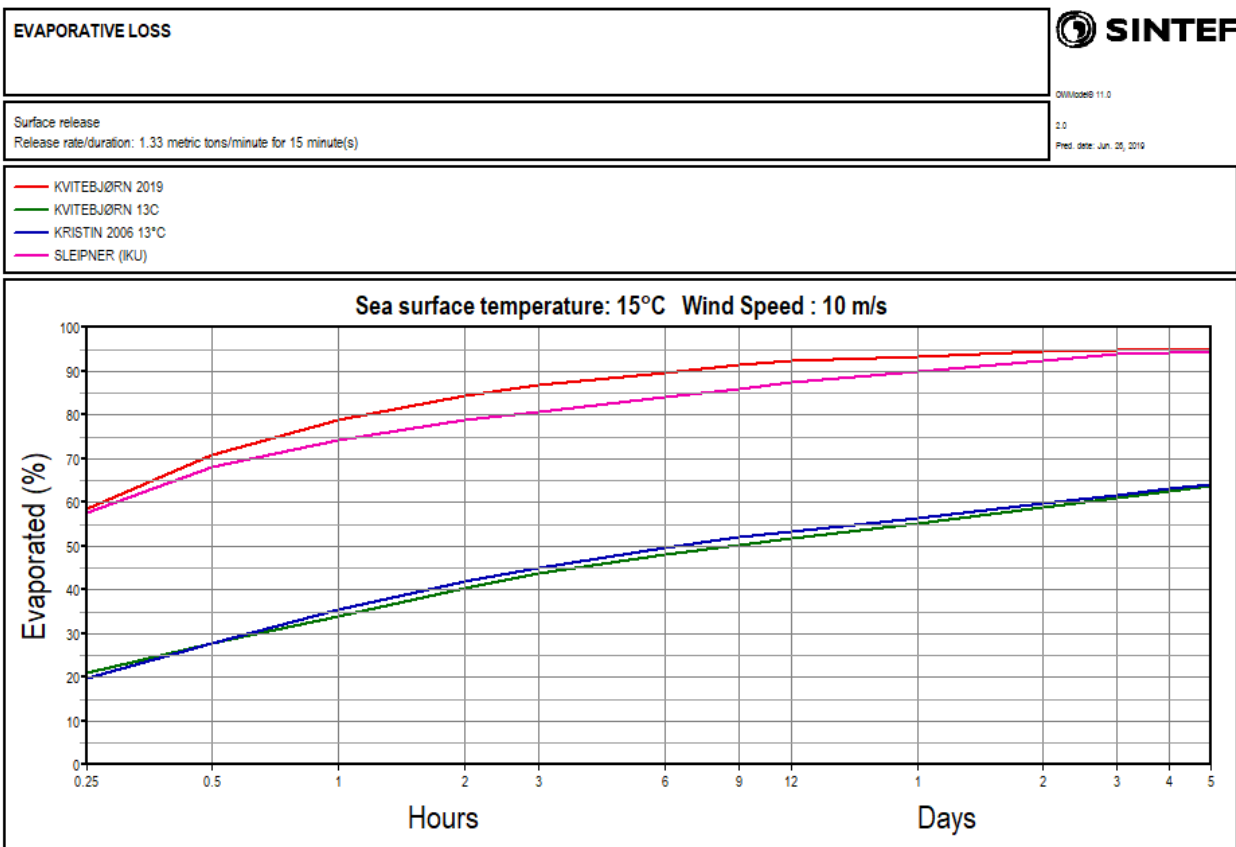
Figure 5-1   Predicted evaporative loss at 15 °C and 10 m/s for Kvitebjørn 2019 compared with other oils

5.2 Flash point

When oil is spilled on the sea surface, the oil will be cooled to the ambient water temperature within a short period. The probability of fire will be high if the flash point of the oil is below the sea temperature. Fire hazard is dependent upon the amounts of volatile components in the oil and the potential for fire is usually over within the first few minutes of a spill due to the rapid evaporation of those components.

The flash points of Kvitebjørn 2019 compared with the other oils are shown in Figure 5-2. The predictions show that only Kristin 2006 is expected to pose a fire hazard 15 minutes after a spill, while the other oils are above the set limit before this time point. Within 30 minutes after spill, Kristin 2006 is predicted to have a flash point above the fire hazard limit.
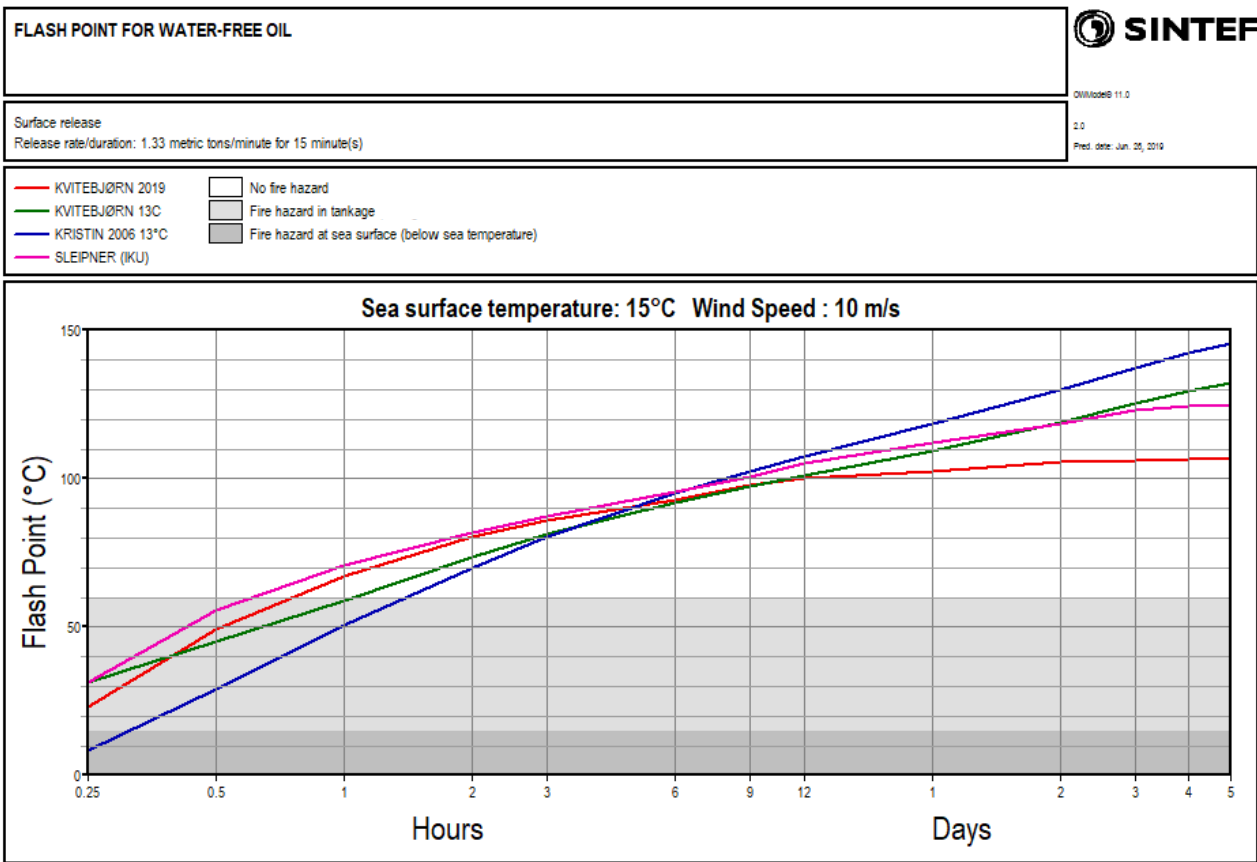
Figure 5-2   *Predicted flash point at 15 °C and 10 m/s for Kvitebjørn 2019 compared with other oils*

PROJECT NO.
302004682

REPORT NO.
OC2019 A-097

VERSION
2.0

25 of 56

5.3 Pour point

The pour point of Kvitebjørn 2019 and the other oils for comparison are given in Figure 5-3. Kvitebjørn 2019 expresses the lowest pour points together with Sleipner 1993, reflecting the low content of wax and will therefore not pose a challenge with solidification. Kvitebjørn 2009 and Kristin 2006 have higher pour points development (higher wax content) with a potential to solidify if spilled at sea.

POUR POINT FOR WATER-FREE OIL

⊙ **SINTEF**

OWModel® 11.0

Surface release
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

2.0
Pred. date: Jun. 26, 2019

— KVITEBJØRN 2019
— KVITEBJØRN 13C
— KRISTIN 2006 13°C
— SLEIPNER (IKU)

☐ Chemically dispersible
☐ Reduced chemical dispersibility
☐ Poorly / slowly chemically dispersible

Sea surface temperature: 15°C   Wind Speed : 10 m/s

Pour Point (°C)

60 · 40 · 20 · 0 · -20

0.25   0.5   1   2   3   6   9   12   1   2   3   4   5

Hours   Days

Figure 5-3   Predicted pour point at 15 °C and 10 m/s for Kvitebjørn 2019 compared with other oils

PROJECT NO.
302004682

REPORT NO.
OC2019 A-097

VERSION
2.0

26 of 56

5.4 Water content

The water uptake of the oils for comparison are shown in Figure 5-4. Neither Kvitebjørn 2019 nor Sleipner 1993 have emulsifying properties with a negligible water content, if any. Kvitebjørn 2009 and Kristin 2006 reach relatively high content of water approx. 40 and 50 %, respectively after 9 hours of weathering.
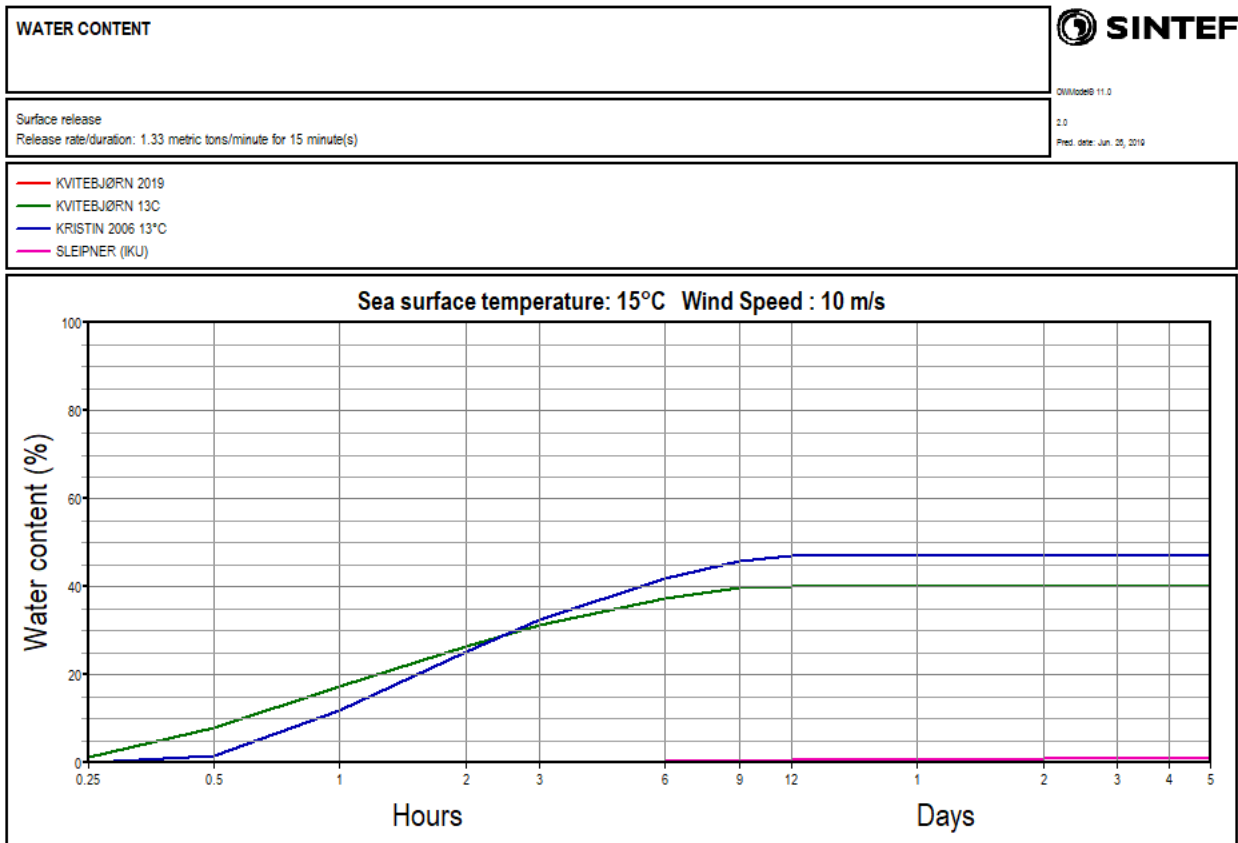
Figure 5-4   Predicted water content at 15 ℃ and 10 m/s for Kvitebjørn 2019 compared with other oils

