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Report

Utgard condensate – Weathering properties and behaviour at sea

In relation to oil spill response

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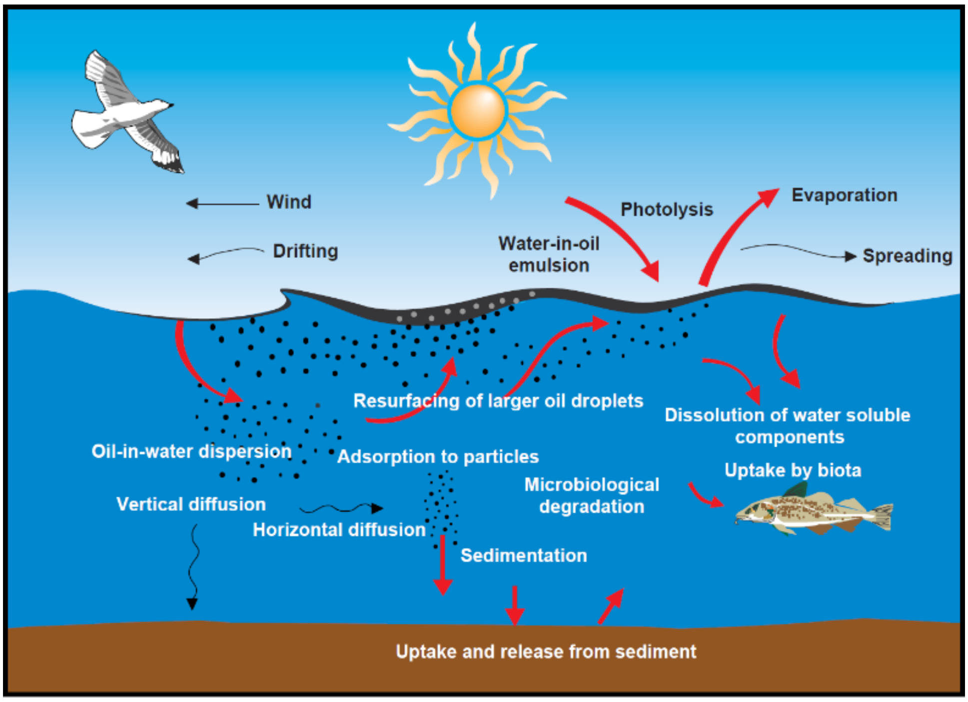

SINTEF Ocean AS

2021-07-07

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Report

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ABSTRACT

A weathering study has been conducted on Utgard condensate. The weathering study is based on a small-scale laboratory testing at 13 °C. The SINTEF Oil Weathering Model (OWM) is used to predict the weathering properties of Utgard at sea. The weathering properties of Utgard are discussed in relation to oil spill response.

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Table of Contents

1 Executive summary

Spilled oils undergo changes when weathered on the sea surface. These changes affect oil behaviour and consequently oil spill preparedness. Oil weathering varies over time and with different environmental conditions. The lifetime of an oil spill at sea depends on the oil's composition, the release conditions and environmental conditions (temperature, wind, waves). Natural dispersion and evaporation are the main weathering processes that remove an oil spill from the sea surface. Based on input from the experimental weathering data of the oil, the SINTEF Oil Weathering Model (OWM) has been used to predict the properties of oil as it weathered over time.

1.1 Surface release

This summary gives a brief overview of the main changes predicted for Utgard condensate when weathered on the sea surface after a surface release.

Compared to many other Norwegian crude oils, this weathering study of Utgard shows the following properties relevant for the behaviour, if spilled at sea:

- Utgard is a condensate with low density (0.772 g/mL) and high content of volatile (80 vol %, 250°C+) that cause a rapid and high degree of evaporative loss: E.g. after 3 hours the evaporative loss is in the range of 60-65 wt.% at 5 °C, and 60-75 wt. % at 15 °C.
- The combination of the very low contents of wax (0.86 wt.%) asphaltenes (0.02 wt.%), and low density, the condensate may form unstable low viscous emulsions (e.g.< 100 mPa.s after 6 hours) that has a high degree of natural dispersion in breaking waves conditions (> 5-10 m/s).
- The OWM predictions indicate a relative short lifetime in breaking waves conditions (10-15 m/s) of 2 to 6 hours. In calm weather conditions (2-5 m/s) the lifetime is predicted to be >2 days
- In summer conditions, the low emulsified residue (visc. < 100 mPa.s) will likely not solidify, however, in very calm weather and winter conditions the residue may form semi-solid lumps/material due to the high pour point of the 200 and 250°C+residues (+15 to + 21 °C) after about 6 hours to 2 days weathering at sea.

The low-viscous loose emulsions will easily release water during recovery and storage due to the low stability of the emulsions and use of emulsion breaker is therefore not considered as an option on recovered emulsions of Utgard.

The mass balance show that the oil/emulsion is naturally removed from the sea surface within 2 hours in high wind speeds (15 m/s) at winter (5 °C) and summer conditions (15 °C), due to evaporative loss and natural dispersion/entrainment. After 5 days in very calm weather conditions (2 m/s wind speed) at 5 and 15 °C about 10-15 % of the oil may still remain on the sea surface.

If free gas is not associated with an oil release (e.g. surface release of stabilized oil at 1 atm.), the flash point of the oil is the most important parameter when evaluating the potential for fire /explosion hazard. Spilled oil on the sea surface assumes to reach the ambient water temperature within a short time. 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 Utgard, the flash point is predicted to exceed the sea temperature within the first 15 minutes at wind speeds (10-15 m/s), and within 1-1.5 hours at lower winds speeds (2-5 m/s). However, for larger surface 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. Utgard reaches this limit (60 °C) in 4-5 hours after a spill at calm wind speed (2 m/s) at summer and 6 hours in winter conditions respective, and more rapidly at higher wind speeds. A "safety" zone should be established early and downwind from the spill site before any response actions in case of an acute oil spill involving free gas. In a response operation, explosimeters should be utilized to measure concentrations of free gas to minimize the risk for fire and explosion hazard at the spill site.

The risk for boom leakage in a mechanical recovery operation is more of a concern for low viscous oils (lower than 1000 mPa.s) compared to emulsions that are more viscous. Boom leakage is also influenced by other factors such as operational speed and weather conditions. This study shows that the emulsion viscosities of

Utgard is well below 1000 mPa.s for several days if spilled at sea in calm conditions at 5 and 15 °C. The abovementioned factors should therefore be taken into account to minimalize the risk for boom leakage during mechanical recovery e.g. reducing the towing speed.

Utgard is assumed to have a high degree of natural dispersion in the water column, particularly in breaking waves conditions (> 5 wind speeds). In calm weather conditions (non-breaking waves < 2-5 m/s wind speed), the use of artificial energy (water flushing /Fi-Fi monitors) may increase the dispersion efficiency for thin oil films (< 0.2-0.3 mm). Due to the expected high degree of natural dispersion the benefit for use of dispersant may be limited, but could be used with following high-capacity water flushing in calm weather conditions (non-breaking waves, where the oil film thickness can be > 0.2-0.3 mm.

Short summary response options for surface release

Lifetime of surface oil with no response: The OWM predictions indicate short lifetime in breaking waves conditions (10-15 m/s) of 2-6 hours. In calm weather conditions (2-5 m/s) the lifetime is predicted to be > 2 days.

Mechanical recovery:
- In calm weather conditions (< 5m/s) Utgard has a potential for mechanical recovery given a film thickness > 0.1mm.
- However, the efficiency may be reduced because of the risk of boom leakage due to low emulsion viscosities (< 1000 mPa.s)

Use of chemical dispersants:
- Limited efficiency for use of chemical dispersant in breaking waves (10-15 m/s) due to high degree of natural dispersion of the oil film into the water column.
- In calm weather (< 2-5 m/s) with film thickness > 0.05-0.1 mm, the use of chemical dispersant may be a possible option in combination with water-flushing (e.g., from Fi-Fi monitor) to enhance effective dispersion of oil droplets into the water column.

High-capacity water flushing (mechanical dispersion):
- Water flushing may be a stand-alone method if the film thickness is <0.2-0.3 mm.

1.2 Subsea release

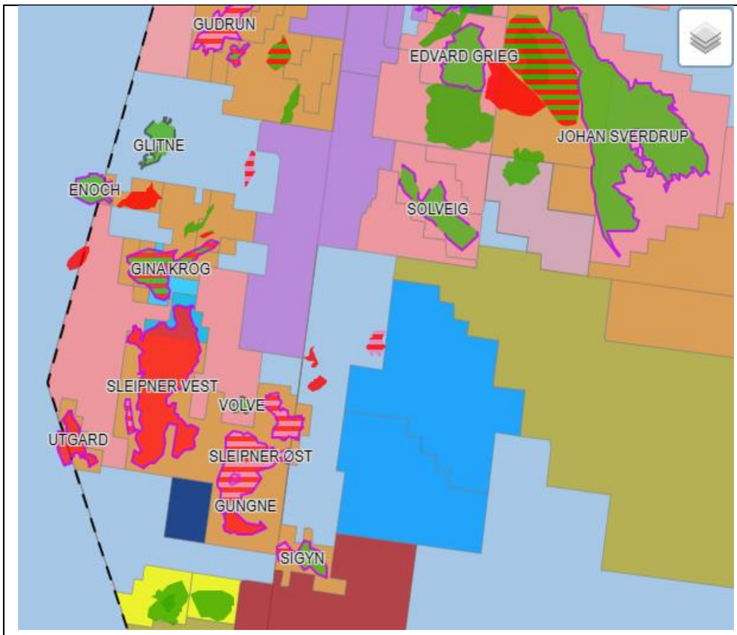
In this study, the OWM Subsea module was used to predict the oil film thicknesses and weathering properties and behaviour after a subsea release of Utgard at 5 and 15 °C, assuming that the momentum and buoyancy of the released plume of oil and gas is sufficient to reach the surface, where the plume will spread the oil out over the sea surface.

For a specified subsea blowout release with free gas present, the predicted initial film thickness (5-10 micron) of Utgard is to too low for emulsification and neither mechanical recovery nor dispersant application are therefore not considered to be an efficient response option. However, high-capacity water flushing can be suitable in spill situations with calm sea conditions (non-breaking waves < 2-5 m/s wind speeds) to enhance the naturally dispersion of surfaced oil in an early phase.

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 time after the release. These past experiences and other incidents 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 oil spilled on the sea surface.

According to the Norwegian Environment Agency and the Petroleum Safety Authority Norway (Ptil) regulations for petroleum activities (Aktivitetsforskriften §59), the characterization of oils with respect to their weathering properties and fate in the marine environment should be performed for all oils coming into production. SINTEF Ocean has performed a standardized small-scale weathering study on Utgard condensate at 13 °C. The obtained laboratory data were further customized to predict the weathering properties of Utgard by use of the SINTEF Oil Weathering Model (OWM). Information about the Utgard field is given, below (Figure 2-1).



Utgard (PL 433) is a field in the North Sea, straddling the sector boundary between Norway and the UK.

Utgard is located 20 kilometres west of the Sleipner area. The water depth is 110-120 metres. T

The field was discovered in 1982 and the plan for development and operation (PDO) was approved in 2017. *Production from Utgard started in September 2019.*

The development concept is a 4-slot subsea template with two wells tied-back to the Sleipner T facility for processing and reduction of the CO_2 level in the gas. The subsea template is located in the Norwegian sector.

The gas is exported to the Gassled pipeline system. Unstable condensate is transported via the existing condensate pipeline to the Kårstø terminal for further processing and export.

Figure 2-1 *https://www.norskpetroleum.no/en/facts/field/utgard/*

3 Small-scale laboratory testing of Utgard condensate

Description of the oil sample of Utgard for testing and the experimental setup for the small-scale weathering are described in Appendix B. Physico-chemical parameters and weathering properties of Utgard condensate were compared with a selection of other oils located in the same area: Gudrun crude oil, Sigyn condensate and Sleipner condensate (Table 3-1). The oils in comparison were selected in agreement with Equinor ASA.

*Table 3-1 Oils compared with Utgard **

Oil name	SINTEF ID	Report number	Reference
Gudrun	2018-6115	OC2019 A-59	Hellstrøm, 2018
Sigyn	2017-113	OC2017 A-137	Øksenvåg et al. 2017
Sleipner	-	93.126	Almås, 1993

**Utgard : SINTEF ID 2021-879*

3.1 Gas chromatographic (GC-FID) characterization

The hydrocarbon profile of Utgard was analysed by use of gas chromatography (GC) coupled with Flame Ionization detector (FID). Figure 3-1 illustrates the GC-FID outputs (gas chromatograms) of the fresh oil of Utgard and the corresponding evaporated residues at three different degrees of evaporative loss of volatiles at 150, 200 and 200°C+ (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.

Utgard is light paraffinic condensate with high degree of light compounds of n-alkanes, cyclic and aromatic hydrocarbons, and a minor content of some heavier wax paraffins >C_{20}. Utgard has also a characteristic feature where the pristane peak is higher than the nC_{17} peak (Table 3-2), which is typically for oils that have undergone a biodegradation process in the reservoir. However, the biodegradation is not very distinct compared with highly biodegraded oils that lack or have minor content of n-alkanes. This is also a similar feature as observed for the Sigyn condensate, as shown in Figure 3-2. Gudrun is a typical (light) paraffinic crude oil with a main range of n-alkanes from nC_5 to nC_{30}.

GC/FID is an important tool for oil characterization and for oil spill identification as an initial step. Common screening parameters used for identification, as well as for the degree of biodegradation, are the nC_{17}/Pristane and nC_{18}/Phytane ratios. Table 3-2 shows the ratios of Utgard in comparison with the other oils.