PROJECT NO.
302004682

REPORT NO.
OC2019 A-097

VERSION
2.0

27 of 56

5.5 Viscosity

Figure 5-5 shows the predicted (emulsion) viscosities of the oils in comparison. Kvitebjørn 2019 and Sleipner 1993 have very low viscosities max. 10 mPa.s. Kvitebjørn 2009 and Kristin 2006 produce higher viscosities, where the viscosities are predicted to increase gradually throughout 5 days of weathering.
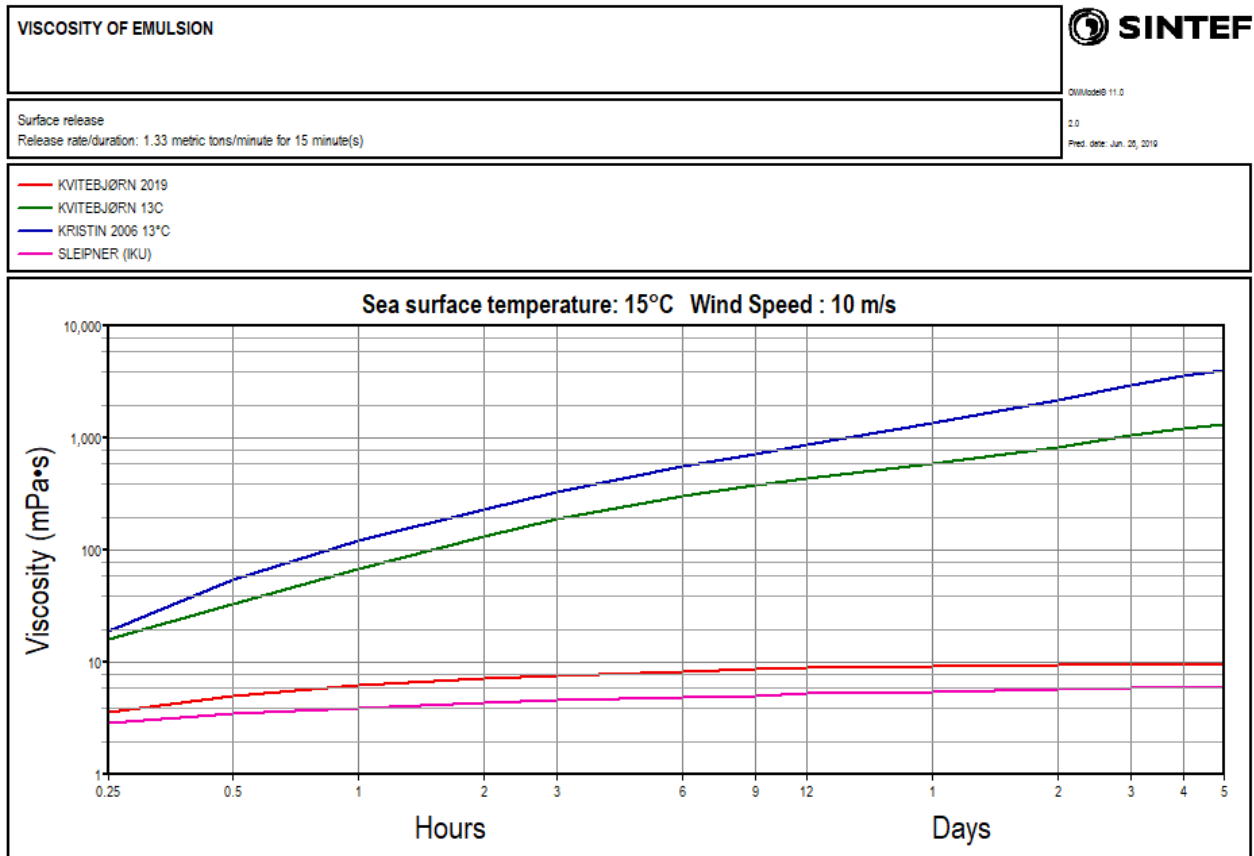
Figure 5-5   *Predicted (emulsion) viscosity at 15 °C and 10 m/s for Kvitebjørn 2019 compared with other oils*

PROJECT NO.
302004682

REPORT NO.
OC2019 A-097

VERSION
2.0

28 of 56

5.6 Surface oil

Due to evaporative loss and natural dispersion/entrainment, the amount oil (assumed no emulsification) on the sea surface will gradually be reduced. Figure 5-6 shows the predicted mass balance of remaining surface oil as a function of weathering. The light condensates Kvitebjørn 2019 and Sleipner 1993 are predicted to be rapidly removed from the sea surface due to evaporation and natural dispersion within 2 hours. The emulsifying oils (Kvitebjørn 2009 and Kristin 2009) are predicted to have a longer lifetime on the sea surface being removed within 2 days.

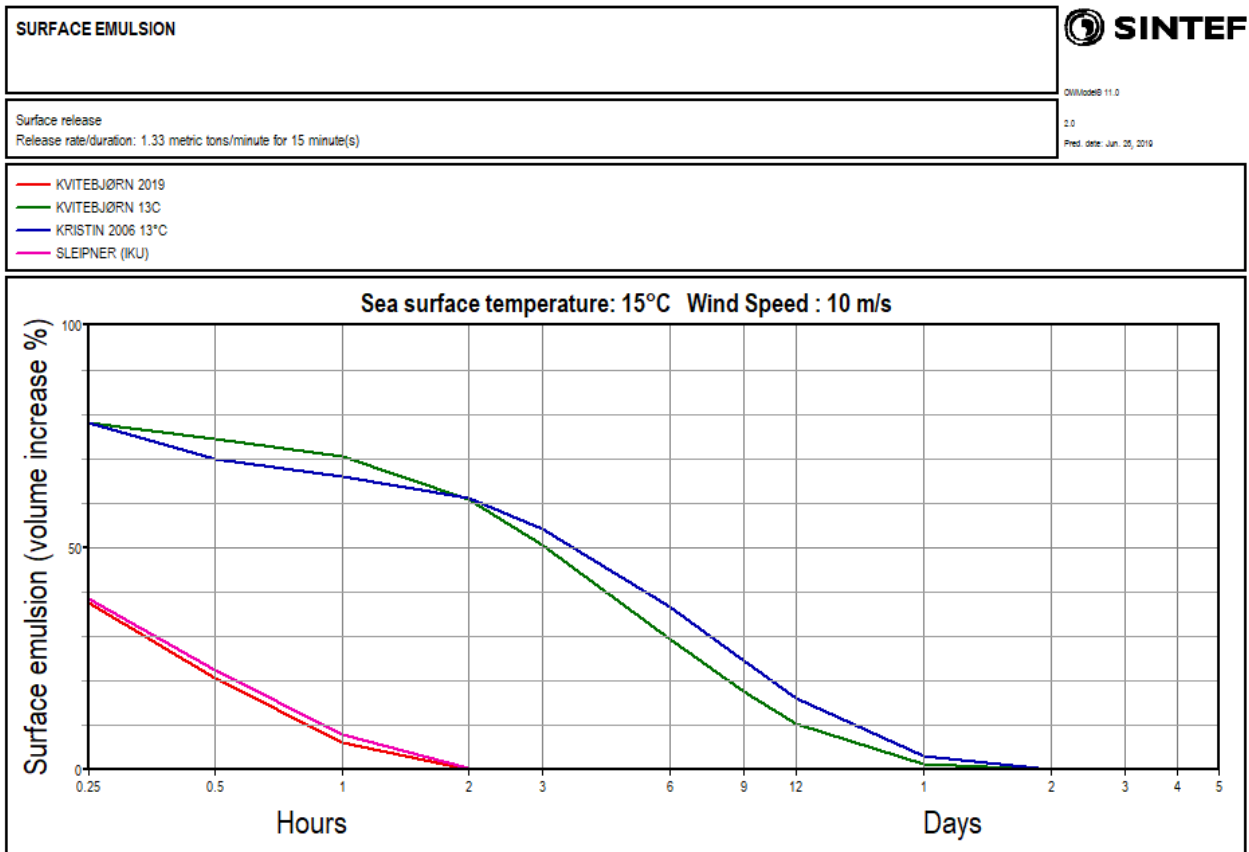*Figure 5-6   Predicted remaining surface oil at 15 °C and 10 m/s for Kvitebjørn 2019 compared with other oils*

29 of 56

PROJECT NO.
302004682

REPORT NO.
OC2019 A-097

VERSION
2.0

6 Weathering properties of Kvitebjørn 2019 when spilled at sea

The relative concentration of heavy oil components within a spilled oil increases due to weathering, and the physical and chemical properties of the oil will change over time. Knowledge about how the oil's properties change during weathering is therefore important in the management of oil spill response. Currently, mechanical recovery and the use of oil spill dispersants are the main oil spill response options at sea in the Norwegian sector, today.

The potential of using water-flushing to disperse the oil is briefly discussed in this report. Moreover, the weathered oil is expected to have a window of opportunity for ignitibility / in-situ burning, but this response option has not been evaluated in this study.

6.1 Oil properties

Kvitebjørn 2019 is categorized as a light condensate with a density of 0.752 g/mL, with very low contents of wax (0.14 wt. %) and asphaltenes (0.01 wt. %). The condensate has a high evaporative loss and the weathering properties indicate that such oil will rapidly be spread on the sea surface and exhibit a low water uptake. Kvitebjørn 2019 has no expected emulsifying properties, and the physico-chemical properties are very similar to other non-emulsifying condensates such as Sleipner 1993. The fresh oil and its 150, 200 and 250°C+ residues exhibit very low viscosities ranging from 1-26 mPa.s at shear rate $10s^{-1}$ (13 °C). The chromatographic characterization shows the hydrocarbon profile with a high extent of light compounds as systematic peaks (*n*-alkanes; paraffins). In addition, the fresh condensate has a low pour point of -36 °C that extends to +9 °C (250°C+ residue) with evaporation of the lightest compounds.

6.2 Flash point – Fire/explosion hazard

Flash point refers to the lowest temperature at which a fuel or oil can vaporize to form an ignitable mixture in the air. In case of an oil spill on the sea surface, the (heated) oil rapidly will be cooled to the ambient seawater temperature within a short period of time. The fire/explosion hazard will be at its greatest if the flash point of the spilled oil is below the seawater temperature
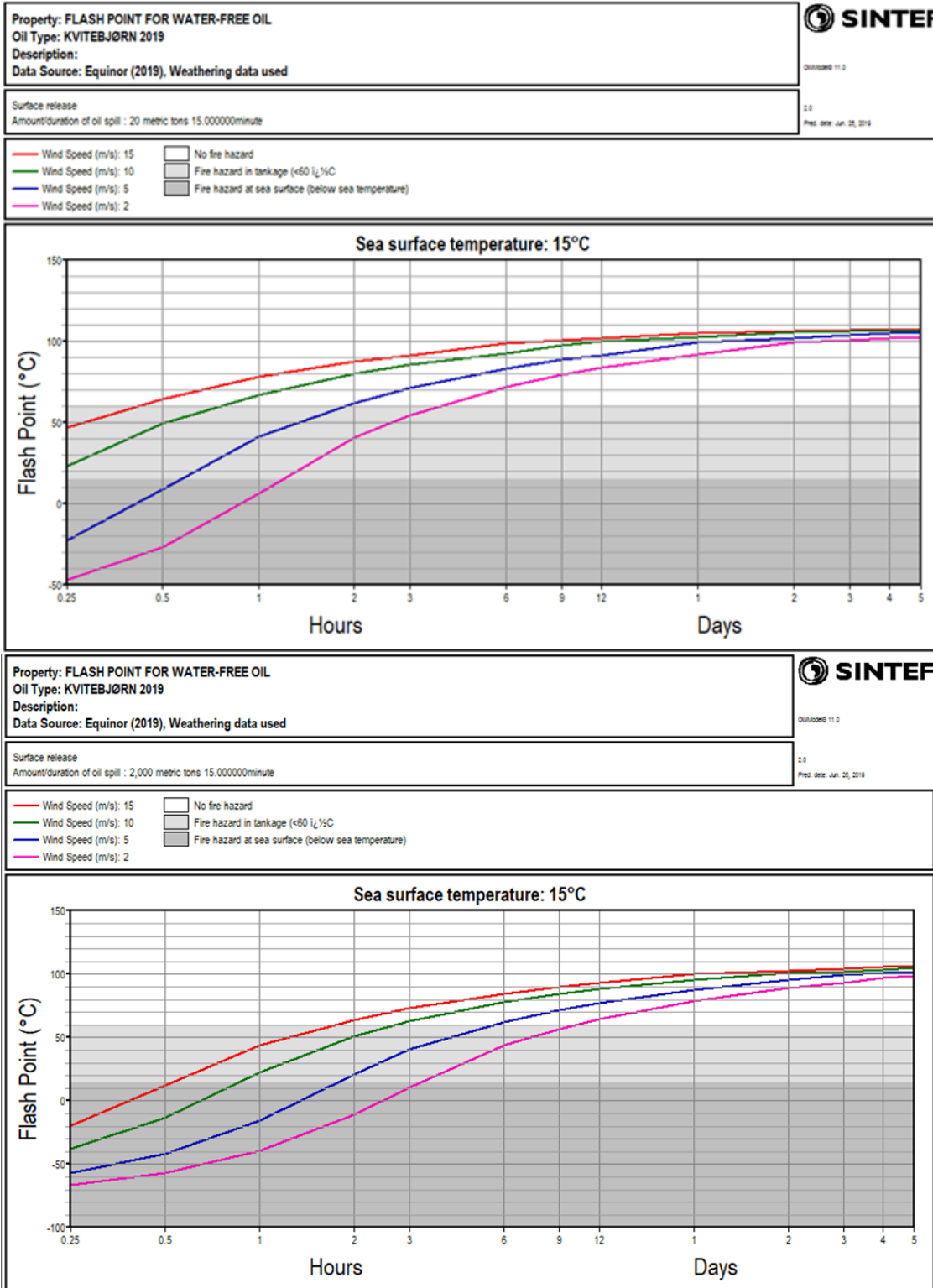
The flash points for Kvitebjørn 2019 is expected to surpass the sea temperature within a few minutes at 5 and 15 °C, at wind speeds of 10 and 15 m/s predicted with the standardized surface release as shown in Figure 4-3 At calmer weather conditions (2 and 5 m/s) care should be taken during the first 0.5 to 1.5 hours. However, the release rate may influence on the rate of evaporation, and for considerably larger (batch) release rates e.g. 100 times higher (8000 m³/h), the rate of evaporative loss is reduced as shown in Figure 6-1B. The time when the flash point has surpassed the sea temperature has now increased from 1.5 to 3 hours at 2 m/wind speed.