*Table 3-2 nC_{17}/Pristane and nC_{18}/Phytane ratios**

Oil name	nC_{17}/Pristane* *	nC_{18}/Phytane**
Utgard	0.96	2.05
Gudrun	2.09	2.82
Sigyn	0.74	2.91
Sleipner	-	-

**Ratios > 1 typical for paraffinic oils, ratios < 1 typical for biodegraded /naphthenic oil.*
-: no data obtained

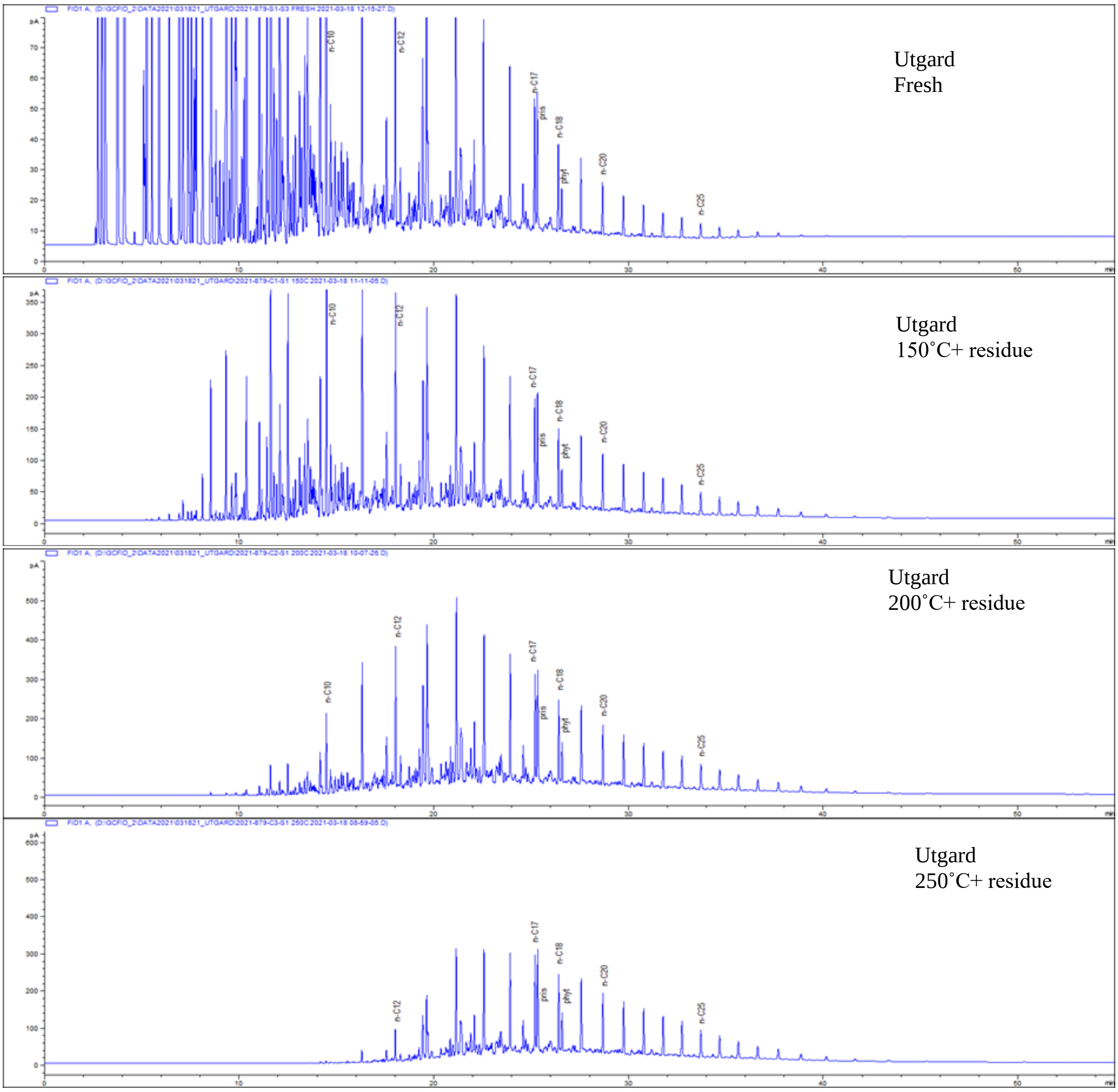


Figure 3-1 GC-FID chromatograms of fresh sample and evaporated residues of Utgard.

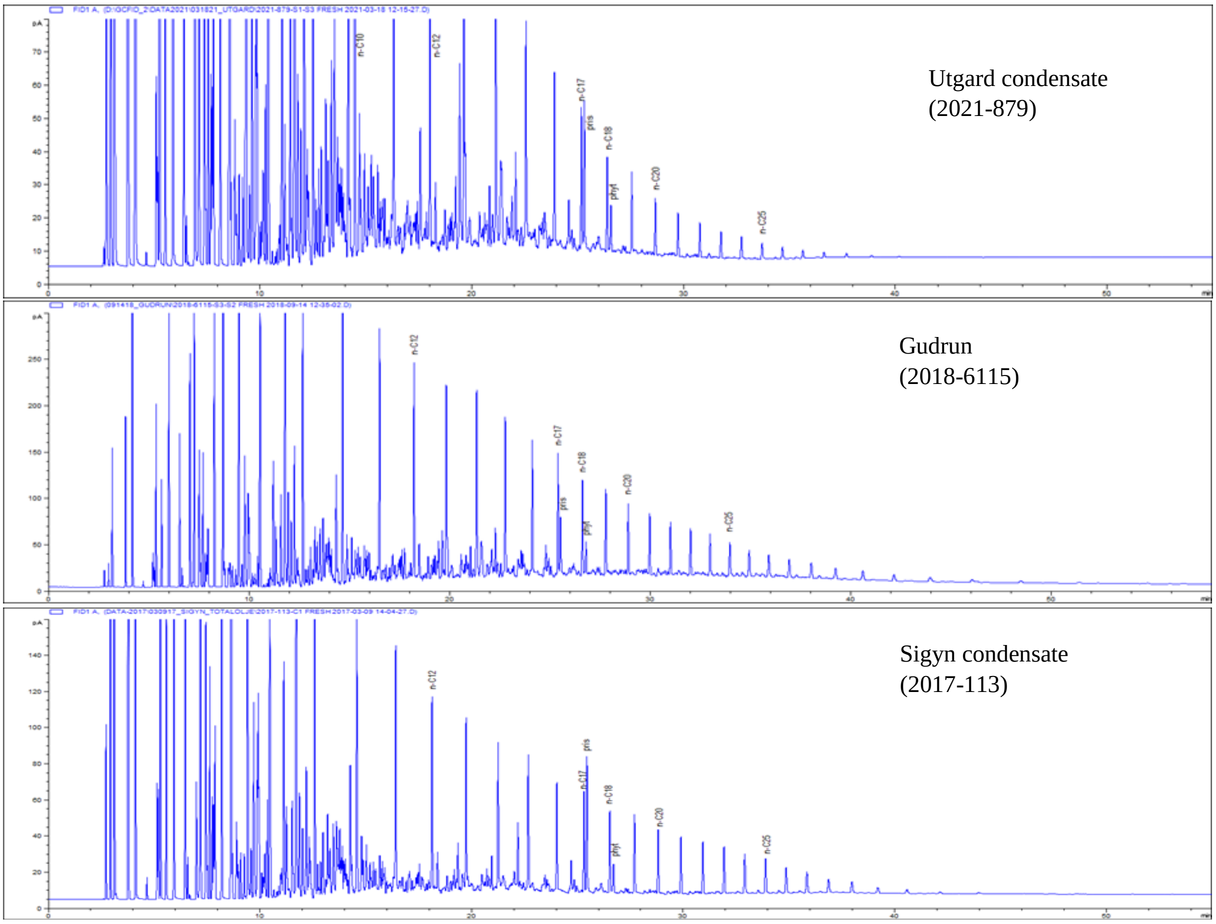


Figure 3-2 *GC-FID chromatograms for fresh oils of Utgard in comparison with Gudrun and Sigyn. A chromatogram of Sleipner has not been obtained for this comparison. The retention times differ between the chromatograms due to different temperature programs (relative comparison).*

3.2 Asphaltenes and wax content of the fresh and weathered residues

The content of asphaltene and wax of Utgard in comparison with the other oils are given in Table 3-3. Utgard (fresh oil) has a very low content of wax (0.86 wt.%) and a low content of asphaltenes (0.02 wt.%). The wax content of Utgard is most like Sleipner, whilst the low asphaltene is in the same range as Gudrun, Sigyn and Sleipner.

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

Oil type	Residue	Asph* (wt. %)	Wax (wt. %)
Utgard	Fresh	0.02	0.86
	150°C+	0.05	1.9
	200°C+	0.07	2.7
	250°C+	0.10	4.0
Gudrun	Fresh	0.03	2.9
	150°C+	0.05	4.1
	200°C+	0.06	4.9
	250°C+	0.07	6.1
Sigyn	Fresh	0.01	3.1
	150°C+	0.03	7.4
	200°C+	0.05	11
	250°C+	0.07	16
Sleipner	Fresh	<0.1	0.85
	150°C+	<0.1	2.1
	200°C+	<0.1	3.4
	250°C+	<0.1	5.3

**n-heptane (nC_7) precipitation*

3.3 Physical properties of the fresh and weathered residues

The physical properties of Utgard are listed in Table 3-4 in comparison of the other oils Gudrun, Sigyn and Sleipner. Figure 3-3 shows the fresh oil and the evaporative residues of Utgard.

Utgard has an evaporative loss of 80 vol.% (250°C+) residue that is most similar with Sigyn of 82 vol. %. All the oils in comparison have low densities in the range of 0.739-0.810 g/mL. Utgard has low pour point -27 °C (fresh oil) that increases rapidly to considerably higher pour points with increasing evaporative loss (range +6 to +21 °C for the residues). Gudrun and Sigyn also exhibit high pour points, particularly for the 250°C+ residues (+27°C). The viscosity of the fresh oil of Utgard increases with increasing evaporation and decreasing temperature. The viscosity of the 250°C+ residue of Utgard is relatively low (269 mPa.s at $10s^{-1}$) compared with Gudrun and Sigyn at 13°C (5029 and 1120 mPa.s, respective), but the viscosity is higher compared with Sleipner.

Figure 3-3 Utgard from left to right: Fresh oil, 150°C+, 200°C+ and 250°C+ residue.

Table 3-4 Physical properties of Utgard in comparison with others oil (Gudrun, Sigyn, and Sleipner)

Oil type	**Residue**	**Evap. (vol. %)**	**Residue (wt. %)**	**Density (g/mL)**	**Flash point (°C)**	**Pour point (°C)**	**Visc. (mPa.s) 13°C (10 s^{-1})**	**Visc. (mPa.s) 5°C (10 s^{-1})**
Utgard	Fresh	0	100	0.772	-	-27	1	1
	150°C+	56	48	0.843	38	6	3	180
	200°C+	70	33	0.860	75	15	36	352
	250°C+	80	22	0.875	112	21	269	1386
Gudrun	Fresh	0	100	0.810	-	-9	17	100
	150°C+	32	71	0.847	41	6	130	815
	200°C+	45	59	0.861	75	18	849	2048
	250°C+	56	48	0.875	110	27	5029	11822
Sigyn	Fresh	0	100	0.739	-	-3	1	-
	150°C+	62	42	0.817	35	18	53	-
	200°C+	74	30	0.834	76	21	266	-
	250°C+	82	20	0.841	111	27	1120	-
Sleipner	Fresh	0	100	0.745	-	-30	1*	-
	150°C+	63	40	0.815	38	-9	2.5*	-
	200°C+	78	25	0.830	69	3	4*	-
	250°C+	86	16	0.839	98	12	6*	-

*-:No data * Measured at 100s^{-1}*

The True Boiling Point curves (TBP) of Utgard in comparison with Gudrun, Sigyn, and Sleipner are shown in Figure 3-4. The TBPs clearly show similarities of Utgard and Sigyn, whilst Sleipner has the highest evaporative loss, and Gudrun the lowest TBP among these oils.

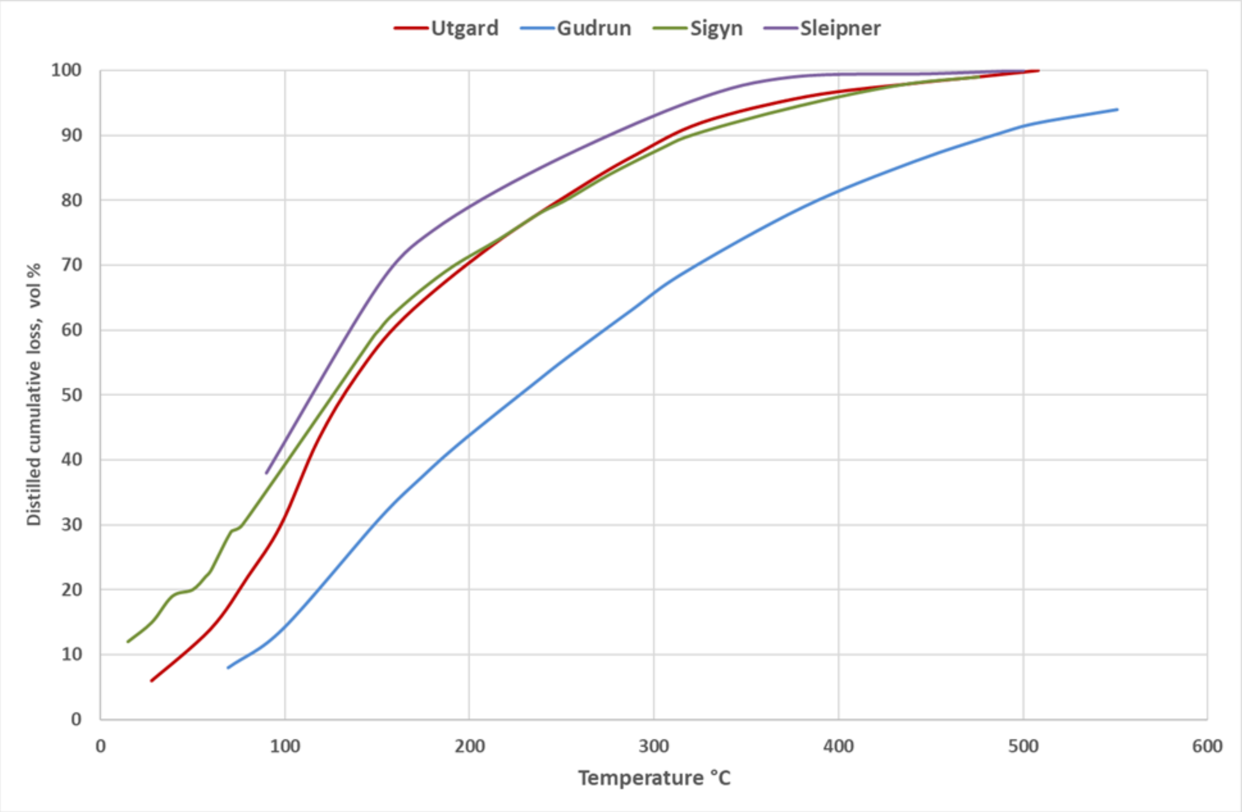


Figure 3-4 TBP of Utgard in comparison with other oils.

3.4 Viscosity of fresh oil and water-free residues with different shear rates

The viscosity describes the oils' ability to resist gradual deformation by increasing shear, where viscosities of so-called *Newtonian* oils remain constant independent on the applied shear rate (s^{-1}) at a given temperature. The opposite when shear is applied on so-called *non-Newtonian* oils the viscosity of such oils decreases. The dynamic viscosities (mPa.s) of Utgard fresh oil and water-free residues are given in Table 3-5 with increasing shear rates (10, 100 and 1000 s^{-1}) at 13 °C. The residues 200 and 250°C+ of Utgard clearly exhibit *non-Newtonian* behaviour at 13 °C, i.e., viscosities depending on the shear rates.

Table 3-5 Viscosities of fresh oil and residues of Utgard with increasing shear rates (s^{-1}) at 13 °C.

Oil type	**Residue**	**Visc. (mPa.s) 13°C (10 s^{-1})**	**Visc. (mPa.s) 13°C (100 s^{-1})**	**Visc. (mPa.s) 13°C (1000 s^{-1})**
Utgard	Fresh	1	1	1
	150°C+	3	3	4
	200°C+	36	14	9
	250°C+	269	83	31

3.3 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. The procedure for maximum water uptake is described in Hokstad et al., 1993 (Appendix B).

Formation of stable emulsions is not likely for Utgard based upon the oil is a light condensate with negligible content of stabilizing components like the asphaltenes and the very low content of wax. A simple emulsification test (maximum water) on the 250°C+ residue was conducted for verify this assumption. The 250°C+ residue formed a very unstable emulsion with large oil droplets after 24 hours rotating, and almost all the incorporated water was released upon stand still within 1-hour (Figure 3-5). The viscosity of the unstable emulsion was very low ~45 mPa.s ($10s^{-1}$). Further testing for emulsifying properties on Utgard was not performed.

Figure 3-5 *Left: Loose emulsion formation for 250°C+ residue of Utgard after 24 hours rotation time. Right: Released water from the 250°C+residue of Utgard within 1-hours stand still.*

3.2 Chemical dispersibility

No standardized dispersibility testing was conducted on Utgard due to negligible emulsification. However, a simple dispersibility test was performed on the "emulsified" 250°C+ residue using the MNS test reflecting typically breaking waves conditions (> 5 m/s wind speed) (Mackay and Szeto, 1980). As shown in Figure 3-6 (Left), the "emulsion" was easily dispersed into the water column without adding dispersants. However, lager oil droplets may arise to the surface in calm sea states. The dispersant, Dasic NS, was also added to the oil/emulsion and produced even smaller oil droplets (< 70-100 μm) that remained in the water phase, see Figure 3-6 (Right).

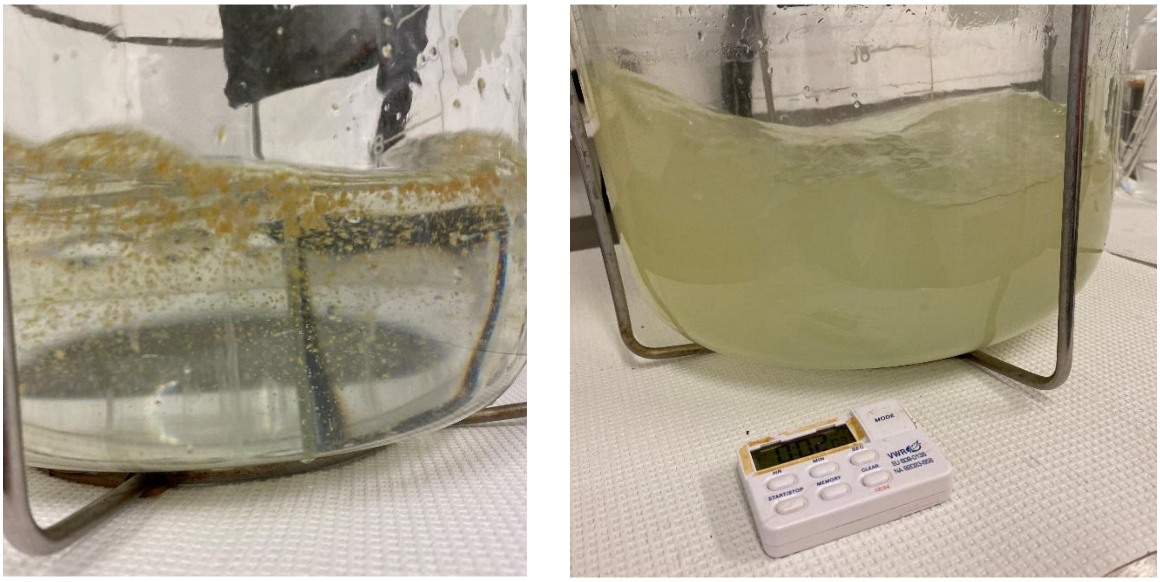


Figure 3-6 *Left: No adding dispersant of 250°C+ residue of Utgard.* .
Right: Dispersion after adding Dasic NS (DOR 1:50) on 250°C+ residue of Utgard.

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 Utgard was conducted at 13 °C, and the analytical data were further used as input to the SINTEF Oil Weathering Model (OWM). The experimental design for the study is described in Appendix B. The input data of Utgard to the SINTEF OWM are 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.

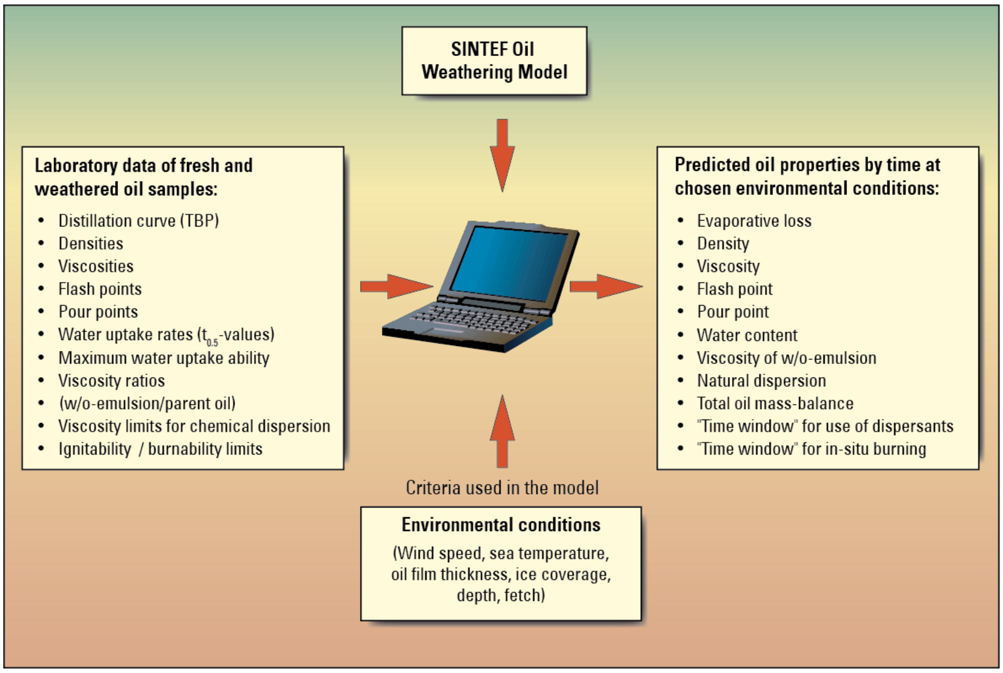


Figure 4-1 Schematic input data to the SINTEF OWM and the predicted output oil properties

Oil film thickness

Oils in OWM are categorized as condensate (non-emulsifying oil), low emulsifying oil/condensate, emulsifying oil, heavy bunker fuel or refined distillate. The categorization is based on the experimental results obtained in the laboratory. The terminal film thicknesses vary among these categories based on experimental (field) experience. Utgard is categorized as a condensate.

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 temperatures chosen for Utgard was 5 and 15 °C, reflecting typically winter and summer conditions.

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 Utgard from surface release

A standard surface release was used as a spill scenario. 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.

Input to SINTEF OWM

Oil type:	Condensate
Geographical area:	North Sea
Terminal oil film thickness:	0.05 mm
Release rate:	1.33 metric tonnes per min. in 15 min, a total of 20 metric tonnes (80 m^3/hour or 1900 m^3/day)
Seawater temperatures:	5 and 15 °C
Wind speeds:	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 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 of predicted weathering properties for Utgard.

Table 4-2 Example of weathering properties of Utgard obtained from the OWM predictions after 3 hours of weathering at 2, 5 and 10 m/s wind speed at 15 °C.

Weathering properties	**3 hours 15 ˚C 2 m/s**	**3 hours 15 ˚C 5 m/s**	**3 hours 15 ˚C 10 m/s**
Evaporation, wt. %	59	66	72
Flash point, °C	55	75	94
Pour Point, °C	10	14	18
Water content, vol.%	-	-	-
Viscosity, mPa.s *	23	35	52
Mass balance / Oil on surface wt.%	41	32	5

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

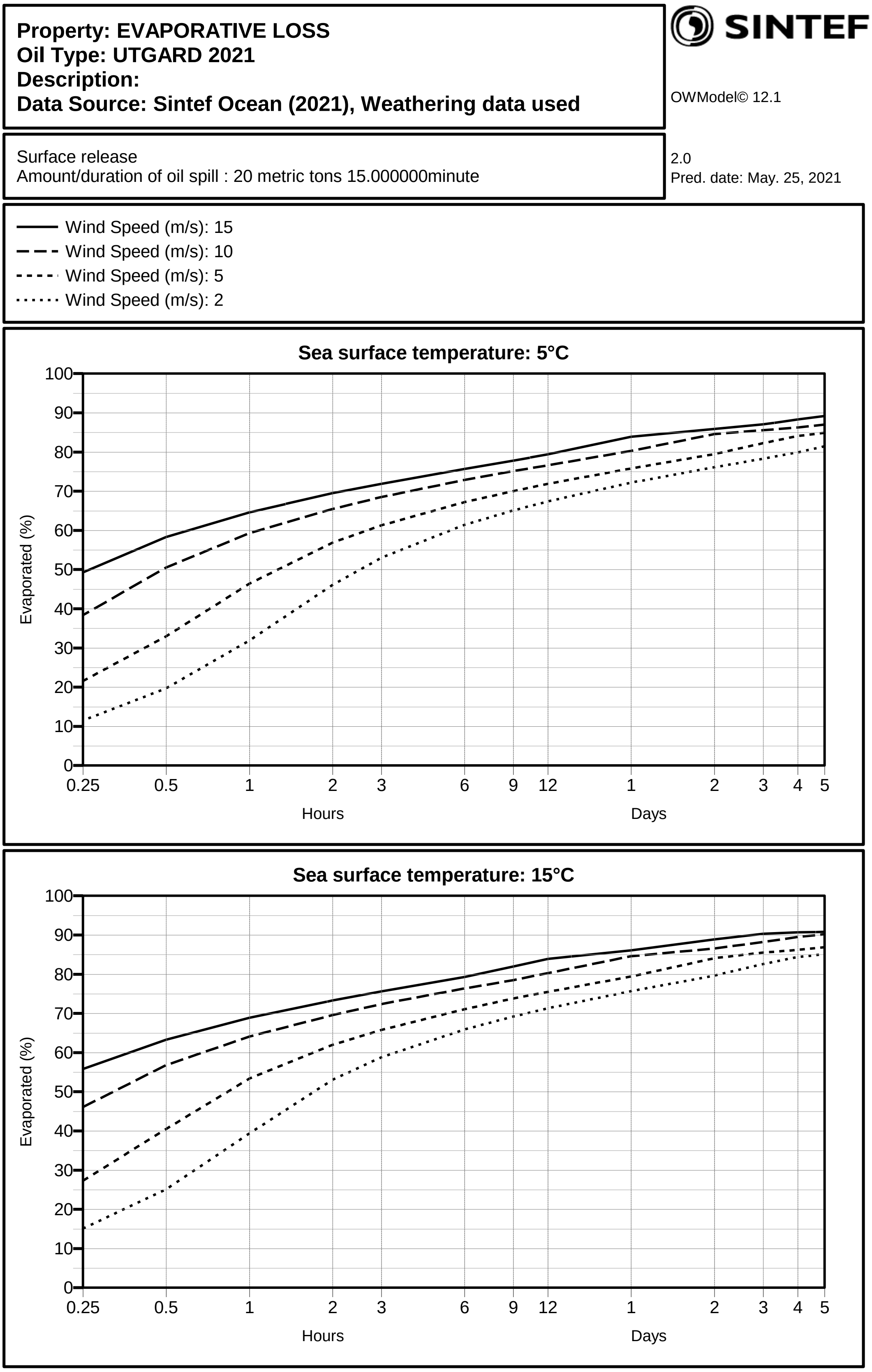


Figure 4-2 Evaporative loss of Utgard predicted at sea temperatures of 5 and 15 °C.

Property: VISCOSITY FOR WATER-FREE OIL
Oil Type: UTGARD 2021
Description:
Data Source: Sintef Ocean (2021), Weathering data used