Moreover, some vessels/storage tanks engaged in oil recovery operations may not be classified to carry liquids with flash points lower than 60 °C, e.g. towing vessels, smaller cargo or other vessels available in the emergency. This means that fuels or oils with the flash point less than 60 °C, are for those type of vessels not permitted as cargo. However, this limit is not considered as relevant for oil recovery vessels with A-class certification for transport of liquids (Class I/II, flashpoints < 60 °C), according to NFPA classification of Flammable and Combustible Liquids (http://www.thetankshop.ca). At low wind speed (2 m/s) this limit is reached within 3.5 hours (80 m³/h), shorter time for the higher wind speeds as shown in Figure 6-1 A. For a larger batch release rate (8000 m³/h) the flash point limit of 60 °C is stretched to 9 hours at 2 m/s wind speed (Figure 6-1 B).

As a general recommendation after an acute oil spill involving free gas (e.g. from a subsea release), a "safety" zone should be established early on and downwind from the spill site before response actions are initiated. 1-hour drifting time of slick (from the source) has e.g. been suggested in Norway before oil spill response operations are initiated in open sea waters. Shorter waiting times have been predicted related to fire/explosion hazard related to the flash point. The following precautions should be taken:

- Prior to the initiation of spill response operations, an evaluation of fire/explosion hazard must always be conducted at the site

- Explosimeters should be utilized continuously and one should be aware of the possibility for varying release rates if "free" gas is involved

Figure 6-1   A (Above): Predicted flash points at different wind speeds for Kvitebjørn 2019 at 15 ℃ (80 m³/ h). B (Below): Predicted flash points at different wind speeds for Kvitebjørn 2019 at 15 ℃ (8000 m³/ h)

PROJECT NO.
302004682

REPORT NO.
OC2019 A-097

VERSION
2.0

31 of 56

6.3 Solidification

Pour point depends on the oil's wax content and the amounts of light components that can keep the wax components dissolved in the oil phase. In addition, high asphaltene content prevents precipitation and lattice formation and hence lowers the pour point. High pour points may prevent the dispersant to soak into the oil slick and influence the dispersant effectiveness and may reduce the potential for flowability towards weir skimmers.

In cases when high viscosity of the oil/emulsion is not a limiting factor, high pour point may cause solidification (elastic properties) when oil is spilled on the sea surface. High pour point may therefore imply solidification on the sea surface immediately after the release, and this is pronounced when the pour point is typically 5-15 °C above sea temperature.

Kvitebjørn 2019 exhibits low pour points and is not expected to pose any solidification (elastic properties) when weathered at sea at 5 and 15 °C within 5 days after a spill, see also the predictions in Figure 4-4.

6.4 Natural dispersion and evaporation

The lifetime of an oil spill at sea depends on the oil's composition, the release conditions (e.g. on the surface, underwater) and environmental conditions (temperature, wind, waves). Natural dispersion and evaporation are the main weathering processes that remove an oil spill from the surface. Figure 6-2 shows the remaining surface oil over time for different wind speeds and temperatures for Kvitebjørn 2019. There is minor difference in lifetime between 5 and 15 °C for this oil.

At high wind speed of 15 m/s, no oil remains on the sea surface after 1-hour weathering, but at calmer weather conditions 2-5 m/s wind speeds (no-breaking waves), the remining surface oil is 30-50 %. The variation of remining surface oil after a release is strongly dependent on the wind speeds and typically oils are more persistent on the sea surface with lower wind.
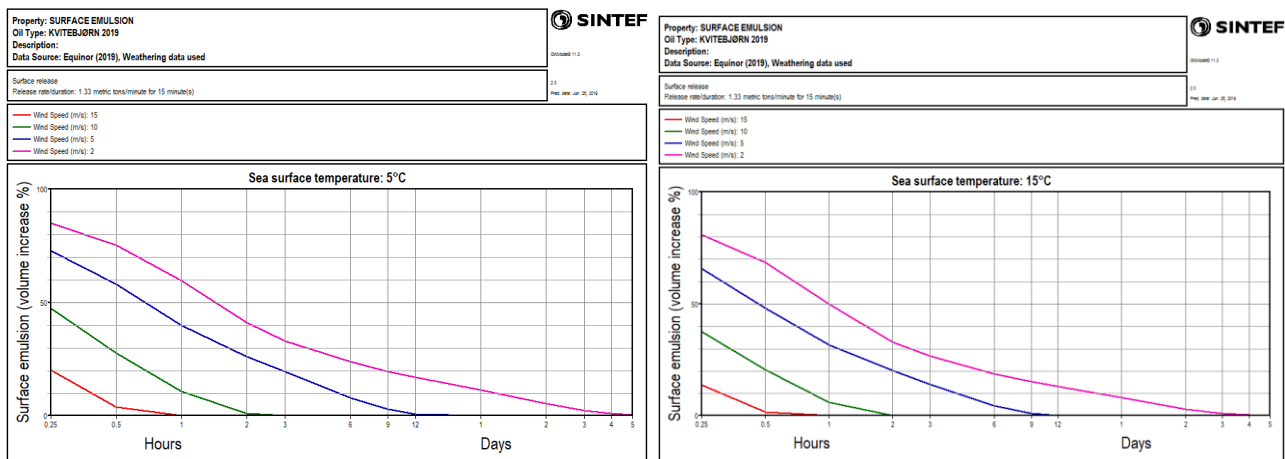
Figure 6-2   Remaining surface oil for Kvitebjørn 2019 at 5 and 15 °C

6.5 Film thickness of surface release

Mechanical recovery requires normal minimum film thicknesses > 0.1-0.2 mm. Film thicknesses > 0.05-0.1 mm are considered for application of oil spill dispersants, as lower film thicknesses are likely to disperse naturally. However, other factors than film thickness should be considered when evaluate response options, as described in the next chapters. Figure 6-3 shows the predicted film thicknesses at different wind speeds.
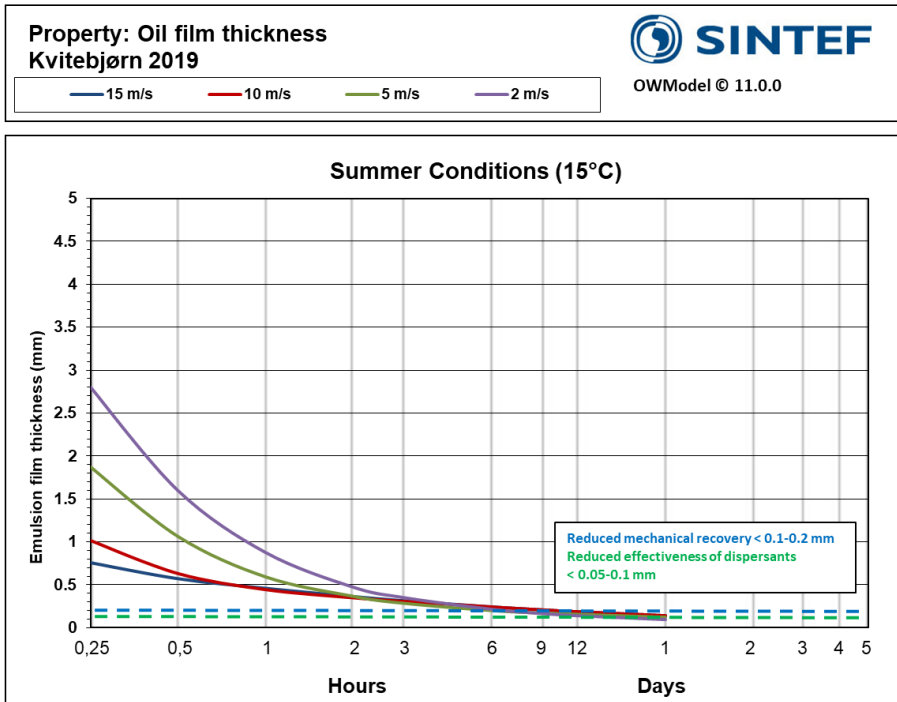
Figure 6-3: Predicted film thickness of Kvitebjørn 2019 after 5 days of weathering (surface release)

6.6 Mechanical recovery by boom and skimmer

Experiences from Norwegian field trials with booms have demonstrated that the effectiveness of various mechanical clean-up operations may be reduced due to the high degree of leakage of the confined oil or emulsion from the oil spill boom. The mass balance has shown that Kvitebjørn 2019 has short lifetime at sea with high degree of natural dispersion and high evaporative loss. However, and the remaining oil/residue has low viscosities (no emulsification), low pour point (no solidification) and exhibit low oil film thickness (after few hours). Due to low viscosities (around 10 mPa.s) and low film thickness, Kvitebjørn 2019 is assumed to be little available for mechanical recovery due to considerable boom leakage with a limit of 1000 mPa.s (Norvik et al., 1992) and low efficacy for containment. Moreover, previously studies at SINTEF have shown that weir skimmers may reduce recovery rates (m³/h) when skimming oils with viscosities in the range 15-20 000 mPa.s (Leirvik et al., 2001). Kvitebjørn 2019 has viscosities far less than this limit and reduced skimmer efficiency would in any case not be an issue for this oil, see Figure 4-5.

6.7 Chemical dispersion

Dispersant testing was not been conducted on this oil in agreement with Equinor. High degree of natural dispersion and evaporative loss indicate that the lifetime at sea is short for Kvitebjørn 2019, particularly in high wind speeds (breaking waves > 5 m/s). Use of dispersants could reduce the lifetime at sea in non-breaking waves conditions (< 5 m/s), but due to vast spreading and expecting low film thicknesses (< 0.1 mm) in few hours after a release application of dispersant would not be optimal in a spill situation. It is expected low efficiency potential, as the dispersant droplets may fall through the oil phase into the sea water. Applying dispersants assuming a very thin oil film < 0.05-0.1 mm is not normally recommended due to high degree of herding.

6.8 Mechanical dispersion by high-capacity water flushing

Mechanical dispersion by high-capacity water flushing could have a potential for oil spill with thin (initial) film thickness up to 0.2 - 0.3 mm and viscosities < 150 - 300 mPa.s. In such cases, water flushing from high-capacity water flush boom and/or firefighting (Fi-Fi) systems could possibly break up the oil/residue into smaller droplets and enhance the dispersion into the water column. Water flushing could also be used in combination with application of dispersant in calm weather condition to enhance dispersant efficiency with use of artificial energy. This technology was tested in a full-scale trial (NOFO Oil-on-Water trial) in 2016 and described by Daling et al., 2017 and Sørheim et al., 2017 but is not implemented as a part of the oil spill response in Norway, today.

For Kvitebjørn 2019, water flushing could be an option in a subsea release in cases where the initial film thickness is below 0.2 mm, or during few hours (2-3) from a batch release used in this report when the oil rapidly has been spread on the surface and produce thin film < 0.2 - 0.3 mm (see Figure 6-3). Prediction from a subsea release has not been performed in this study.