SINTEF

OWModel© 12.1

Surface release
Amount/duration of oil spill : 20 metric tons 15.000000minute

2.0
Pred. date: May. 25, 2021

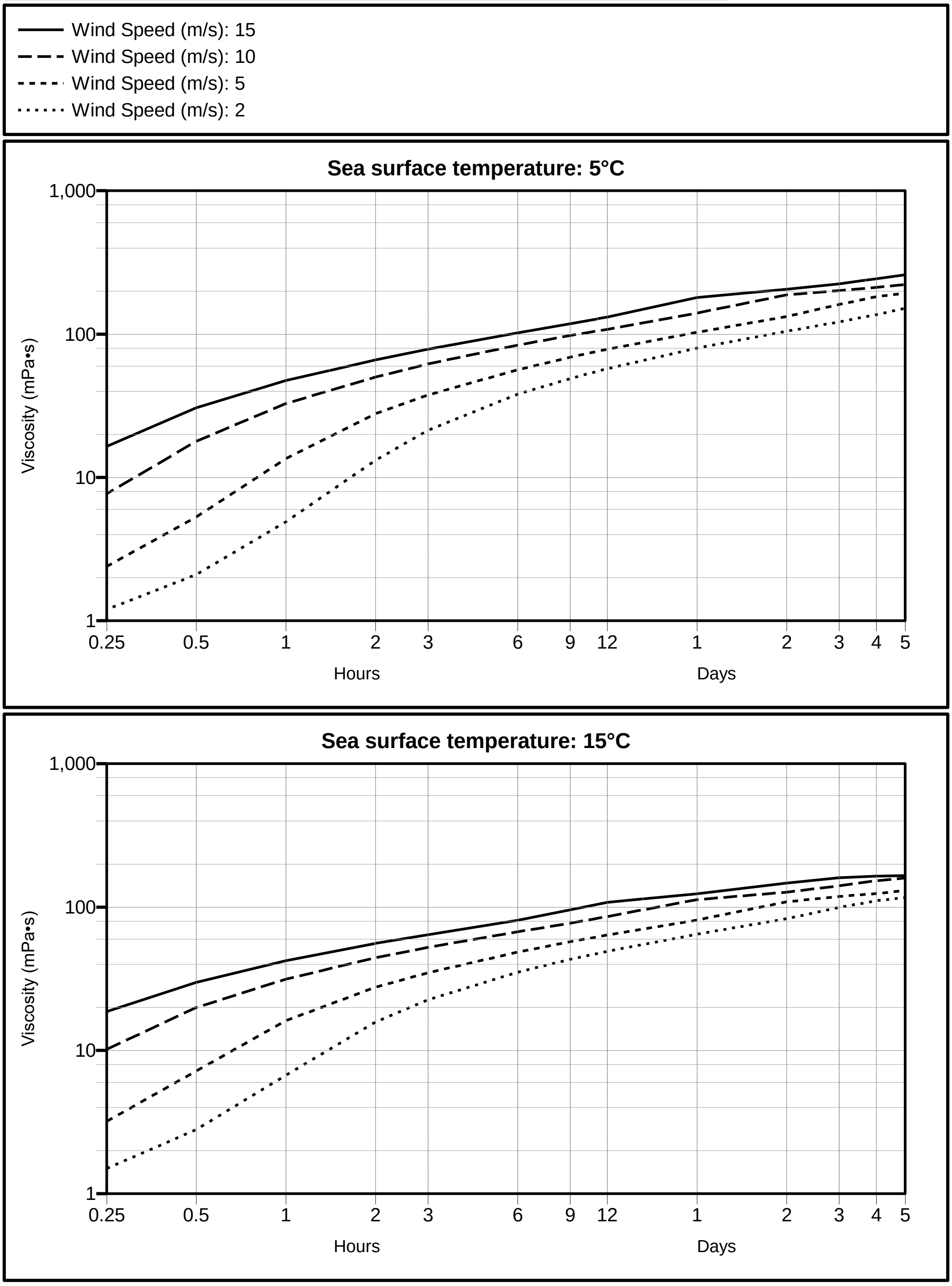
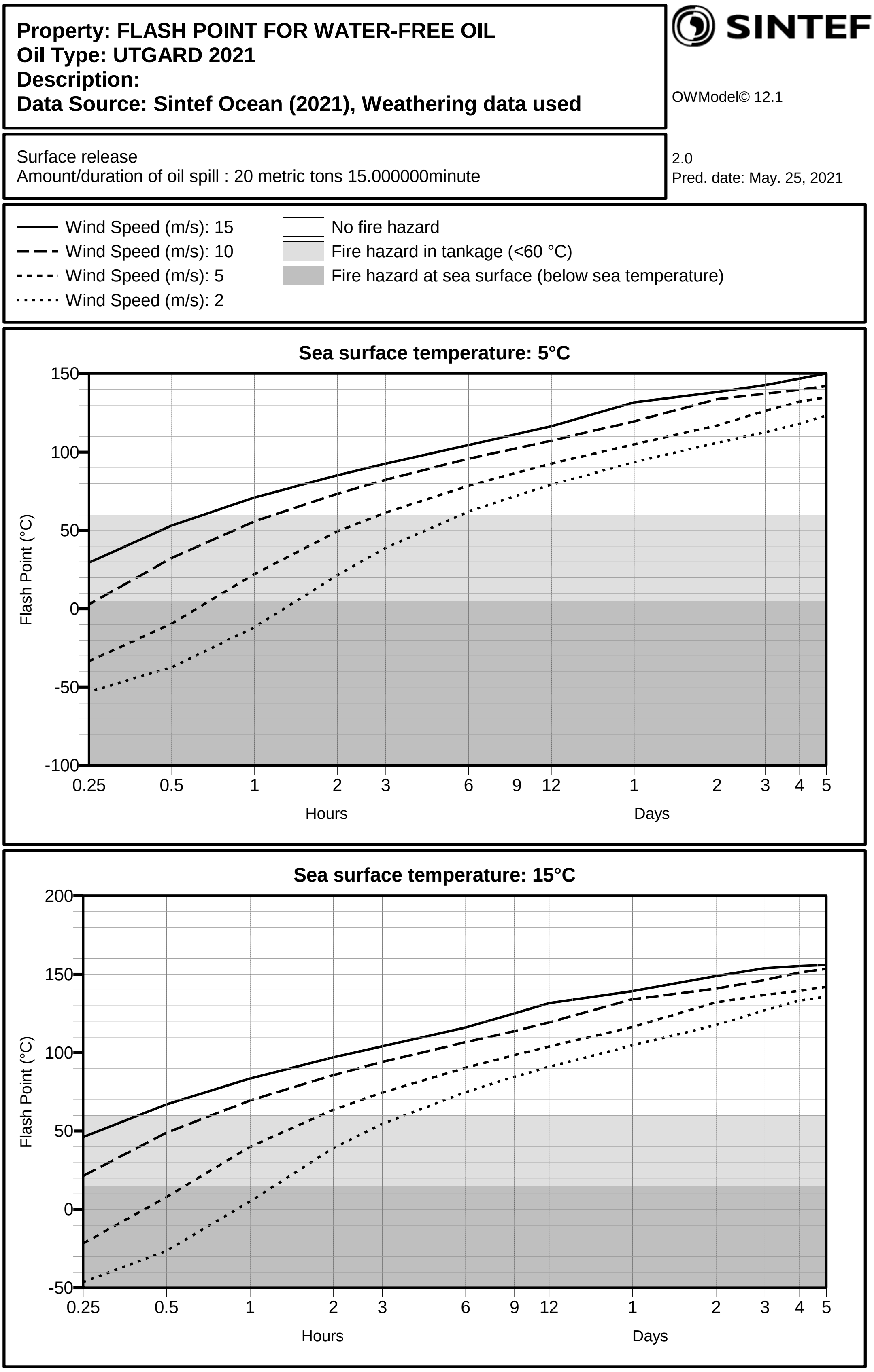


Figure 4-3 *Viscosity of Utgard predicted at sea temperatures of 5 and 15 °C, shear rate 10* s^{-1}.



Property: FLASH POINT FOR WATER-FREE OIL
Oil Type: UTGARD 2021
Description:
Data Source: Sintef Ocean (2021), Weathering data used

OWModel© 12.1

Surface release
Amount/duration of oil spill : 20 metric tons 15.000000minute

2.0
Pred. date: May. 25, 2021

Figure 4-4 *Flash point of Utgard predicted at sea temperatures of 5 and 15 °C.*

Property: POUR POINT FOR WATER-FREE OIL
Oil Type: UTGARD 2021
Description:
Data Source: Sintef Ocean (2021), Weathering data used

SINTEF

OWModel© 12.1

Surface release
Amount/duration of oil spill : 20 metric tons 15.000000minute

2.0
Pred. date: May. 25, 2021

—— 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	

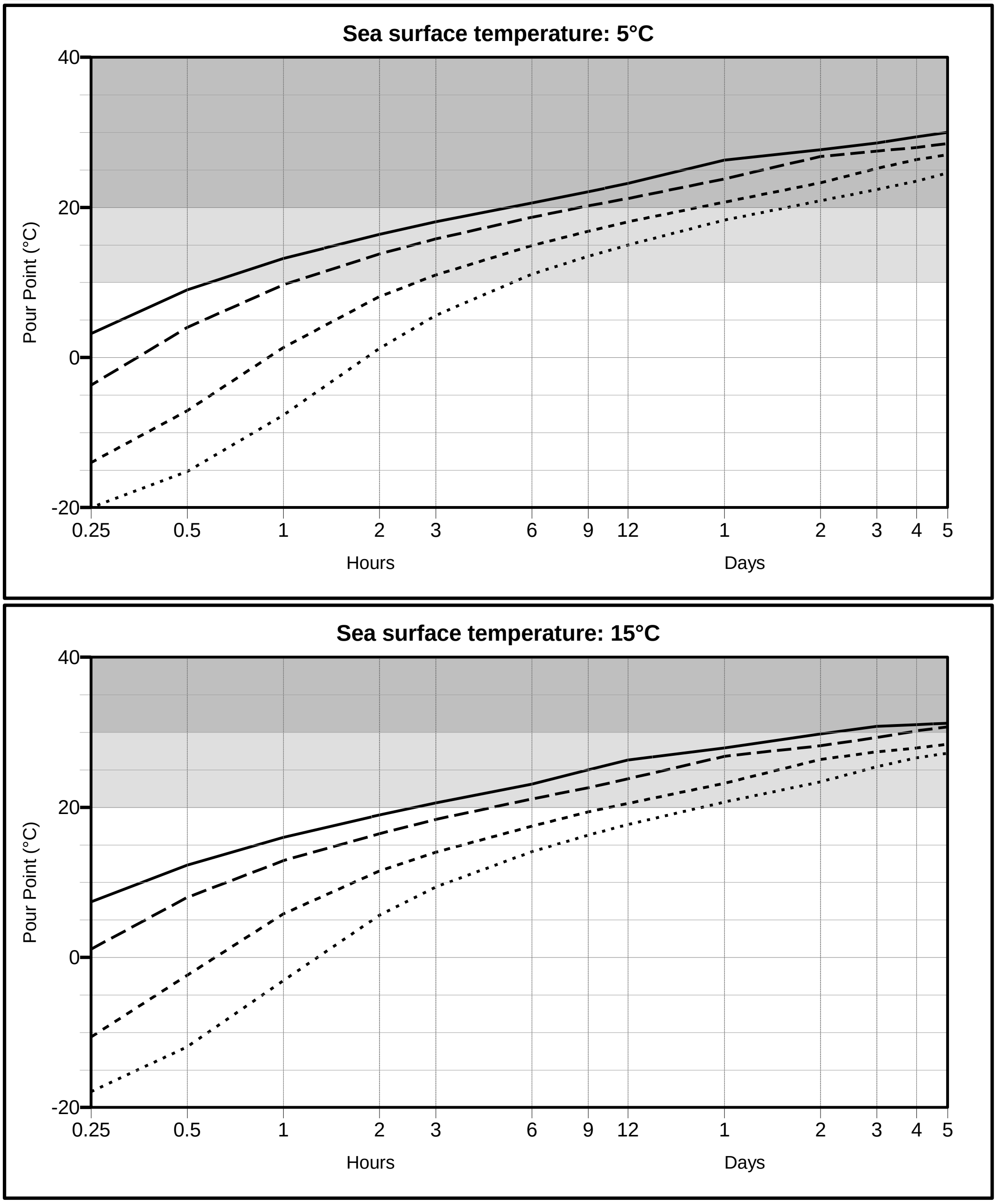


Figure 4-5 Pour point of Utgard predicted at sea temperatures of 5 and 15 °C.

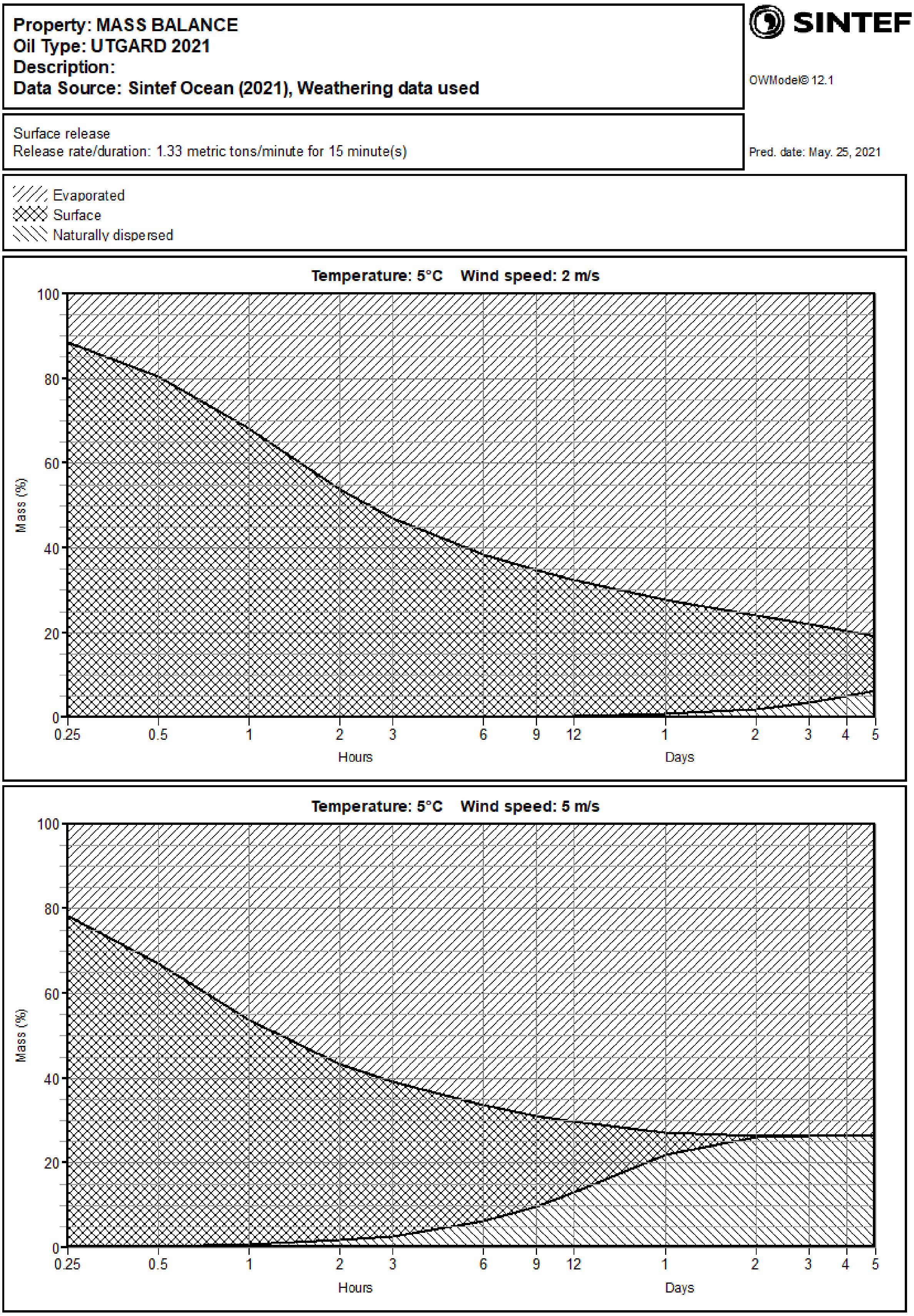


Figure 4-6 Predicted mass balance of Utgard predicted 5 °C, wind speeds of 2 and 5 m/s.

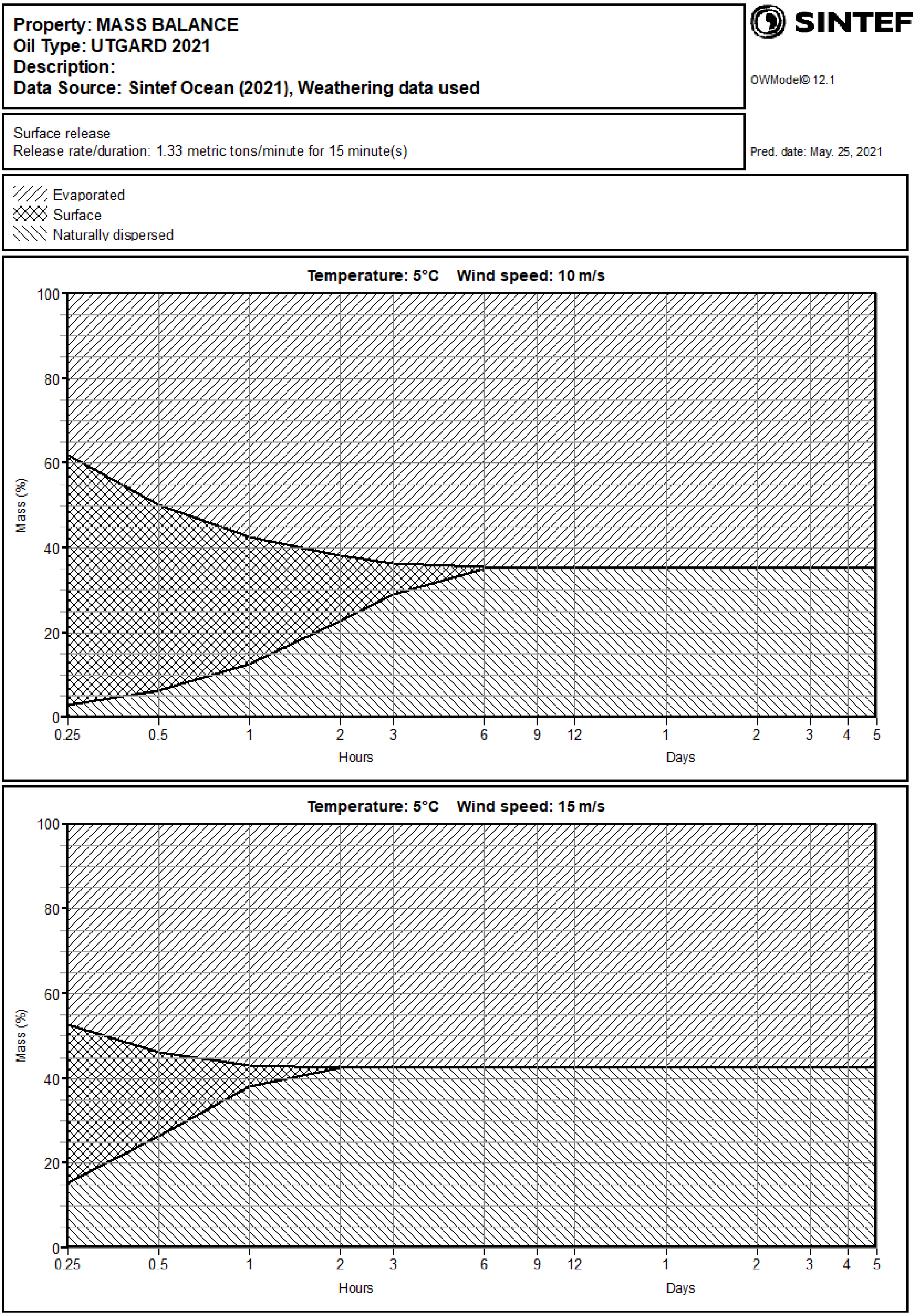


Figure 4-7 *Predicted mass balance of Utgard predicted 5 °C, wind speeds of 10 and 15 m/s.*

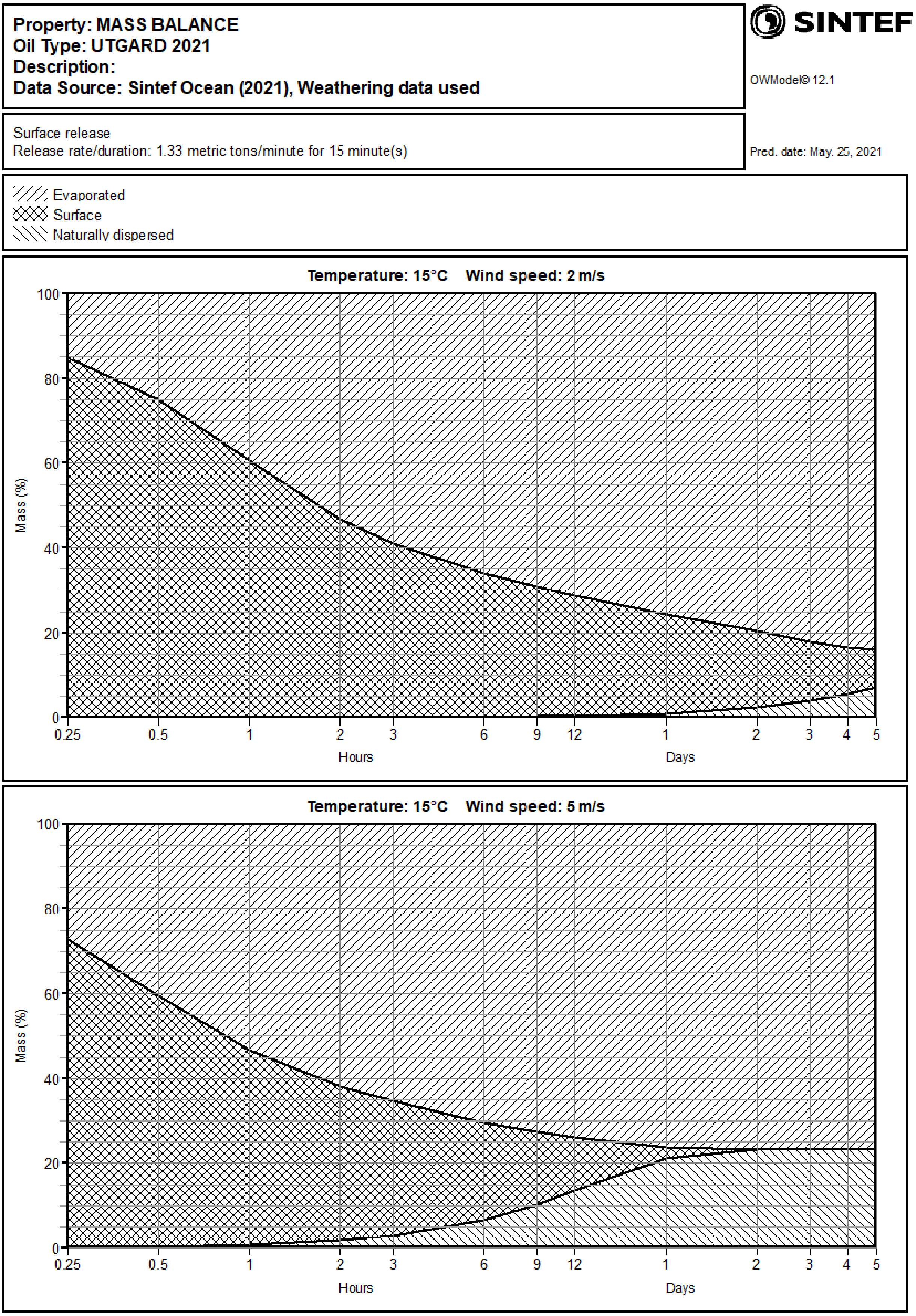


Figure 4-8 *Predicted mass balance of Utgard predicted 15 °C, wind speeds of 2 and 5 m/s.*

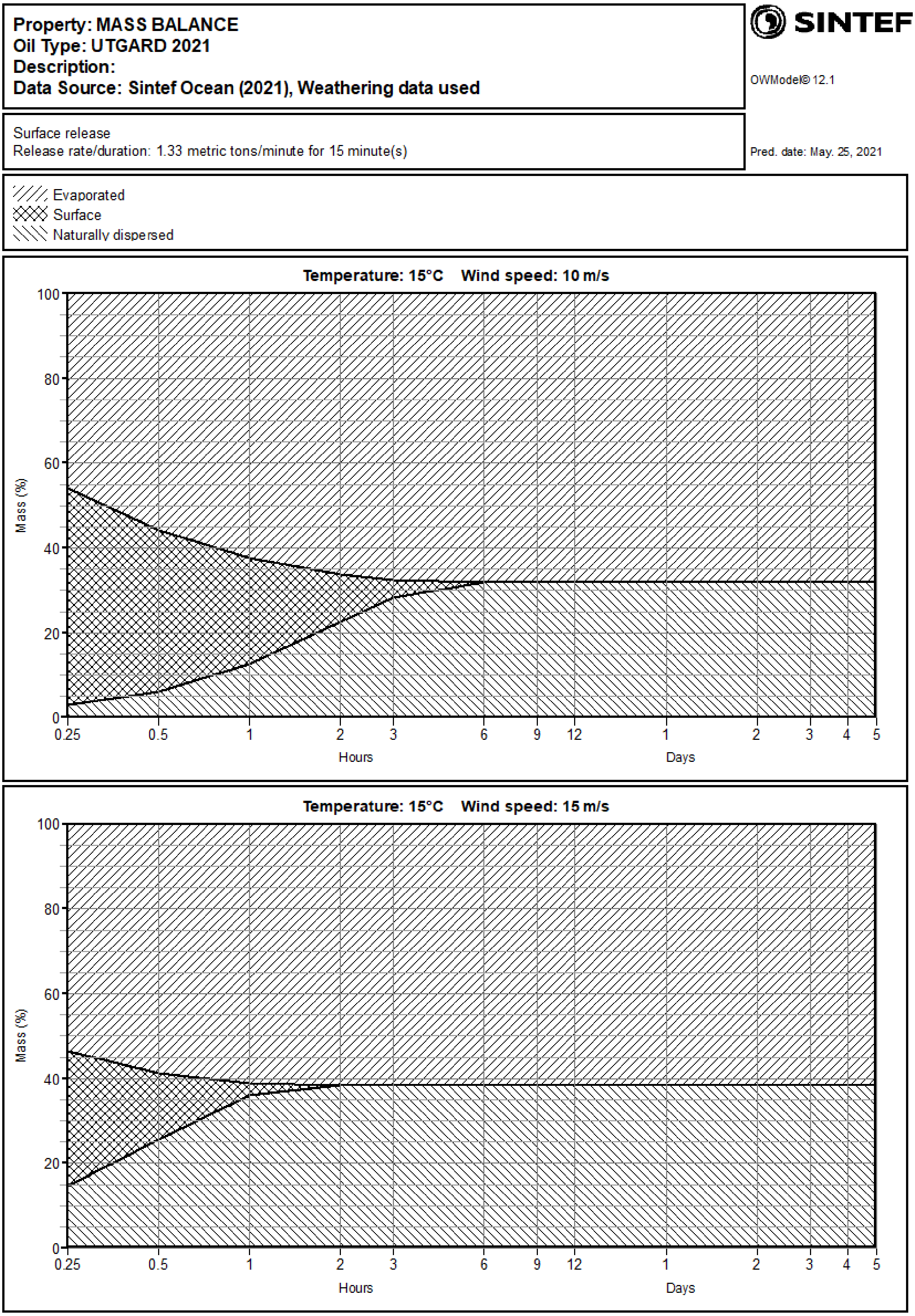


Figure 4-9 Predicted mass balance of Utgard predicted 15 °C, wind speeds of 10 and 15 m/s.

5 Comparison of OWM predictions

Weathering predictions from surface release of Utgard were compared with predictions of Gudrun, Sigyn and Sleipner. The predictions are based on sea temperature of 15 °C and wind speed of 5 m/s.

5.1 Evaporative loss

Evaporation is one of the natural process that helps removing spilled oil from the sea surface. Utgard, Sigyn and Sleipner have significantly higher evaporative loss compared with Gudrun (Figure 5-1). Utgard and Sigyn are most similar compared with the oils. The evaporative loss reflects the characteristics of the oils where condensates normally exhibit higher evaporative loss and have lower densities compared with crude oils.

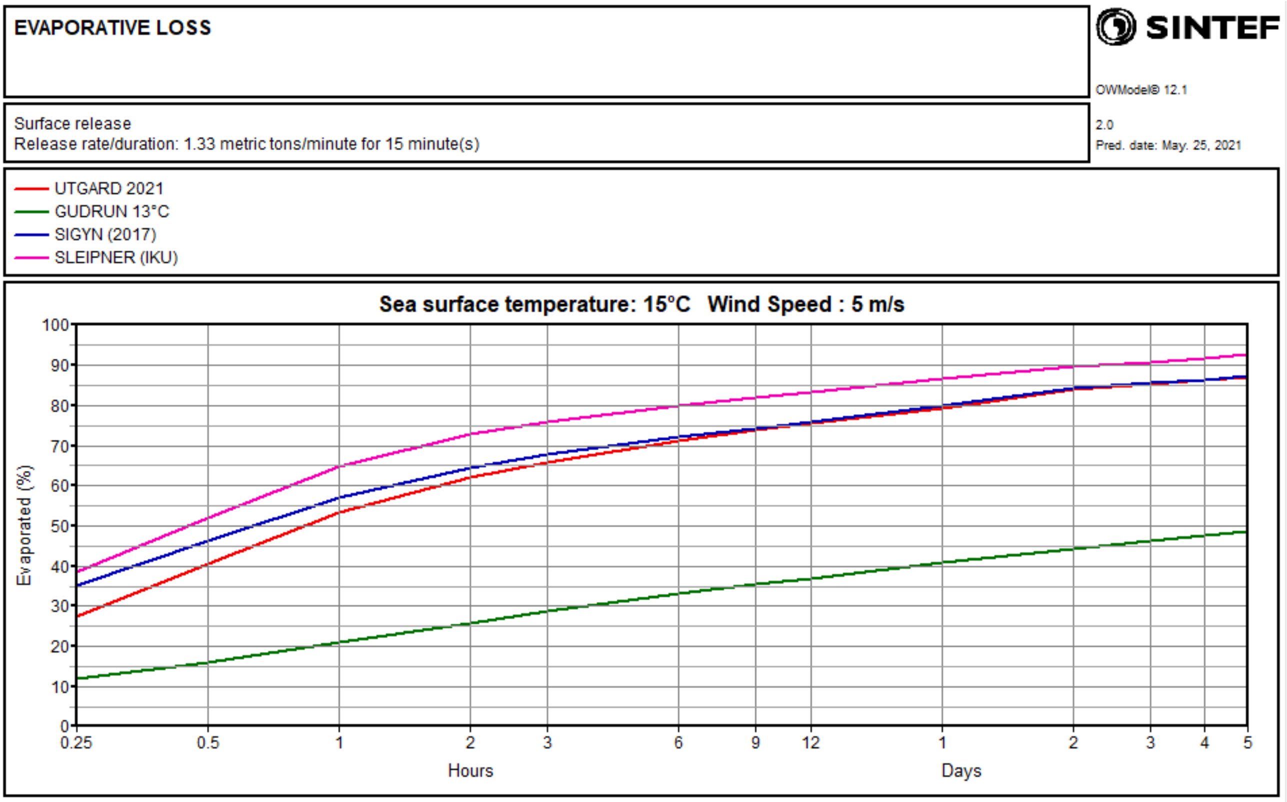


Figure 5-1 Predicted evaporative loss at 15 °C and 5 m/s for Utgard compared with other oils.

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 is high if the flash point of the oil is below the seawater 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 the oils in comparison are shown in Figure 5-2. The initial Flash points of the condensates Utgard, Sigyn and Sleipner are below the seawater temperate the first 0.5-1 hour, whilst Gudrun has surpassed the flash point seawater temperature within 15 minutes. Utgard and Sigyn reach the highest flashpoints among these oils.

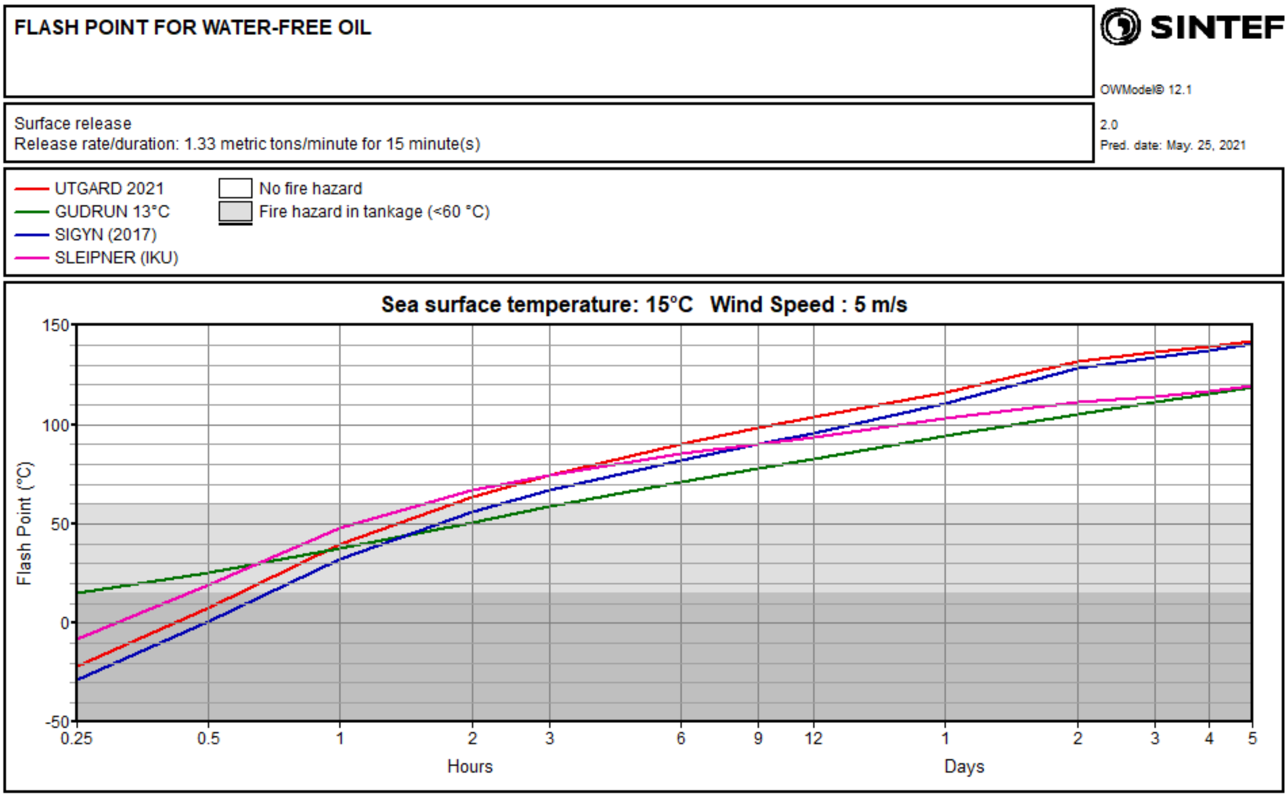


Figure 5-2 Predicted flash point at 15 °C and 5 m/s for Utgard compared with other oils.