6.9 Summary recommendation of response options

Kvitebjørn 2019 is a light condensate that is expected not to form water-in-oil (w/o) emulsions if spilled at sea. The condensate will have a high degree of spreading on the sea surface if spilled at sea. In high wind speeds (breaking waves, 10-15 m/s) the condensate will naturally be dispersed into to the water column within few hours. In low wind speeds (non-breaking waves, 2-5 m/s) natural dispersion will be slower. The viscosity will be low for any remining oil/residue on the sea surface, and the low pour points will not cause the oil/reside to solidify.

- Mechanical recovery:
  - The viscosity is low even at some days on the sea surface, and it is too low for confinement in a booming operation.
  - Mechanical recovery is judged to have low efficiency
- Use of chemical dispersant:
  - Film thickness < 0.1 mm is too low for effective dispersant treatment
  - For a surface release dispersant may be possible in an early phase (few hours), as the initial thickness can be > 0.1 mm, however other factors as flash point and degree of natural dispersion must also be considered
- High-capacity water flushing:
  - The predicted viscosity is well below 150-300 mPa.s which is the estimated upper limit for treatment of water flushing
  - The predicted film thickness is below 0.2-0.3 mm after few hours which is the upper limit for effective use of water flushing
  - Water flushing is therefore an option to be considered for the remining oil/residue after few hours
- Monitoring and remote sensing:
  - Short lifetime at sea is expected in increasing wind speeds(> 5 m/s) and monitoring and remote sensing can be evaluated as a sufficient practical "response" option

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A The behaviour of oil on the sea surface

A.1 The chemical composition of crude oils and condensates

Crude oil is a complex mixture of thousands of chemical components. The relative compositions vary, giving rise to crude oils with different chemical and physical properties. The components found in crude oil are classified into two main chemical groups: hydrocarbons and non-hydrocarbons see Figure A-1.
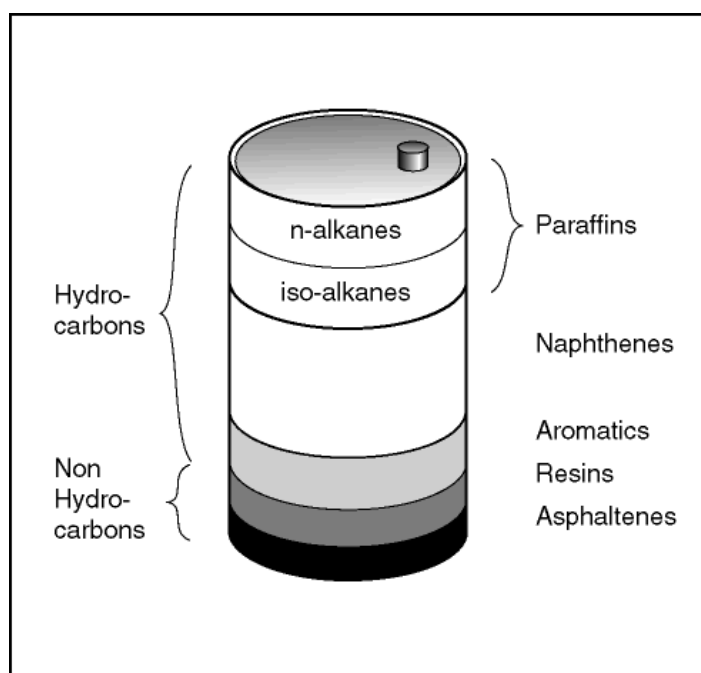

Figure A-1The chemical composition of crude oils

A.1.1 Hydrocarbons

Most compounds in crude oils are hydrocarbons, which are composed of hydrogen (10-15 wt. %) and carbon (85-90 wt. %). These range from simple, volatile gases, such as methane with only one carbon atom to large, complex molecules with more than 100 carbon atoms. The hydrocarbons in crude oils include saturated and unsaturated molecules in linear, branched and cyclic configurations.

Hydrocarbons are further classified into aliphatic and aromatic compounds. The two main groups of aliphatic compounds are paraffins and naphthenes.

Paraffins
Paraffins include *n*-alkane and *iso*-alkane aliphatic compounds. Waxes are an important subgroup of paraffins, containing more than 20 carbon atoms. The wax components of a crude oil will be present in a solution at elevated temperatures. At low temperatures, they may precipitate from the solution. These are principally n-alkanes. The wax content of crude oils can vary from 0.5 wt.% up to 40 or 50 wt.% in extreme cases, although the majority of the world's crude oils have a wax content of 2-15 wt.%.

Naphthenes
This group includes cycloalkanes containing one or more saturated rings. Each ring may have one or more paraffinic side chains, which are chiefly five- and six-membered rings.

Aromatics

Aromatics are a specific type of unsaturated cyclic hydrocarbons. Benzene, toluene and xylenes are examples of mono-ring aromatics, naphthalenes are di-ring aromatics and polycyclic aromatic hydrocarbons (PAH) contain three or more aromatic rings.

A.1.2 Non-hydrocarbons

In addition, hydrogen and carbon, some organic compounds in crude oils also contain small amounts of oxygen, nitrogen or sulphur, as well as some trace metals such as vanadium and nickel. These compounds are referred to as heteroatom organic compounds because they contain a heteroatom, which is any atom that is not carbon or hydrogen. The two most important groups of heteroatom organic compounds are resins and asphaltenes.

Resins

Compared to the hydrocarbons, resins are relatively polar and often have surface-active properties. Resins have molecular weights ranging from 700-1000. Carboxylic acids (naphthenic acids), sulphoxides and phenol-like compounds can be found in this group as well.

Asphaltenes

Asphaltenes are is a complex group of poorly characterized chemical compounds that consist of condensed polycyclic aromatic compounds. They are large molecules with 6-20 aromatic rings and side chains (molecular weight 1,000-10,000). Asphaltenes may be classified as "hard" or "soft" based on the method of determination. Crude oils may contain up to 6 wt. % "hard" and 10 wt. % "soft" asphaltenes (Peregrino:13.4 wt.%)

A.2 Main oil categories – Related to weathering

Different oil types can have extremely different compositions, which impact their physical properties and effect their behaviour after a spill at sea.

Oils that are subject to weathering can roughly be divided into 3 main categories:

- Crude oils
- Light oils
- Condensates

Crude oils contain relatively more of the heavier components than light oils or condensates. Crude oils can be weathered in the laboratory to mimic natural weathering that occurs on the sea surface. The laboratory weathered crude oil identified as 250˚C+ residue, corresponds to 0.5 to 1 week after a spill at sea, and contains less than 50% of its original volume due to evaporation. The heavier components allow the formation of stable water-in-oil (w/o) emulsions, which reduces oil spreading at the sea surface. The final (terminal) film thickness of a crude oil depends on the emulsion's physical properties, and will be in the order of 1 mm.

Light oils and crude oils are not specifically differentiated in reservoir terminology. However, it is suitable to deal with the light oils as a separate category when referencing weathering properties. Light oils have a high content of low molecular weight hydrocarbons. When subjected to laboratory weathering, the 250˚C+ residue of light oils may lose 50-70% of their total volume due to evaporation. In contrast to condensates, which only contain light components, light oils contain a mixture of light and heavy components. These heavy components may cause light crudes to emulsify in water, but these w/o emulsions are, however, very unstable. A light oil will spread less than a condensate, with a final film thickness of approximately 0.5 mm.

Condensates only contain low molecular weight hydrocarbons and are considered extremely volatile. Laboratory weathered condensates, such as the 250˚C+ residue, typically lose more than 70% of their initial volume. Condensates do not contain components such as asphaltenes or heavier waxes and will not emulsify significant amounts of water. The spreading of condensates is relatively fast, and can result in a final film thickness of approximately 0.05 mm.

A.3 Physical properties of crude oils

The physical properties of specific oils are a result of their chemical composition. The most important physical properties in oil spill scenarios are discussed below.

Density

The density of a crude oil is dependent on the density of all of its components. The density of hydrocarbons increases with increasing molecular weight. Furthermore, paraffinic oils have lower density than those containing larger amounts of high molecular weight aromatics, such as naphthenic and asphaltenic oils.

Specific gravity is defined as the oil density at 60°F (15.5°C) divided by water density at 60°F. In American literature, the density of the oil is often expressed as °API, where:

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

In the present study, the density of the oil is presented as specific gravity.

The density of fresh crude oils normally lies in the range 0.78 to 0.95 g/mL (50 to 10 °API).

A.3.1 Rheological properties

The viscosity of crude oils expresses its resistance to flow and is of special interest when pumping oil.

Absolute viscosity also known as dynamic viscosity) is a measure of internal resistance. In the SI system, absolute viscosity has units of N s/m^2, Pa s or kg/(m s), where 1 Pa s = 1 N s/m^2 = 1 kg/(m s). Absolute viscosity can also be expressed in the metric CGS (centimeter-gram-second) system as g/ (cm s), dyne s/cm^2 or Poise, where 1 Poise = 1 dyne s/cm^2 = 1 g/(cm s) = 1/10 Pa s = 1/10 N s/m^2. https://www.engineeringtoolbox.com/dynamic-absolute-kinematic-viscosity-d_412.html

The industry often uses centipoise, as the *Poise* is normally too large, 1 Poise = 100 cP and 1 cP = 0.001 N s/m^2. The viscosity of fresh crude oils can vary from less than 1 to more than 2000 mPa.s (cP) at ambient sea temperature. In comparison, water has an "absolute" viscosity of 1 cP and syrup's is 120 000 cP at 20°C.

Kinematic viscosity is absolute viscosity divided by density. 1 centistoke (cSt) = 1 cP / density. Because the density of weathered oils and emulsion are typically 0.9 – 1 g/mL, the units cSt and cP will often have similar values.

Viscosity is temperature dependent. For liquids, the viscosity decreases with increasing temperatures. Viscous and waxy crude oils can exhibit non-Newtonian behaviour (viscosity varies with shear rate), especially close to, or below, their pour point. Water-in-oil (w/o) emulsions exhibits this non-Newtonian behaviour with shear thinning. In an oil spill situation, an emulsion may be liquid under turbulent conditions at sea, but can become much more viscous, or even semi-solid in calmer water conditions, or on beaches. Thus, the measurements of the viscosity of w/o-emulsions must be carried out under strictly controlled conditions (defined shear rates and thermal and mechanical history of the sample). At SINTEF, a shear rate of 10 s^{-1} is routinely used for expressing viscosity data on w/o-emulsions.

The viscosity of an oil increases with evaporation since the heavier, more viscous components remain in the residue (Mackay et al., 1982). The difference in viscosity for crude oils is approximately 3 to 2000 mPa.s for fresh crude oils and several hundred/thousand mPa.s for their residues.

Water-in-oil (w/o) emulsions are generally more viscous than the parent crude oil; this is illustrated in Figure A-2.
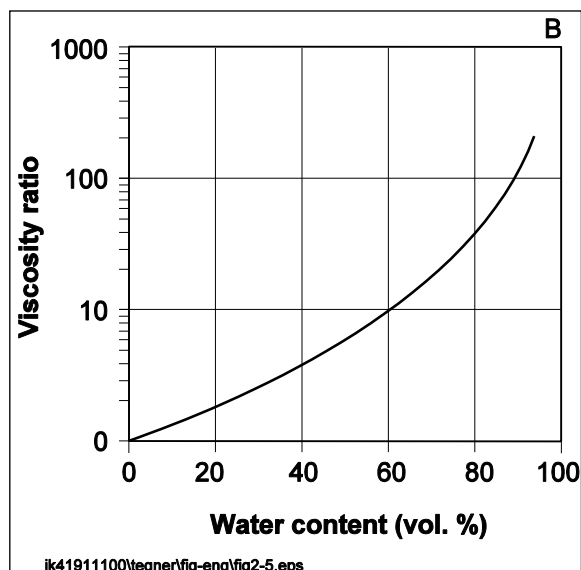
Figure A-2   Example of viscosity ratio as a function of water content

A.3.2 Pour point

The temperature at which oil ceases to flow when cooled without disturbance under standardized conditions in the laboratory is defined as the oil's pour point (ASTM-D97). The method accurately determines the temperature at which the oil become semi-solid under the specified laboratory conditions. Due to the movement at the sea surface, the oil may remain a liquid at sea at temperatures as low as *5 to 15°C lower* than the pour point of the oil. The pour point of oil with high wax content will increase dramatically with evaporation as the lower weight molecules, which contribute to keeping the wax in solution, evaporate. The pour point for oils with high wax contents can reach 30°C, while low viscous naphthenic oils may have pour points as low as - 40°C.

In an oil spill clean-up situation, the pour point provides essential information for when determining the efficiency of various skimmers, pumping rates and the use of dispersing agents.

A.3.3 Distillation curve

The distillation curve, which is obtained by measuring the vapour temperature as a function of the amount of oil distilled, shows the relative distribution of volatile and heavier components in the oil. The boiling point of a chemical component depends on its vapour pressure, which is a function of its molecular weight and chemical structure. Low molecular weight oil components have a higher vapour pressure, thus lower boiling points than higher molecular weight components of a similar type. Aromatic compounds boil at a higher temperature than paraffinic compounds of the same molecular weight, and *iso*-alkanes boil at a lower temperature than the equivalent *n*-alkanes. Hence, the distillation curve is an indicator of the relative amount of different chemical components, principally as a function of molecular weight, but also as determined by the chemical composition.

A.3.4 Flash point

The flash point is the lowest temperature at which the gas or vapour generated by the heating of oil will form an ignitable mixture in air. The flash point depends on the proportion of low molecular weight components. Fresh crude oils normally have a low flash point (from -40°C to 30°C).

From a safety point of view, flash points are most significant at, or slightly above, the maximum temperature that may be encountered in storage or transport. The flash point is an approximate indicator of the relative fire and explosion hazard of oil.

> ***Rule of thumb:***
>
> *In the presence of an oil slick at sea, a fire and/or explosion hazard exists when the oil's flash point is close to or lower than the sea temperature.*

Natural weathering processes such as evaporation and emulsion formation contribute to reducing the potential hazard by increasing the flash point. Thus, it will be a relatively short fire and/or explosion danger in the initial stages of oil spill.

In the laboratory, the flash point is measured in a closed system with the components in the oil and gas equilibrated. In the field, however, the weather situation will influence the flammability of the air above the slick. The gas concentration will be high just above the oil film in calm weather and high temperatures, whereas the concentration will be low in cold and windy weather due to dilution and transport and a lower degree of evaporation.

A.4 The behaviour of crude oil spilled at sea

This chapter gives a general description of the main weathering processes when oil is spilled at sea. There are many natural processes take place that change the volume and chemical properties of the oil. These natural processes are evaporation, water-in-oil (w/o) emulsification, oil-in-water (o/w) dispersion, spreading, sedimentation, oxidation and biodegradation. A common term for all these natural processes is weathering. The relative contribution of each process varies during the duration of the spill. The weathering of oil depends on the oil type (chemical and physical properties), the weather conditions (wind, waves, temperature and sunlight) and the properties of the seawater (salinity, temperature, bacterial flora, etc.).

Figure A-3 illustrates the various weathering processes, and Figure A-4 shows their relative importance over time.
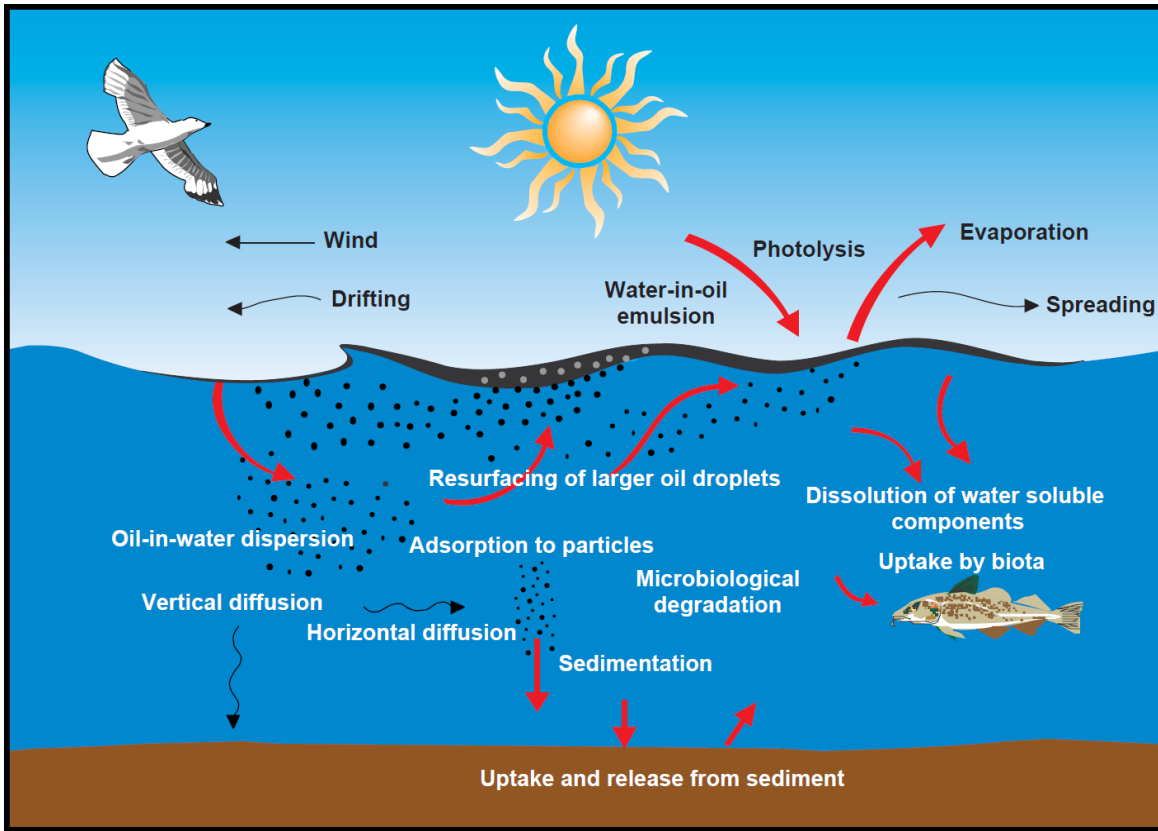
Figure A-3: Illustrating the weathering processes that take place when oil is spilled on the sea surface
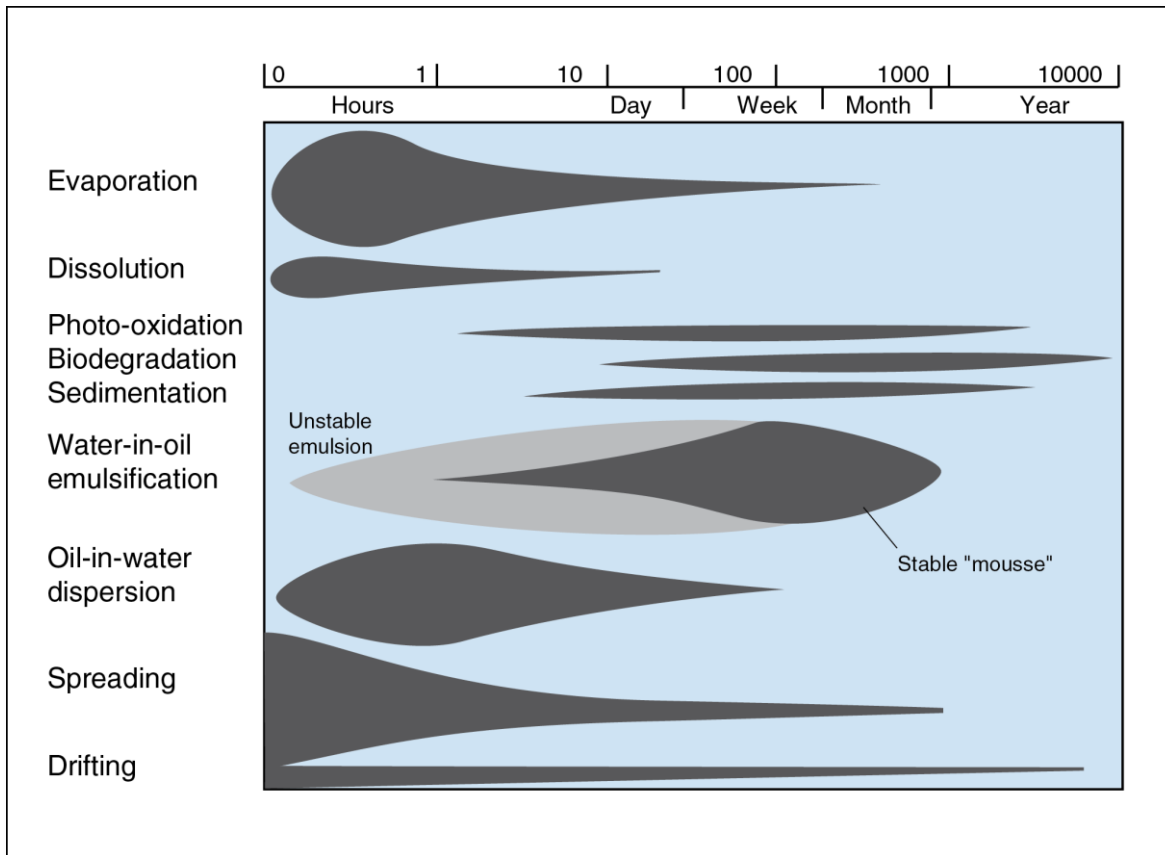
Figure A-4: Weathering processes' relative importance over time. Note: logarithmic scale

A.4.1 Evaporation

Evaporation is one of the natural processes that support the removal of spilled oil from the sea surface. The evaporation process starts immediately after the oil is spilled, and the evaporation rate decreases exponentially throughout the duration of the oil spill.

The evaporated amount depends on the chemical composition of the oil in addition to the prevailing weather conditions, sea temperature and oil film thickness.

The rate of evaporation varies for different oil types. Light refinery products (e.g. gasoline and kerosene) may completely evaporate after a few hours/days on the sea surface. Condensates and lighter crude oils can lose 50% or more of their original volume during the first days after an oil spill.

The most significant difference caused by evaporation is the loss of volatile and semi-volatile compounds, which increases the relative amounts of higher molecular weight compounds.

With evaporations, the chemical and physical properties of the remaining oil will change. The density, viscosity, pour point and wax and asphaltene content, will all increase with increased evaporation.

A.4.2 Spreading

Oil spilled at sea will spread on the sea surface. Spreading is often the dominant process in the initial stages of an oil spill and decreases as the viscosity and density of the remaining oil increases. The spreading process is also reduced if the oil's pour point is 5-15°C below the sea temperature.

Oceanographic conditions (e.g. wind, waves and currents) affect the spreading process. The oil slick will be broken into "wind rows" aligned in the direction of the wind, see Figure A-5. The thickness of the oil slick varies, often differing by a factor of several thousand. Experience has shown that most of the total oil slick area consists of a thin film (<1 μm oil thickness) that only contains 10% of the oil volume. Most of the oil volume (~90%) is located in small patches of w/o emulsions with a film thickness of 1 to 5 mm, which often constitutes less than 10% of the total oil slick area.
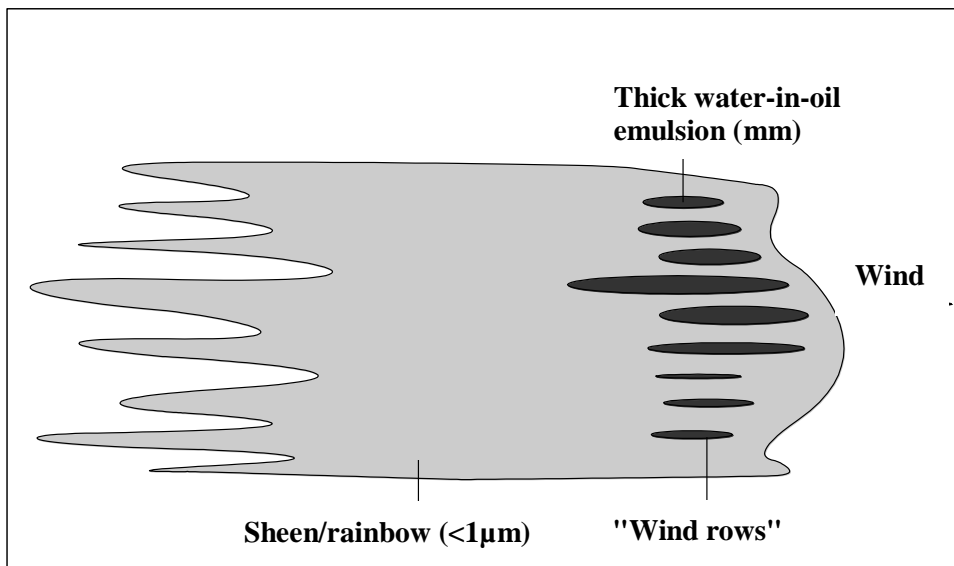

Figure A-5: The spreading of oil spilled on the sea surface and the distribution within the oil slick