5.3 Pour point

The pour points of Utgard and the other oils in comparison are given in Figure 5-3. Sigyn has the highest point, followed by Utgard and Gudrun. Sleipner has very low pour points. Utgard and Sigyn may have a potential to solidify on the sea surface by time if spilled at sea.

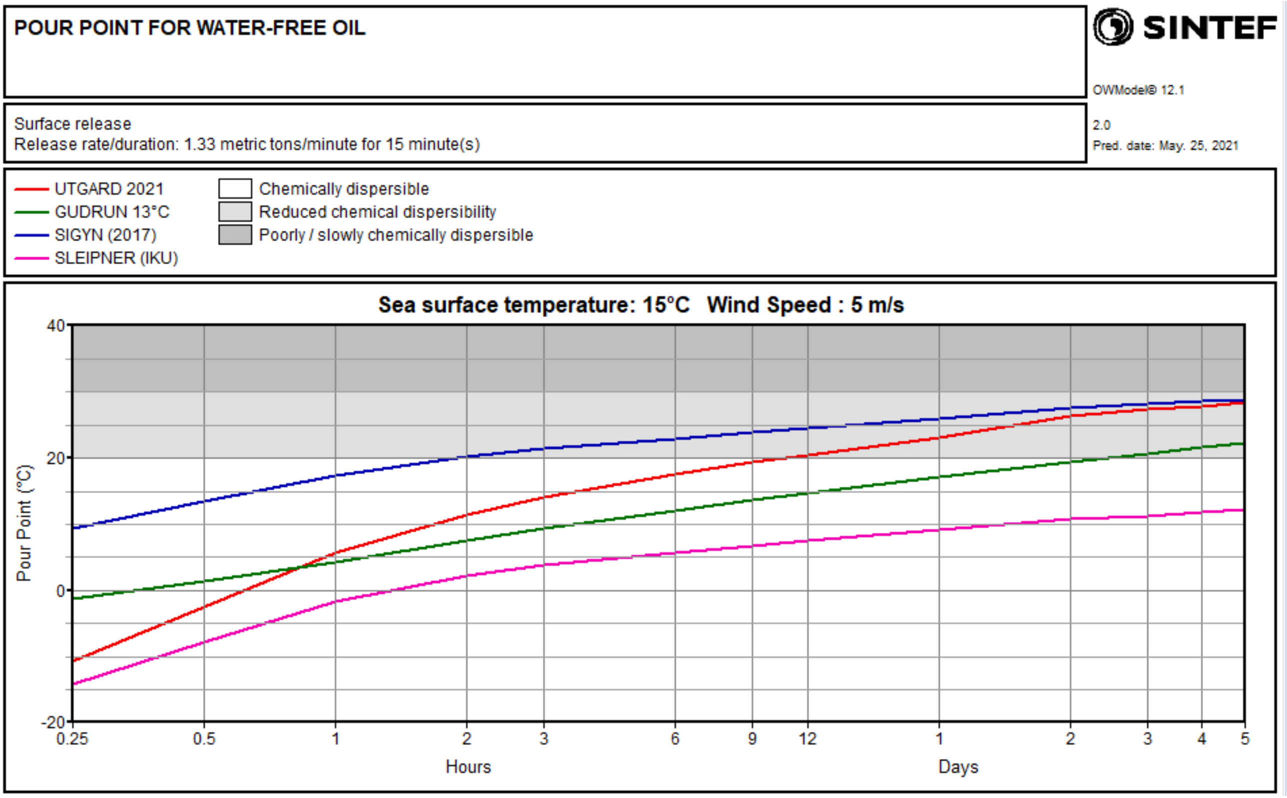


Figure 5-3 Predicted pour point at 15 °C and 5 m/s for Utgard compared with other oils.

5.4 Viscosity

Figure 5-4 shows the predicted (emulsion) viscosities of the oils in comparison. Utgard and Sigyn have the most similar low viscosities in the range of 10-200 mPa.s. Sleipner has very low viscosities < 10 mPa.s. Gudrun has high viscosities where the viscosities are predicted to increase gradually throughout 5 days of weathering up to 10.000 mPa.s. In general, crude oils exhibit significantly higher viscosities than the condensates.

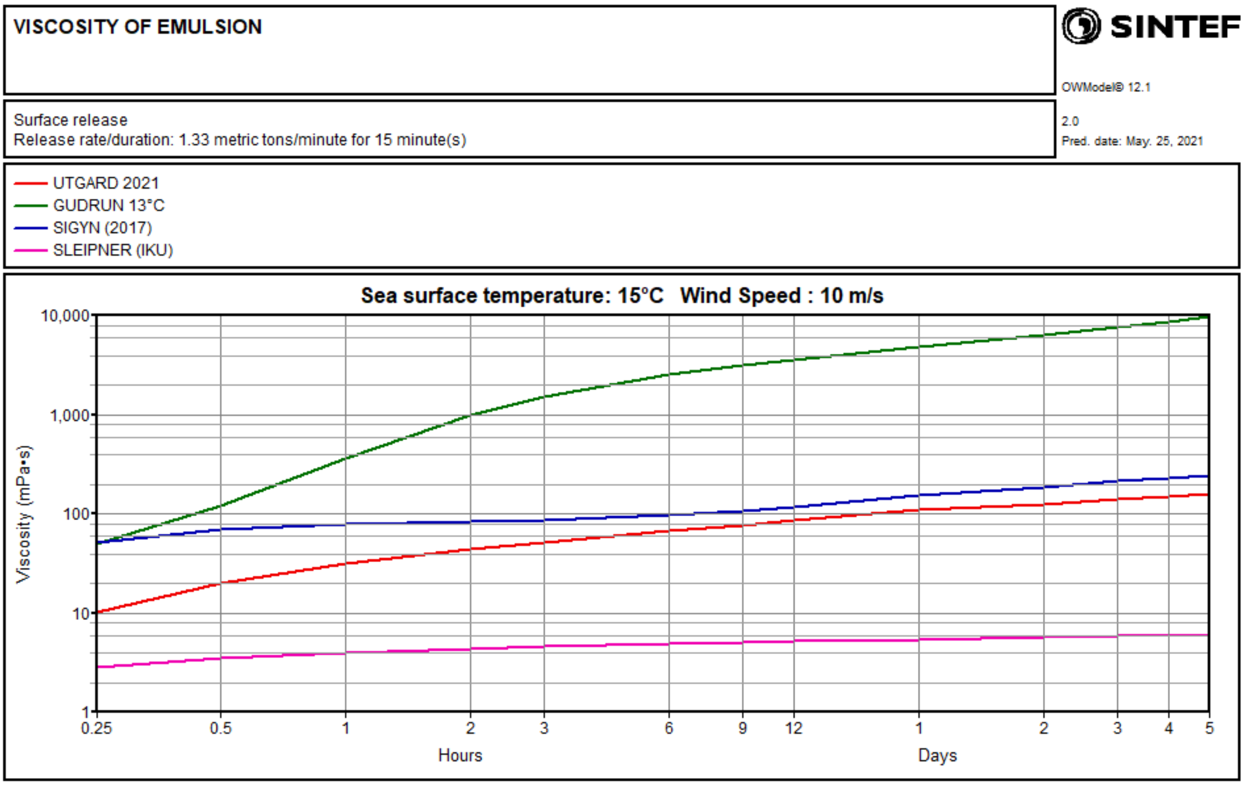


Figure 5-4 Predicted (emulsion) viscosity at 15 °C and 5 m/s for Utgard compared with other oils.

5.5 Surface oil emulsion

The predicted surface oil emulsion is based on the evaporative loss, natural dispersion/entrainment, and emulsification. Figure 5-5 shows the predicted mass balance of remaining surface emulsion as a function of weathering. Utgard, Sigyn and Sleipner condensates are predicted to be removed from the sea surface due to evaporation and natural dispersion within 2-6 hours, whilst Gudrun is more persistent on the sea surface with longer predicted lifetime >5 days. Gudrun has also a significant water uptake and the oil volume can therefore increase subsequently compared with the condensates.

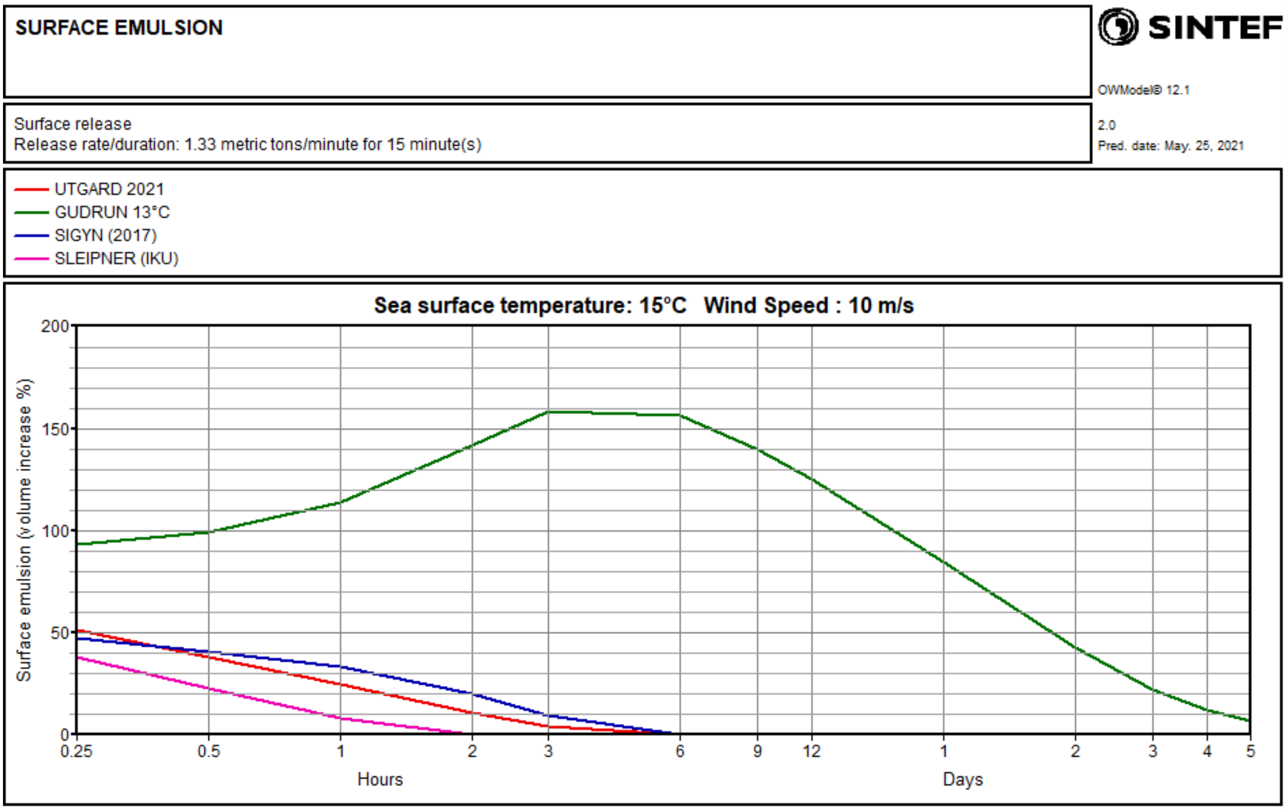


Figure 5-5 *Predicted remaining surface oil at 15 °C and 5 m/s for Utgard compared with other oils.*

6 Weathering properties and response of Utgard from a surface release

The relative content of heavy oil components within a spilled oil increases due to evaporation , 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 (artificial energy) to disperse thin oil films and low viscous oils is also discussed in this report.

6.1 Oil properties

The specific physico-chemical parameters of Utgard are input to SINTEF OWM. The physico-chemical analysis of the fresh and topped residues show that Utgard is a paraffinic condensate with a density of 0.772 g/mL with a low content of asphaltenes (0.02 wt. %) and a low wax content of 0.89 wt. %. Utgard has a high evaporate loss of 80 vol. % of the 250°C+ residue. The fresh oil has a viscosity of 1 mPa.s at shear rate $10s^{-1}$ (13 °C) and increases by evaporation to 269 mPa.s ($10s^{-1}$) for the waterfree 250°C+ residue. The fresh oil has a low pour point of -27 °C, that increases significantly from +6 to + 21 °C upon evaporation (150 to 250 °C+). Moreover, Utgard lacks the ability to form stable water-in-oil emulsions but may form very loose low-viscous emulsions that easily break upon stand still within short time (< 1 hour).

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 potential for 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 Utgard are 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- and Figure 6-1. In calmer weather conditions (2 and 5 m/s), care should be taken during the first 1-2 hours and use of explosimeter is recommended. However, the release rate may influence on the rate of evaporation, and for considerably larger (batch) release rates e.g.100 times higher (8000 m^3/h), the rate of evaporative loss is thus reduced particularly for the first hours after the release. Such high batch release can be e.g. an incident scenario in connection to loading on vessels. For Utgard, the time when the flash point has surpassed the sea temperature has now increased to 2-3.5 hours at 2 and 5 m/wind speed (Figure 6-2).

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). Refers to the flash point predictions in Figure 4-4 and Figure 6-1.

As a general recommendation after an acute oil spill involving free gas (e.g. from a subsea release), a "safety" zone typically 1-2 km from the source should be established early on and downwind from the spill site before response actions are initiated in open seawaters. Less than 1-hour delay time can be predicted related to fire/explosion hazard related to the flash point of the drifting oil itself. 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.