A.4.3 Drift of an oil slick

The oil slick will drift as the weathering processes continue. The wind and current conditions cause the oil slick to drift, as illustrated in Figure A-6. Waves and wind create a current in the mass of water which amounts to approximately 3% of the wind speed at the sea surface. The influence of the wind decreases rapidly with the depth of the water below the surface. At 1 to 2 meters the current reduces to approximately 1% of the wind speed. This means that oil on the surface of the open sea, will move faster than the water below (e.g. Reed and Turner, 1991; Reed et al., 1994). In the absence of wind, the oil drift is governed by the prevailing (background) current.
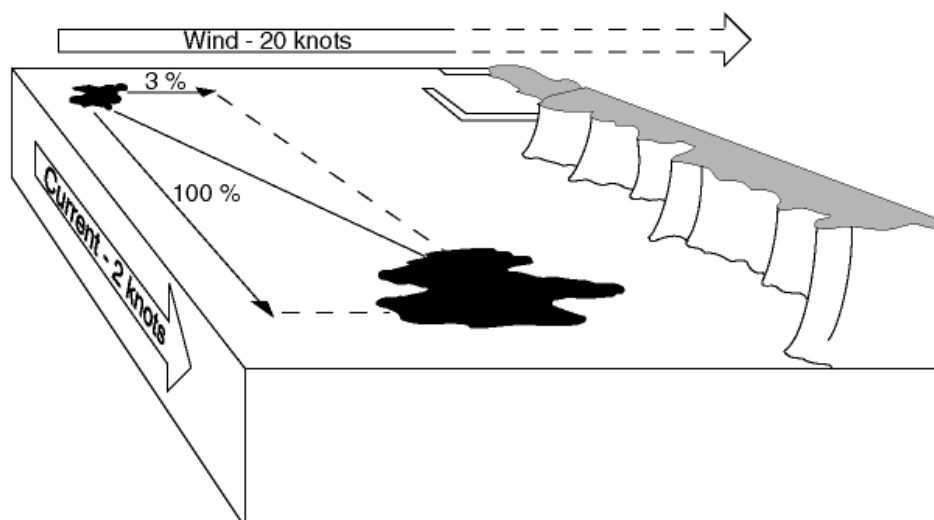
PROJECT NO.
302004682

REPORT NO.
OC2019 A-097

VERSION
2.0

44 of 56

Figure A-6: An illustration showing how wind and current can influence the drifting of an oil slick

A.4.4 Water-in-oil (w/o) emulsion

The formation of water-in-oil emulsions significantly affects the behaviour and clean-up of oil spilled at sea. Because of emulsification, the total emulsion volume may increase to as much as six times the original spilled oil volume depending on the properties of the oil. The formation of w/o emulsions also contributes to keeping oil on the sea surface. A w/o emulsion normally has a higher viscosity than the parent crude oil, so the emulsification process will therefore retard/delay evaporation and the natural dispersion process.

The minimum criterion for the formation of w/o emulsions is the presence of breaking waves (i.e. a wind speed of >5 m/s). Nonetheless, a slow water uptake can also take place during calmer weather. Figure A-7 shows how wind speed influences the w/o formation rate.

Surface active compounds present in crude oil will promote the formation of w/o emulsions and contribute to stabilizing the emulsion. These components contain both hydrophilic and hydrophobic groups.

The maximum water uptake will vary for different crude oils. Tests performed at SINTEF have revealed that the maximum water uptake is independent of the prevailing weather conditions if the lower energy barrier for the formation of w/o emulsions is exceeded. The rate, however, depends highly on the weather conditions. In the laboratory, the $t_{1/2}$-value is determined, which is the time in hours it takes before the oil has emulsified half of its maximum water content.

The w/o emulsion formation rate depends on the oil's chemical composition, which varies for different oil types.
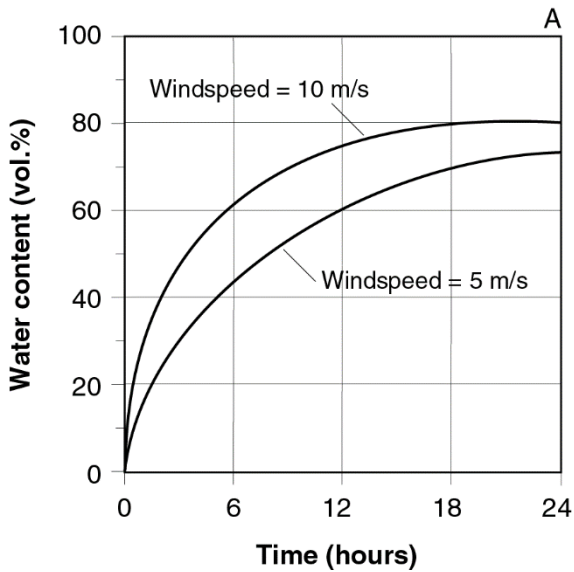
Figure A-7: Example of how weather conditions influence the w/o emulsion formation for typical oils

The stability of the w/o emulsion depends on the water droplet size, since not all water droplets in the emulsion are stable. Larger water droplets may be reduced in size by the flexing, stretching and compressing motion of the slick due to wave action, whereas the largest droplets may coalesce and be squeezed out of the w/o emulsion. After a certain period, the emulsion may only contain small water droplets with diameters of 1 to 10 μm, yielding a more stable emulsion.
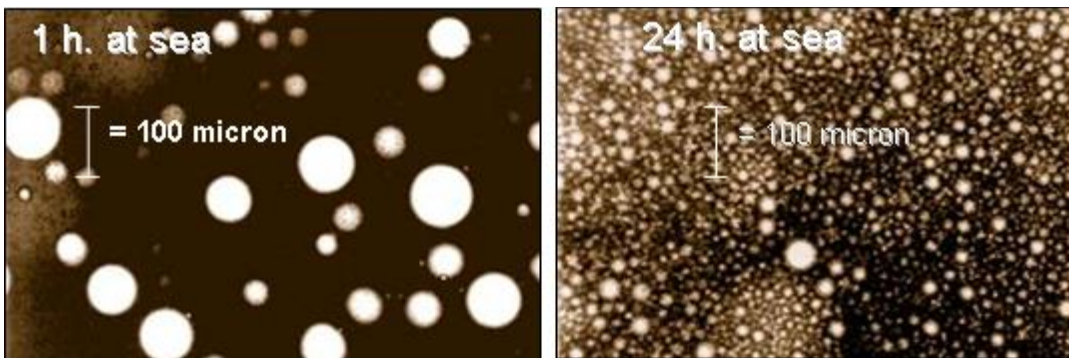

Figure A-8: Microscope pictures of w/o emulsion after (A) 1 h. and (B) 24 h. in a rotating cylinder

Thus, the formation of emulsions is the result of water retention by oil as an effect of both viscous and interfacial forces. The interfacial forces are the most important, and asphaltenes are largely responsible for this. Resins are similar compounds to asphaltenes and can stabilize an emulsion, but not to the same extent.

Resins and asphaltenes have both hydrophobic and hydrophilic properties and will concentrate at the interface between the water and oil, thereby forming a layer that stabilizes the water droplets. The hydrophobic properties can lead to the concentration of wax along the water droplets, which further stabilizes the interfacial "skin" layer. The interfacial layer between the oil and water forms a physical barrier that hinders the coalescence of the water droplets and will stabilize the w/o emulsion. The stabilization of the water droplets by asphaltenes and wax is shown in Figure A-9.

PROJECT NO.
302004682

REPORT NO.
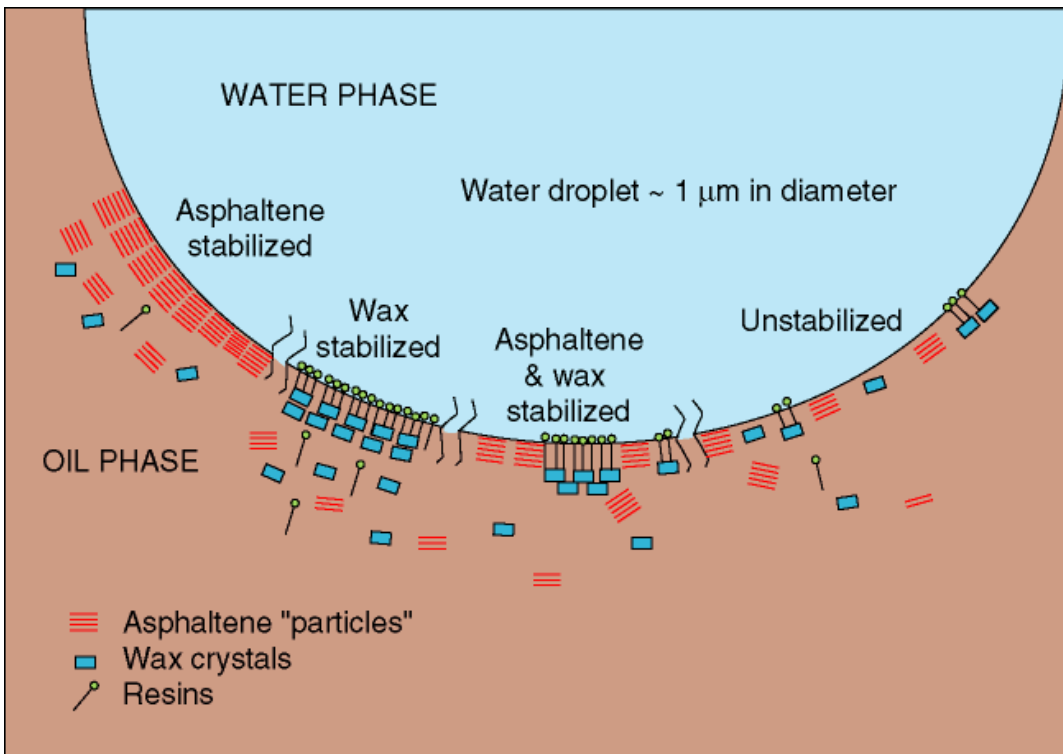OC2019 A-097

VERSION
2.0

46 of 56

Figure A-9: Interfacial layer stabilized by wax and asphaltenes in w/o emulsion

Oils that contain large amounts of wax and small amounts of asphaltenes can form w/o emulsions stabilized by a continuous phase's rheological strength (viscosity and elasticity) due to wax structure formed by precipitated wax. Wax stabilized emulsions are characterized by large water droplets and are fairly stable when stored, although they may break down when stress is applied and/or when the emulsion is heated to, e.g. 40-50°C.

Crude oil and sea water interfacial tension (IFT) plays a key role in the process of oil droplet formation. The need to understand and control droplet formation in dispersant system is extremely important. Addition of dispersants reduces the interfacial tension between oil and water that subsequently promotes the formation of a larger number of small oil droplets when surface waves entrain oil into the water column. These small submerged oil droplets are then subject to transport by subsurface currents and other natural removal processes, such as dissolution, volatilization from the water surface, biodegradation, and sedimentation resulting from interactions with suspended particulate material.

A.4.5 Oil-in-water (o/w) dispersion

Natural oil-in-water (o/w) dispersion will take place if there is sufficient energy on the sea surface, i.e. if there are breaking waves present. The waves will break the slick into small oil droplets (~1 µm - 1 mm in diameter), which are then mixed into the upper water column. The largest oil droplets will resurface and form a thin oil film (typically <50 µm). This thin oil film will be rapidly dispersed again by breaking waves as smaller droplets into the water column and will be available for rapid biodegradation.

The natural dispersion rate depends highly on oil type and can be one of the main processes that determine the lifetime of an oil slick on the sea surface. Natural o/w dispersion will gradually decrease with time since the evaporation of the lighter compounds will increase the viscosity of the remaining oil.

The purpose of applying chemical dispersing agents is to increase, or enhance, the natural dispersion rate. Dispersants reduces the interfacial tension between water and oil and thus promote natural o/w dispersion. When effective chemical dispersion is achieved, small oil droplets are formed, with typical diameters ranging from 5

PROJECT NO.
302004682

REPORT NO.
OC2019 A-097

VERSION
2.0

47 of 56

to 100 µm. These are retained in the upper layers of the water column by the prevailing turbulence of wave action.

A.4.6 Water solubility

The water solubility of saturated hydrocarbons is generally very low, while lower molecular weight aromatic compounds are water-soluble to some extent; particularly aromatics, such as BTEX, 2-ring PAH and paraffin's up to C_7) have a potential to be dissolved in the water column (McAuliffe, 1987). Within the various types of hydrocarbons, the water solubility decreases from aromatics to naphthenes and from *iso*-alkanes to *n*-alkanes. In each series, the water solubility decreases with *increasing* molecular weight.

Evaporation and the release of oil components into the water mass are competitive processes since most of the water-soluble components are also volatile. The evaporation process is approximately 10 to 100 times faster than the release in the water column. The concentration of soluble oil components into the water column during an oil spill is quite low (< 1 mg/L), while the dissolution of oil components into the water column does not contribute to removing the oil from the sea surface. However, the water-soluble fraction is of great interest since it has a high bioavailability and thus the potential to cause acute toxic effects on marine organisms.

A.4.7 Photo-oxidation

Under the influence of sunlight, some of the oil components will slowly oxidize to resins and finally asphaltenes. The photo-oxidized components will stabilize the w/o emulsions and influence the oil's persistence on the sea surface. After a long period of weathering at sea, tar balls (mainly consisting of asphaltenes) may be formed. These tar balls break down very slowly, both at sea and on beaches.

A.4.8 Biodegradation

Seawater contains an abundance of microorganisms that can break down all types of oil components. Various microorganisms prefer specific oil components as their energy source. Bacteria prefer to degrade oil in contact with water and the rate of biodegradation depends on the water/oil interface area. The interface area increases as the oil is spread over the sea surface in a thin layer or by chemical or natural dispersion of oil into the water column.

Important factors influencing the biodegradation rate are temperature, the concentration of available nutrients (i.e. nitrogen and phosphorus), oxygen, oil type and the degree of weathering. Low molecular compounds are degraded more rapidly than the high molecular weight/heavier compounds in the oil, thus giving the following order for biodegradation: straight-chain *n*-alkanes > branched *iso*-alkanes > cyclic alkanes > cyclic naphthenes > aromatics> resins > asphaltenes (Perry, 1984).

At sea, the formation of oil droplets by natural or chemical enhanced dispersion will increase the biodegradation rate in the water mass by 10 to >100 times compared to surface oil due to increased water/oil interfacial area. When immobilised on hydrophobic synthetic fabrics, n-alkanes biodegraded within 2-4 weeks at North Sea conditions (13°C; Brakstad and Løding, 2005). Some small PAHs dissolved in water can be degraded within a few days (Brakstad and Faksness, 2000), but high molecular-weight oil compounds associated with particulate oil biodegrade more slowly and some very high molecular-weight compounds (equivalent to the heavy residues in crude oil that are used to make bitumen) may not biodegrade to any significant degree.

A.4.9 Sedimentation

Crude oil and oil residues rarely sink into the water mass since there are few oils that have a density higher than water, even after extreme weathering. Oil can sink by sticking to materials present in the water mass. W/o emulsions that have a higher density value (e.g. emulsified bunker fuel oils) can more easily stick to a material, particularly if coming to the shore, and can sink to the bottom if washed out again from the shore. In connection to sub-sea blowout at the sea bottom, it is assumed that some of the oil droplets generated in the plume may adsorb to suspended particles or encounter with the seabed sediment. This can cause some sedimentation of oil

droplets to the seabed near the release. It is assumed that sub-sea dispersant treatment will reduce the potential for such sedimentation, due to lower adsorption /stickiness to sediment particles.

A.4.10 Deep water releases

Size distribution of the oil droplets formed during a subsurface release strongly influences the subsequent fate of the oil in the environment. Large droplets (typically larger than 5 mm) reach the surface after a couple of hours rise time from a depth of approximately 1000 m, while smaller droplets (down to 0.5 mm) may rise for up to a day before they will come to the surface. Fine droplets (below 100 microns) may stay in the water for weeks or even month before they eventually reach the surface. However, factors like vertical turbulence mixing in the water column, density stratification and cross flows will contribute to keep such fine small droplets submerged for even prolonged periods (Johansen et al., 2003). In case of deep-water releases, large droplets (mm range) will usually rise to the surface and form an oil layer with sufficient thickness to emulsify (form water-in-oil emulsions). This is usually caused by loss of buoyancy and more horizontal entrainment of the gas/oil/water plume due to dissolution of gas, possible hydrate formation, cross currents and density layers. However, large droplets (mm range) will leave the entrained plume and rise to the surface, illustrated in Figure A-10. This was observed both during the "DeepSpill" experiments in 2000 (Figure A-11) and the DWH oil spill in 2010 (Figure A-12). This emulsification will be dependent on oil properties and environmental conditions, such as temperature and sea state.
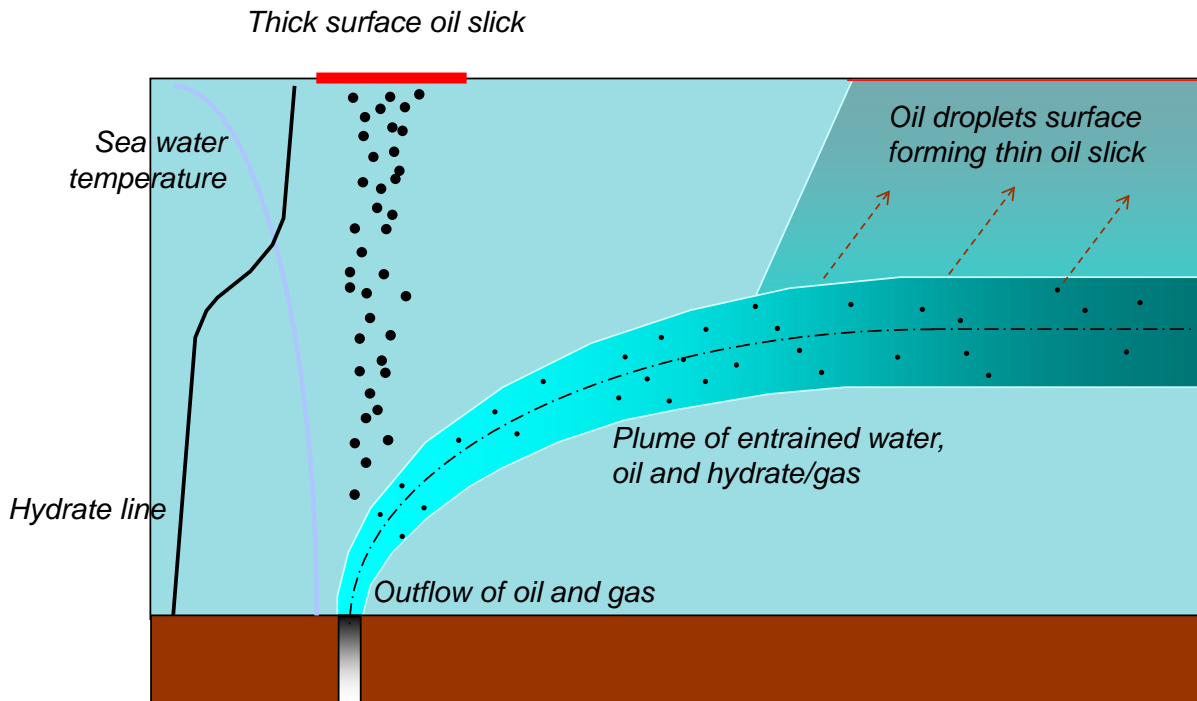

Figure A-10: Illustration of possible creation of thick surface oil slick (> 200 µm) from deep-water release of oil

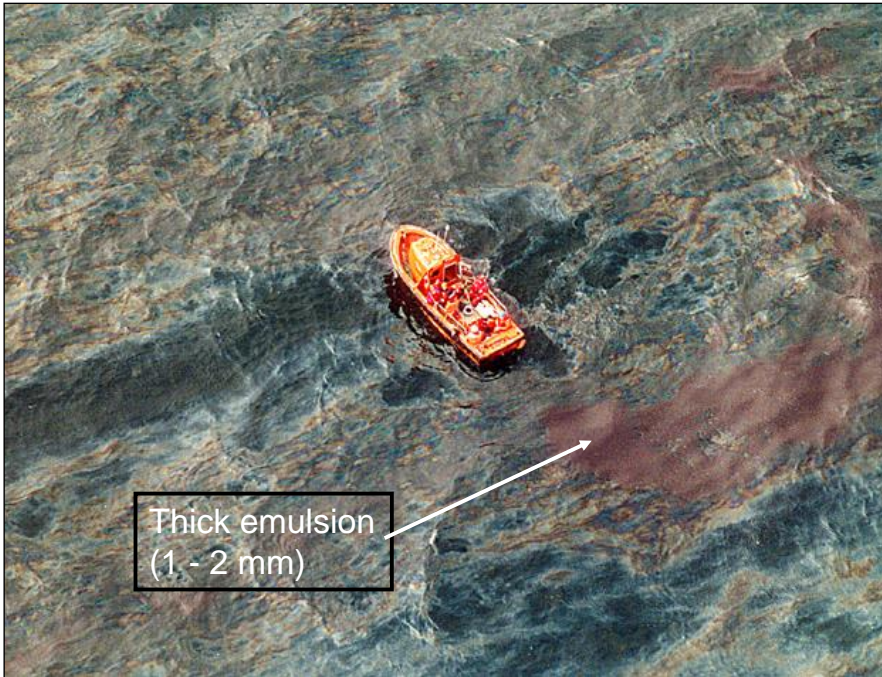*Figure A-11: Surface oil slick (initial thickness > 200 μm) from the experimental deep-water release "DeepSpill" in 2000. Surface oil is emulsifying similar to an oil slick from a surface batch release (from Leirvik et al., 2011)*
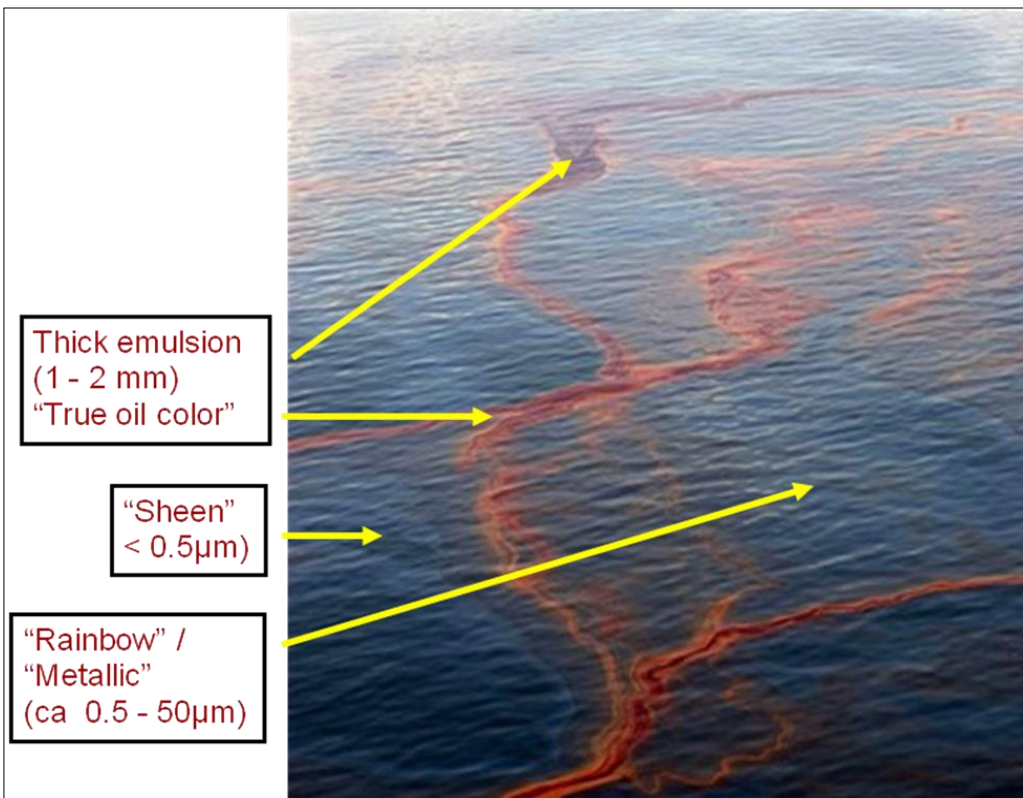

Figure A-12: Surface oil slick (initial thickness > 200 μm) from the DWH deep-water release. Surface oil is emulsifying like an oil slick from a surface batch release