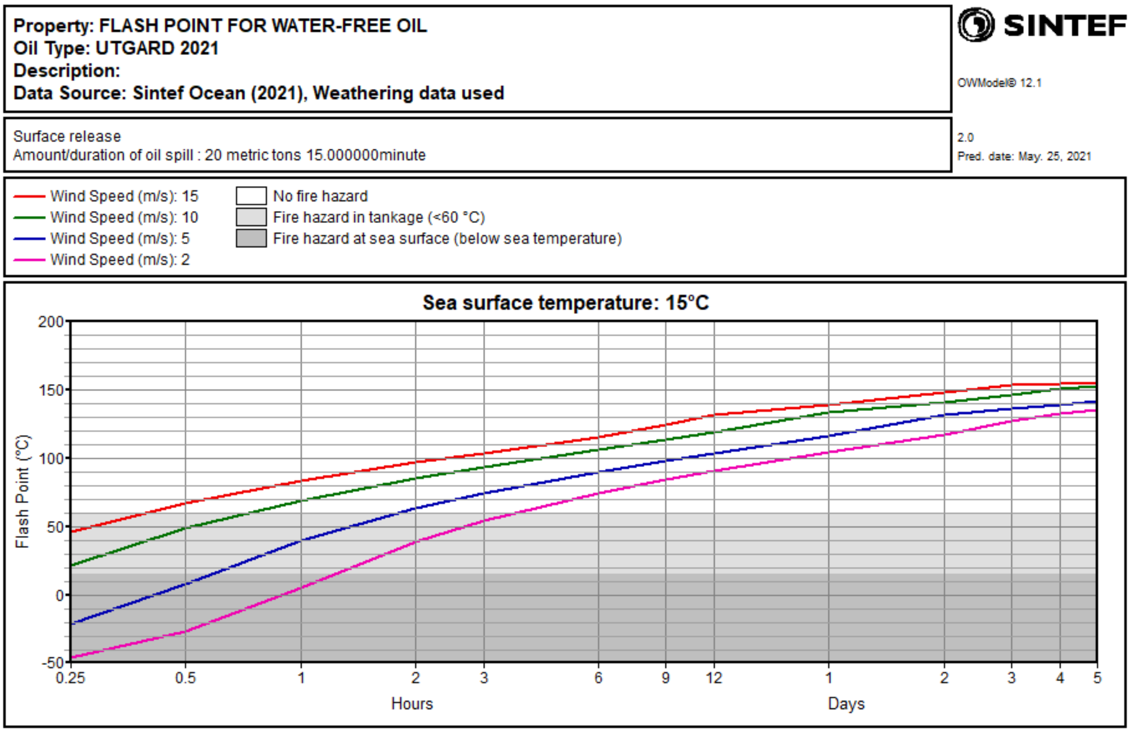


Figure 6-1 Predicted flash points for Utgard at 15 °C (80 m³/ h)

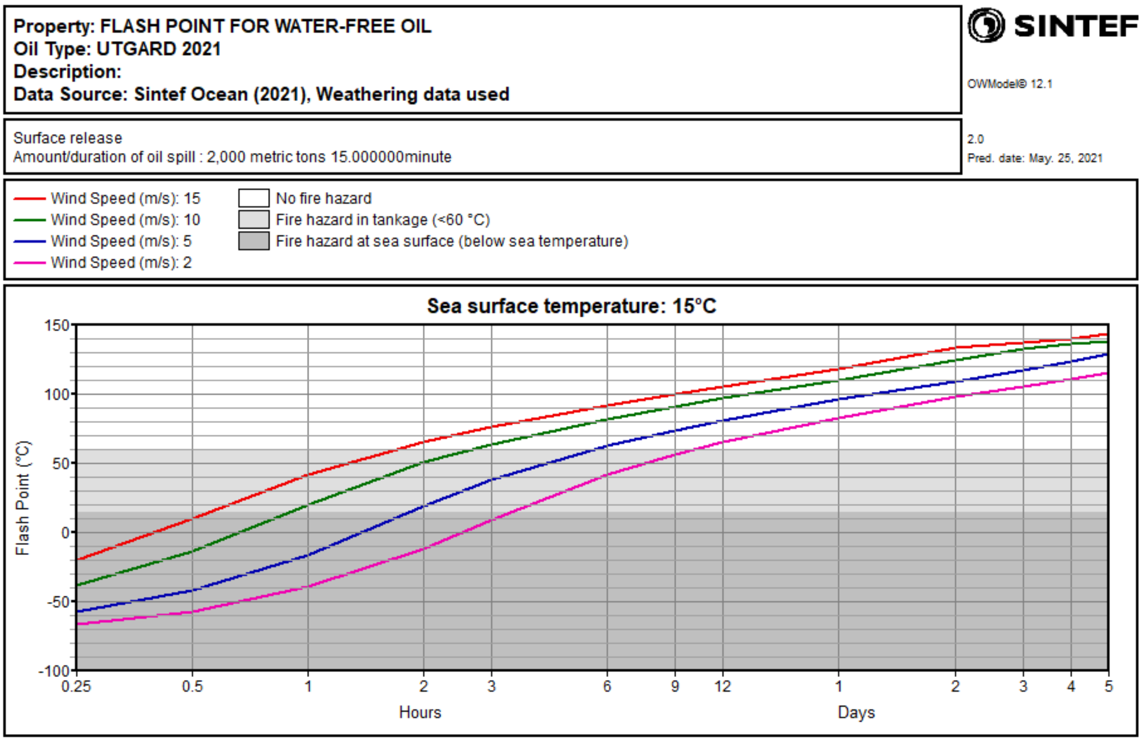


Figure 6-2 Predicted flash points for Utgard at 15 °C (8000 m³/ h)

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, contents of asphaltenes prevent or reduce 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 also reduce the potential for flowability towards weir skimmers. In cases when high viscosities are not a limiting factor, high pour points may cause solidification (elastic properties) of semi-solid patches 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 and in cold temperatures.

If the oil is mixed with the seawater by waves, the wax lattice in the oil will likely be weakened and may break up. This is accordance with the emulsifying properties of the condensate from the laboratory experiments. Utgard has high pour points of its residues, and a remaining residue at sea may have a potential to solidify, particularly in winter condition as shown for the pour point prediction in Figure 4-5.

6.4 Submerged oil 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). Submerged oil (natural dispersion) and evaporation are the main weathering processes that remove an oil spill from the sea surface. The remaining surface oil after a release is dependent on the wind speeds and typically oils are more persistent on the sea surface with lower wind.

Figure 6-3 shows the predicted remaining surface oil over time for different wind speeds and temperatures for Utgard. Only minor difference in lifetime between 5 and 15 °C for this condensate. At high wind speeds of 10-15 m/s, no oil remains on the sea surface after 6 hours of weathering at 10 m/s, and similar 2 hours at 15 m/s wind speed.

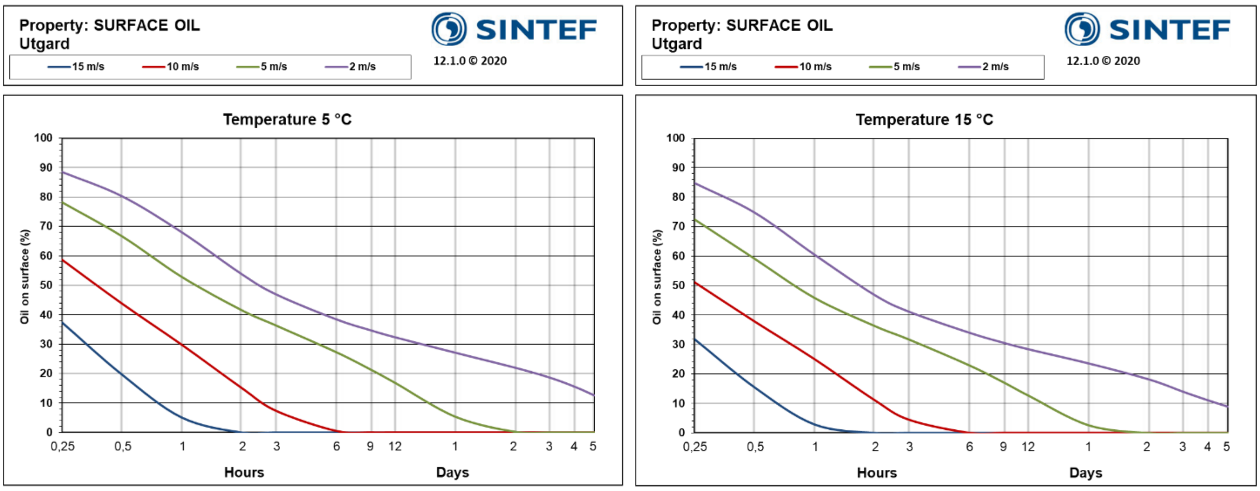


Figure 6-3 Predicted remaining surface oil for Utgard at 5 and 15 °C.

6.5 Film thickness from surface release

In general, 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. Lower film thicknesses are likely to disperse naturally under breaking waves conditions and can be enhanced in non-breaking waves by mechanical dispersion (chapter 6.8). However, other factors than film thickness should be considered when evaluate response options, as described in the next chapters. Figure 6-4 shows the predicted film thickness of Utgard for a surface release.

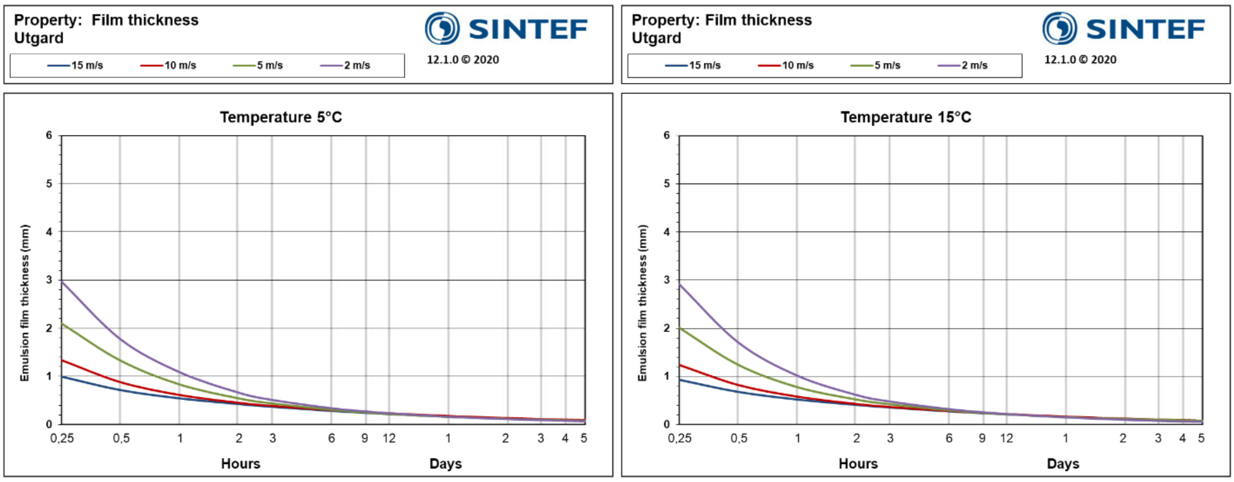


Figure 6-4 Predicted film thickness of Utgard from a surface (batch) release at 5 and 15 °C.

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. Boom leakage is particularly pronounced if the viscosity of the oil or the w/o-emulsion is lower than 1000 mPa.s (Nordvik et al., 1992). The lower viscosity limit for an optimal mechanical clean-up operation has therefore been estimated to 1000 mPa.s. However, other factors like the operational speed of recovery vessel and current weather conditions will also influence on the risk of boom leakage. Weir skimmers may reduce recovery rates (m^3/h) when skimming oils with viscosities in the range 15-20 000 mPa.s (Leirvik et al., 2001). NOFO is operating with viscosity limits for skimmer efficiency as followed: primary use of weir skimmers (< 20 000 mPa.s), combination of weir and high-visc. skimmer (20-50 000 mPa.s), and primary high visc. skimmer (> 50 000 mPa.s).

For Utgard, the emulsion viscosities of are very low, and the risk for boom leakage is highly present during several days at sea, and should be considered in a recovery operation e.g. reducing the towing speed (Figure 6-5).

The predicted mass balance of Utgard indicates that the condensate has short lifetime at sea particularly.
in high wind speeds, with a high degree of evaporative loss and natural dispersion. In calm weather conditions, mechanical recovery may have a potential close to release point assuming film thicknesses >0.1-0.2 mm. However, the remaining oil/residue on the sea surface has low viscosities <200 mPa.s (negligible emulsification). Utgard is therefore assumed to have limited efficiency and low efficacy for containment for mechanical recovery due to considerable boom leakage with a limit of 1000 mPa.s.

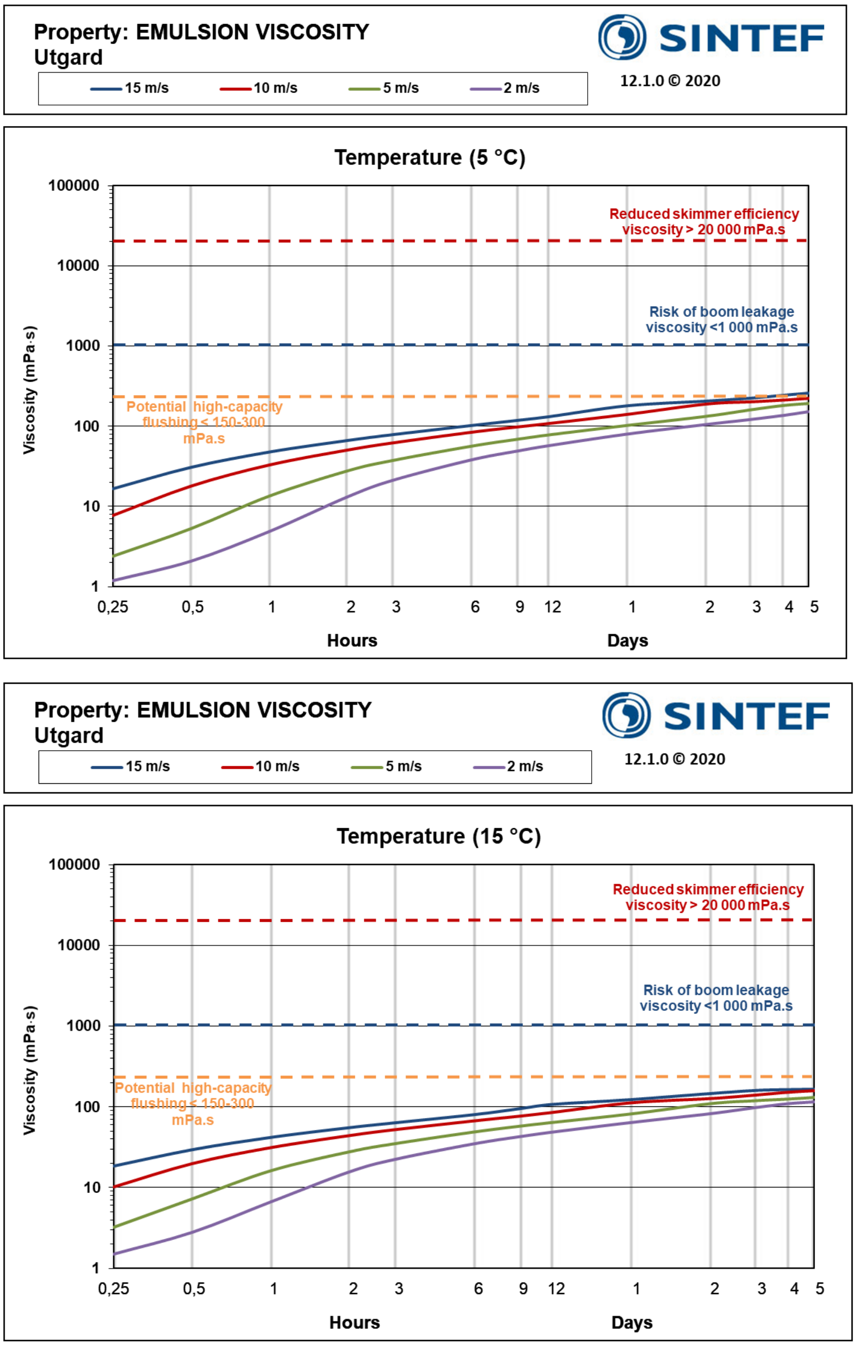


Figure 6-5 Expected time window for effective use of booms and skimmers and high-capacity water flushing (see chapter 6.8) as a function of emulsion viscosity of Utgard at 5 and 15 ºC.