A.4.11 Shallow releases

In case of a sub-surface release of oil and gas in shallower water (<500 meter) the buoyancy of the rising water/gas/oil plume is usually sufficient to reach the surface. The gas will be released to the atmosphere, while the large volumes of water will set up a horizontal current that will create a wide and thin surface oil slick (see Figure A-13, Figure A-14 and Rye et al., 1997). This surface oil slick could be too thin to emulsify (< 200 microns) and evaporation and natural dispersion will be the predominant weathering processes.
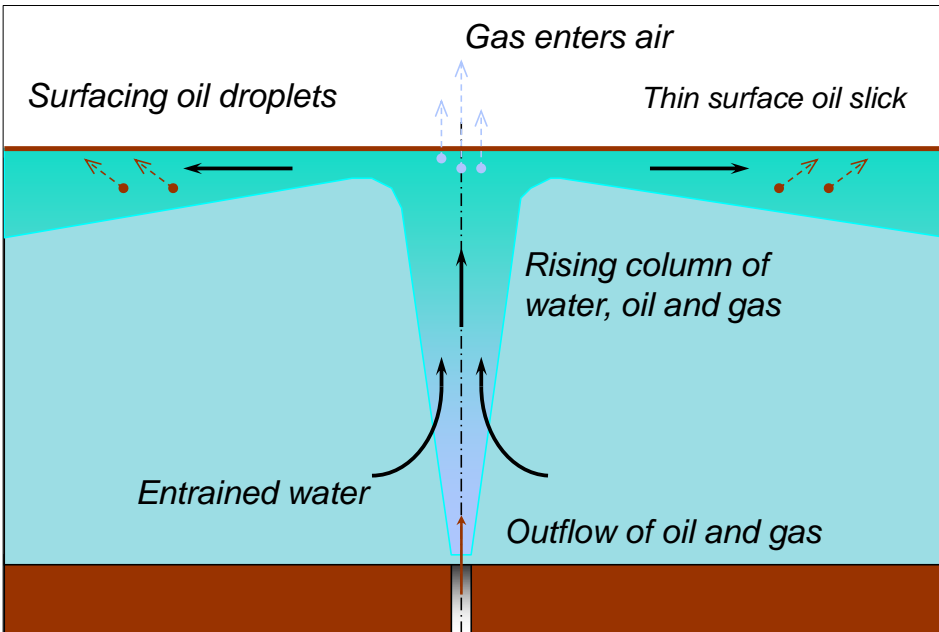
Figure A-13 Illustration of possible creation of thin surface oil slick (< 200 µm) from a shallow subsurface release (<500 m)
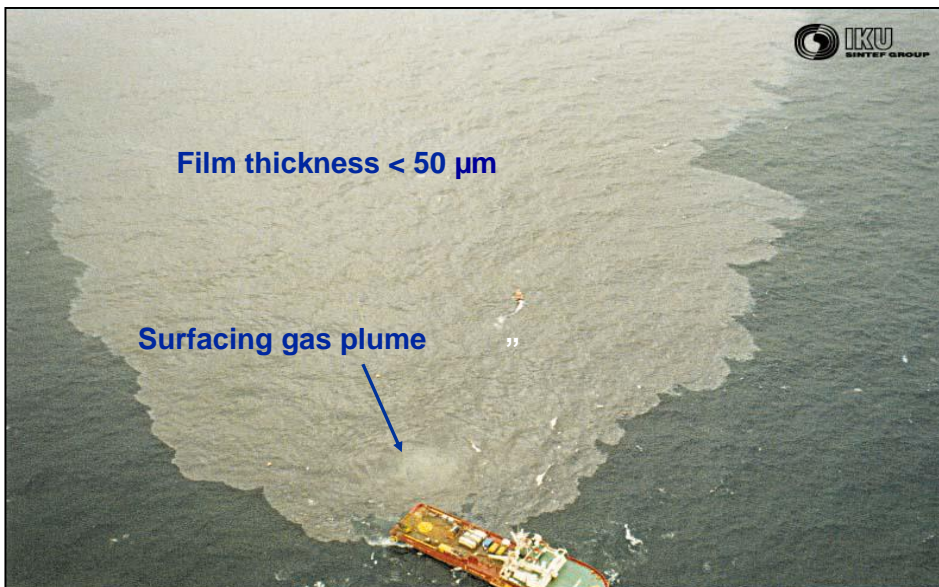

Figure A-14: Surface oil slick (< 50 µm) from experimental subsurface release at 106 m in 1996. The surface oil didn't emulsify and had a very limited life time (hours) due to the low film thickness and high rate of natural dispersion (even at < 10 m/s wind)

B Experimental setup

B.1 Oil samples and test temperature

20 Litres of Kvitebjørn 2019 arrived at SINTEF Ocean AS 2019-02-21 (Figure B-1). The oil was given the unique SINTEF ID 2019-1059. The weathering study (small-scale) were performed at 13 °C.

Figure B-1: 1 x 20 Litres of Kvitebjørn 2019 arrived at SINTEF Ocean

B.2 Small-scale laboratory testing

To isolate and map the various weathering processes at sea, the crude oil was exposed to a systematic, stepwise procedure developed at SINTEF (Daling et al., 1990). The general procedure is illustrated in Figure B-2.
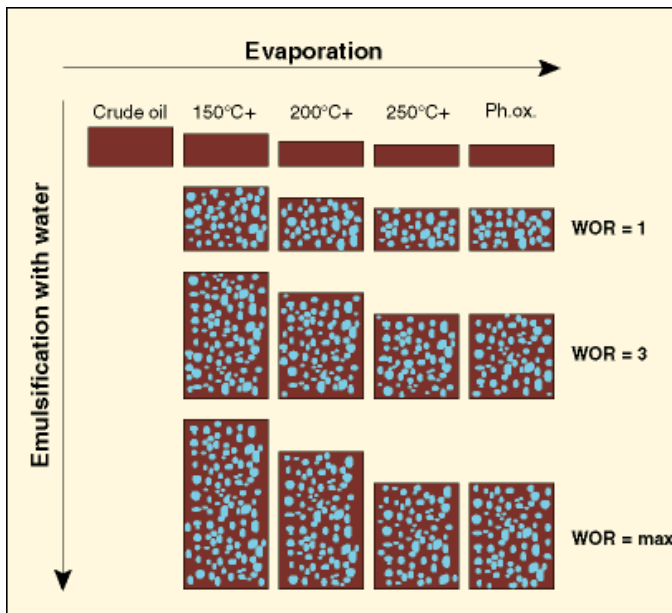
WOR: Water to Oil Ratio

WOR=1: 50 vol.% water
WOR=3: 75 vol.% water
WOR=max: the maximum water content

Figure B-2: Small-scale laboratory weathering flow chart of oil

B.2.1 Evaporation

The evaporation procedure used is described in Stiver and Mackay (1984). Evaporation of the lighter compounds from the fresh oil was carried out as a simple one-step distillation to vapour temperatures of 150 °C, 200 °C and 250 °C, which resulted in oil residues with an evaporation loss corresponding to approximately 0.5-1-hour, 0.5-1 day and 0.5-1 week of weathering on the sea surface. These residues are referred to as 150°C+, 200°C+ and 250°C+, respectively.

B.2.2 Physical and chemical analysis

The viscosity, density, pour point and flashpoint of the fresh and water-free residues was analysed. In addition, wax content and "hard" asphaltenes was measured for the 250°C+ residue. Viscosity for all the w/o emulsions was determined. The analytical methods used are given in Table B-1 and Table B-2.

Table B-1: Analytical methods used to determine the physical properties

Physical property	Analytical method	Instrument
Viscosity	McDonagh et al, 1995	Physica MCR 300
Density	ASTM method D4052-81	Anton Paar, DMA 4500
Pour point	ASTM method D97	-
Flash point	ASTM D 56-82	Pensky-Martens, PMP1, SUR

Table B-2: Analytical methods used to determine the chemical properties

Chemical property	Analytical method
Wax content	Bridiè et al, 1980
"Hard" asphaltene	IP 143/90

Chemical characterization by GC-FID and GC-MS

- The distribution of hydrocarbons (nC_5-nC_{40}) was analysed using a Gas Chromatograph coupled with a Flame Ionisation Detector (GC-FID). The Gas Chromatograph used was an Agilent 6890N with a 30m DB1 column.
- The analysis and quantification of PAHs, phenols and alkylated phenols (C_0-C_4) were completed using an Agilent 6890 Gas Chromatograph coupled with a, 5973 MSD detector (GC-MS) operating in SIM mode (Selected Ion Monitoring)

The volatile components were in the range of nC_5-nC_{10} and were quantified by use of PT-GC-MS (Purge and Trap Gas chromatograph Mass Spectrometer operating in full-scan mode and using a modified version of the EPA 8260 analysis method).

C Input data to SINTEF Oil Weathering Model (OWM)

The laboratory data used as input to the SINTEF OWM for Kvitebjørn 2019 is given in Table C-1 to C-3.The oil weathering predictions were based on the laboratory data at 13 ℃.

Table C-1: Physical and chemical properties for Kvitebjørn 2019

Properties of fresh oil	Value
Density (g/mL)	0.752
Pour point (℃)	-36
Reference temperature (℃)	13
Viscosity at ref. temp. (mPa·s = cP) *	1
Flash point (℃)**	10
Asphaltenes (wt. %)	0.01
Wax Content (wt. %)	0.14
Dispersible for visc. <	-
Not dispersible for visc. >	-

* Measured at shear rate 10 s-1

** Data from Equinor – Råolje og Produktlaboratoriet (CP)- Report 120-0018-R1

Table C-2: True boiling point (TBP) curve for Kvitebjørn 2019

Temp. (℃)	Cumulative yield (vol. %)*
36.5	11.94
69.2	21.02
98.9	37.17
126.1	56.44
151.3	68.74
174.6	74.73
196.4	80.74
217.0	85.32
253.9	91.31
271	93.47
303	96.02
344	97.90
381	98.78
423	99.34
522	99.88

*TBP received Equinor – Råolje og Produktlaboratoriet (CP) - Report 120-0018-R1

PROJECT NO.
302004682

REPORT NO.
OC2019 A-097

VERSION
2.0

54 of 56

Table C-3: Lab weathering data for Kvitebjørn 2019, 13 °C

Properties	Fresh	150°C+	200°C+	250°C+
Boiling Point Temp. (°C)	-	168.8	224.1	288.5
Vol. Topped (%)	0	65	83.5	93.2
Weight Residue (wt. %)	100	37.1	18.0	7.5
Density (g/mL)	0.752	0.797	0.816	0.835
Pour point (°C)	-36	-24	-6	9
Flash Point (°C)	-10	33	72	102
*Viscosity of water-free residue (mPa.s =cP)	1	2	4	26
*Viscosity of 50% emulsion (mPa.s = cP)	-	-	-	-
*Viscosity of 75% emulsion (mPa.s = cP)	-	-	-	-
*Viscosity of max water (mPa.s = cP)	-	-	-	-
Max. water cont. (vol. %)	-	-	-	-
(T1/2) Halftime for water uptake (hrs)	-	-	-	-
Stability ratio	-	-	-	-

* Measured at shear rate 10 s^{-1}

- No data – not measured

PROJECT NO.
302004682

REPORT NO.
OC2019 A-097

VERSION
2.0

55 of 56

D Chemical characterization (OSCAR oil profile)

The method for generating OSCAR oil profile is based on the quantification of semi-volatile organic hydrocarbons (SVOC) and volatile organic hydrocarbons (VOC) by GC-MS. The composition is divided into individual pseudo-component groups (OSCAR groups) representing the oil based on the TBP (True Boiling Point) and GC-MS analysis.

Table D-1: Chemical characterization ("oil profile") of Kvitebjørn 2019 (fresh oil) from GC-MS analysis and TBP oil fraction

SINTEF ID	2019-1059	Kvitebjørn 2019
8.000	1	C1-C4 gasses (dissolved in oil)
8.000	2	C5-saturates (n-/iso-/cyclo)
4.427	3	C6-saturates (n-/iso-/cyclo)
2.573	4	Benzene
12.000	5	C7-saturates (n-/iso-/cyclo)
4.691	6	C1-Benzene (Toluene) et. B
21.309	7	C8-saturates (n-/iso-/cyclo)
3.464	8	C2-Benzene (xylenes; using O-xylene)
5.100	9	C9-saturates (n-/iso-/cyclo)
1.436	10	C3-Benzene
5.000	11	C10-saturates (n-/iso-/cyclo)
0.050	12	C4 and C4 Benzenes
7.950	13	C11-C12 (total sat + aro)
0.000	14	Phenols (C0-C4 alkylated)
0.370	15	Naphthalenes 1 (C0-C1-alkylated)
6.630	16	C13-C14 (total sat + aro)
0.000	17	Unresolved Chromatographic Materials (UCM: C10 to C36) 0 0 0
0.000	37	metabolite 1
0.000	38	metabolite 2
0.288	18	Naphthalenes 2 (C2-C3-alkylated)
2.712	19	C15-C16 (total sat + aro)
0.097	20	PAH 1 (Medium soluble polyaromatic hydrocrbns (3 rings-non-alkyltd;<4 rings)
1.903	21	C17-C18 (total sat + aro)
2.000	22	C19-C20 (total sat + aro)
0.963	23	C21-C25 (total sat + aro)
0.037	24	PAH 2 (Low soluble polyaromatic hydrocarbons (3 rings-alkylated; 4-5+ rings)
1.000	25	C25+ (total)

The SINTEF OSCAR model is a 3-dimensional <u>O</u>il <u>S</u>pill <u>C</u>ontingency <u>A</u>nd <u>R</u>esponse model system that calculates and records the distribution (as mass and concentrations) of contaminants on the water surface, on shore, in the water column and in sediments. The model allows multiple release sites, each with a specified beginning and end to the release. This allows time-variable releases at a given location, as well as throughout the study area. The model computes surface spreading, slick transport, entrainment into the water column, evaporation, emulsification and shore interactions to determine oil drift and fate at the surface. In the water column, horizontal and vertical transport by currents, dissolution, adsorption, settling and degradation are simulated. By modelling the fate of individual pseudo-components, changes in the oil composition due to evaporation, dissolution and degradation are accounted for. OSCAR may compute oil weathering from crude assay data, although the most reliable results are produced if the target oil has been through a standardized set of laboratory weathering procedures established by the SINTEF laboratories. Alternatively, the model may use oil-weathering properties from oils for which data already exist, selecting the oil in the oil database that most closely matches the composition of the oil of concern