6.7 Mechanical dispersion by high-capacity water flushing

In general, mechanical dispersion by high-capacity water flushing without using dispersants 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 some minutes after the dispersant treatment. 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 (NOFO), today.

For Utgard, mechanical dispersion by high-capacity water flushing can be considered as a possible strategy in calm weather conditions from a surface release due to low emulsion viscosities (< 150-300 mPa.s) even up to some days at sea (Figure 6-5). However, the oil film thickness in the early stage from a surface release can be > 0.2-0.3 mm (Figure 6-4) that may limit the efficiency of mechanical dispersion. In such cases a combined response strategy with use of chemical dispersant application followed by water-flushing could be beneficial particularly in non-breaking waves (<2-5 m/s wind speed).

6.8 Chemical dispersion

Dispersibility testing on Utgard was not conducted in agreement with Equinor. High degree of natural dispersion and evaporative loss indicate that the lifetime at sea is short for Utgard, 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). In a spill operation (batch release) the use of dispersants may have a potential assuming that the thickness is higher than 0.1 mm to enhance natural dispersion. However, it is expected low efficiency potential for low film thicknesses, as the dispersant droplets may fall through the oil phase into the seawater. In addition, applying dispersants assuming a very thin oil film < 0.05-0.1 mm is not normally recommended due to high degree of herding.

7 Subsea release (blowout)

Earlier studies simulating spill from subsea releases have shown formation of initial thin oil films at sea (< 0.1 mm) due to the horizonal spreading of gas /oil plume and the oil will be rapidly initially spread out on the sea surface. This phenomenon is however highly dependent on the release conditions, e.g. GOR (gas-oil ratio), release rate, water depth etc.

In this study, the OWM Subsea module was used to predict the oil film thicknesses and weathering properties and behaviour after a subsea release of Utgard at 5 and 15 °C, assuming that the momentum and buoyancy of the released plume of oil and gas is sufficient to reach the surface, where the plume will spread the oil out over the sea surface. Alternatively, the oil and gas plume will be trapped in the water column and only the oil droplets will rise to the surface through their own buoyancy alone. Simulation with use of the 3-D plume model (OSCAR) were not included in this study.

The input parameter for OWM predictions of Utgard from a subsea release is given in Table 7-1, in addition to the experimental weathering data of Utgard.

Table 7-1 Input parameters used for OWM predictions of Utgard from a subsea release.

Parameter	**Value**
Seawater temperature (°C)	5 and 15
Wind speed (m/s)	2, 5, 10 and 15
Gas to Oil ratio (GOR) (Sm^3/Sm^3)	2940
Release oil flowrate (m^3/day)	1165
Duration of release (days)	115
Water depth (m)	115

7.1 Film thickness and mass-balance of surfaced oil

The predicted initial film thicknesses of the surfaced oil were about 5-10 micron, i.e. rainbow or metallic appearance, and too thin for emulsion formation. In a release situation, the oil film on the sea surface will be subjected to oceanic processes and may form films with varying thicknesses due to wind and wave movement. It is expected that possible formation of windrows or fragmentation of the film will have thickness lower than 50-100 µm.

The mass-balance predictions of surfaced oil (Figure 7-1 to Figure 7-4) show that in breaking waves conditions (10-15 m/s), the very thin film has been evaporated or dispersed into the water column short time after the oil-gas plume has reached the surface. In non-breaking waves (2-5 m/s) remaining oil is predicted on the sea surface within 1-2 day at 2 m/s, and 1-2 hours at 5 m/s at and 2 hours at 5 m/s and 3-4 days at 2 m/s, at 5 and 15 °C.

7.2 Response options from subsea release

The general criteria for evaluation of possible response options from a subsea release are given in Table 7-2 (Singsaas et al. 2017). Here, only the film thickness is used for evaluation, as the rheological properties (viscosity/pour point) are not assumed relevant for metallic thicknesses <50 µm.

Table 7-2 General criteria for evaluation response from a subsea release based on film thickness.

	Mechanical recovery	Chemical dispersion	Water flushing
Not applicable	Film thickness < 0.1 mm	Film thickness < 0.05 mm	Film thickness > 0.2 mm
Feasible	Film thickness = 0.1-0.2 mm	Film thickness = 0.05-0.1 mm	-
Applicable	Film thickness > 0.2 mm	Film thickness > 0.1 mm	Film thickness < 0.2 mm

General, a safety zone of 1-hour downwind from the spill site should be considered before any response action, and a separate model prediction of the atmospheric dilution of the gas plume could be considered with respect to explosion hazard for the specific scenario. Explosimeters should be utilized to measure concentrations of free gas to minimize the risk for fire and explosion hazard at the spill site.

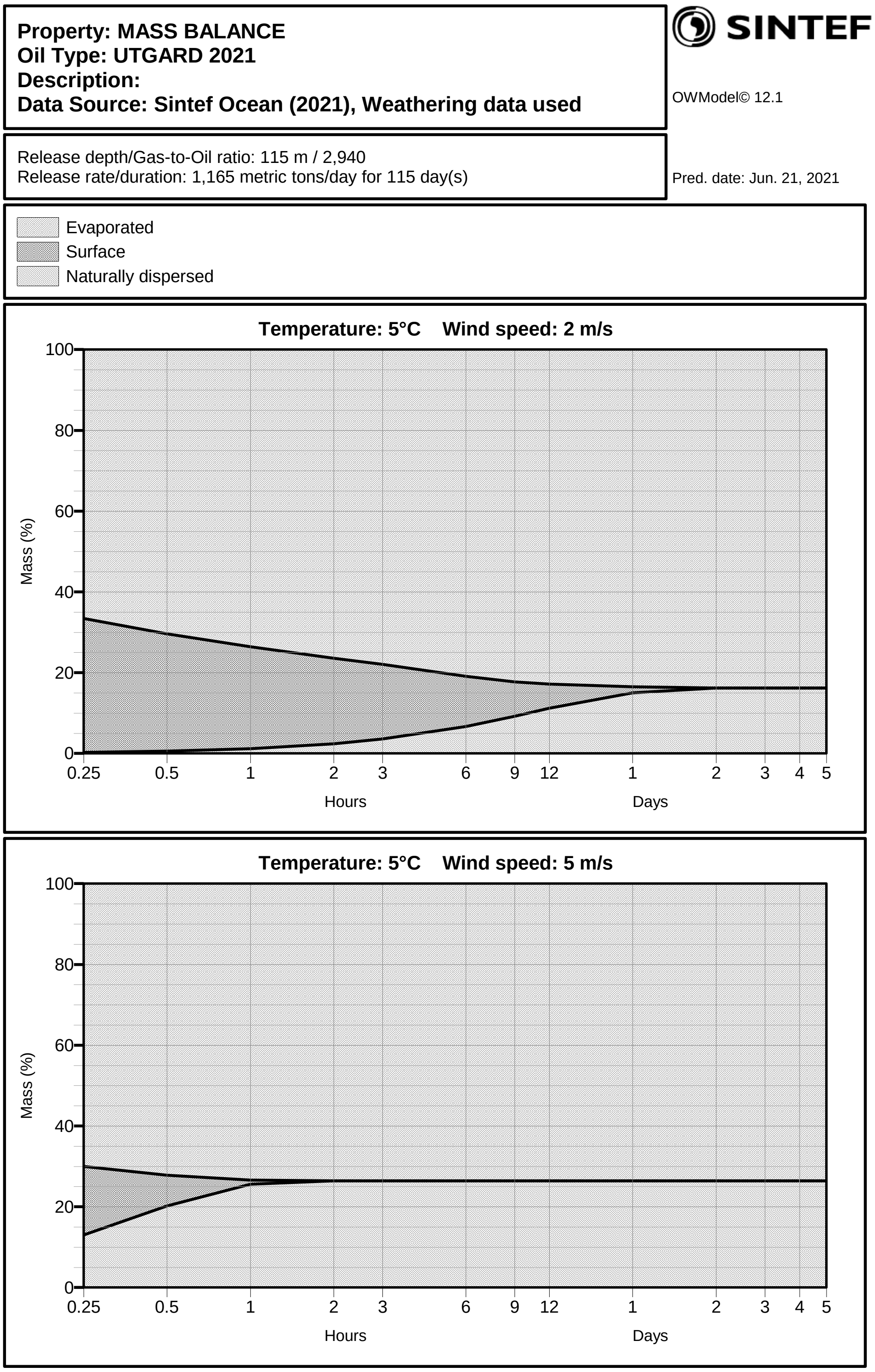
Monitoring and remote sensing:
In case of an oil spill, remote sensing and monitoring should be used as support in any response operation.

Mechanical recovery:
For mechanical recovery to be efficient, the oil film or emulsion thickness should generally be thicker than 0.1-0.2 mm. Mechanical recovery is not assumed applicable for the given subsea scenario for Utgard.

Use chemical dispersants:
Application of chemical dispersants requires oil film thickness >50-100 µm to prevent the dispersant droplets from penetrating the oil film and being diluted in the water beneath. The predicted film thicknesses of the subsea release of Utgard are well below this limit in the presented scenario, and chemical dispersion is not recommended. It is expected that possible formation of windrows will have thickness lower than 50-100 µm.

Mechanical dispersion with high-capacity water flushing:
High-capacity water flushing e.g. from Fi-Fi monitor is suitable for oil films with thicknesses <0.2 mm. The predicted film thicknesses for Utgard are well below this limits and water flushing is therefore applicable for this scenario. The decision for initiating mechanical dispersion is relevant in spill situations with calm sea conditions (non-breaking waves < 2-5 m/s wind speed) to enhance the naturally dispersion in an early phase. Water flushing will not be efficient on solidified flakes with high pour points.

7.3 Predictions from subsea release



Property: MASS BALANCE
Oil Type: UTGARD 2021
Description:
Data Source: Sintef Ocean (2021), Weathering data used

OWModel© 12.1

Release depth/Gas-to-Oil ratio: 115 m / 2,940
Release rate/duration: 1,165 metric tons/day for 115 day(s)

Pred. date: Jun. 21, 2021

Figure 7-1 Mass balance of Utgard from a subsea release at 5 °C and wind speeds of 2 and 5 m/s

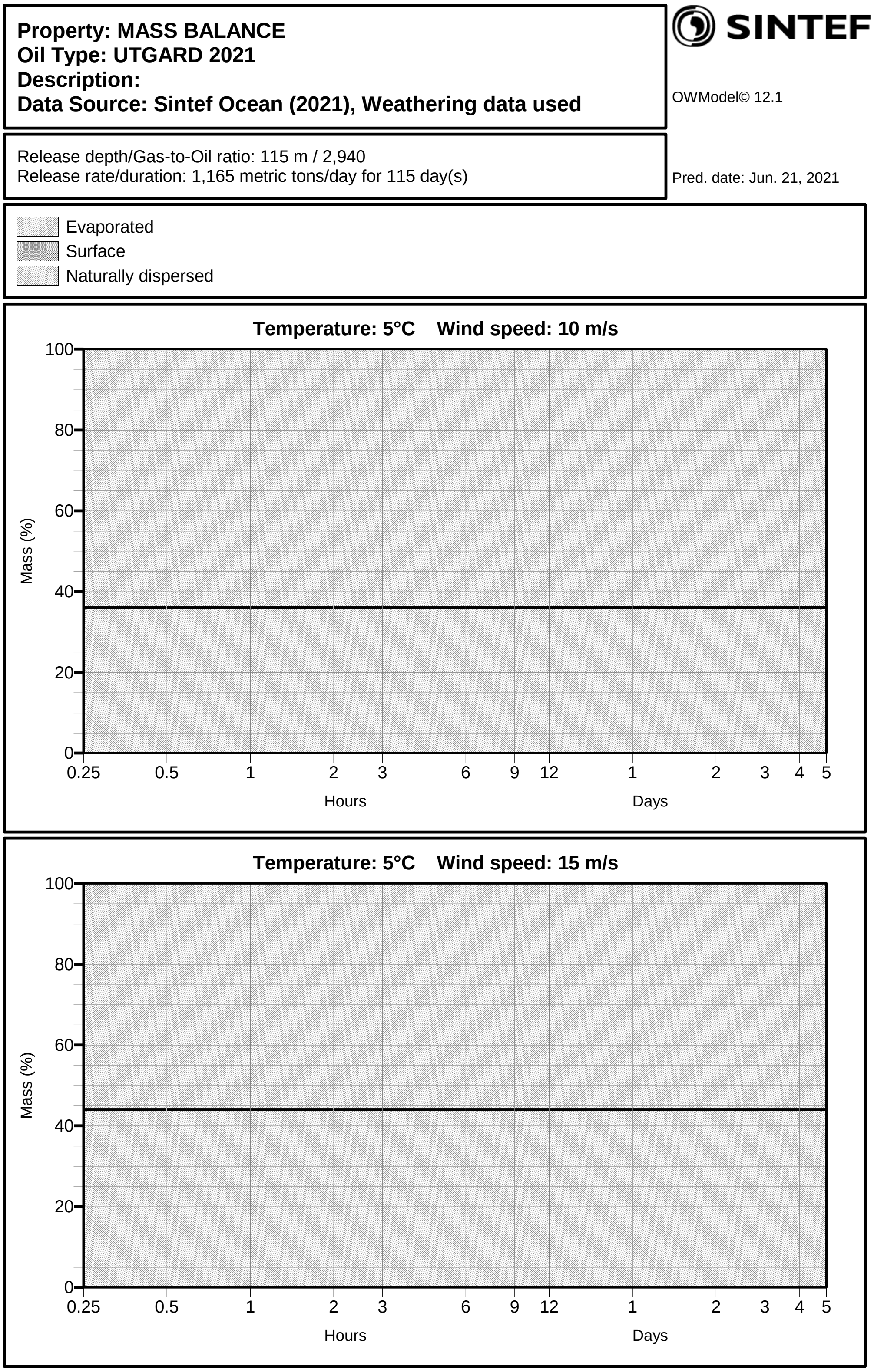


Figure 7-2 Mass balance of Utgard from a subsea release at 5 °C and wind speeds of 2 and 5 m/s

Property: MASS BALANCE
Oil Type: UTGARD 2021
Description:
Data Source: Sintef Ocean (2021), Weathering data used

SINTEF
OWModel© 12.1

Release depth/Gas-to-Oil ratio: 115 m / 2,940
Release rate/duration: 1,165 metric tons/day for 115 day(s)

Pred. date: Jun. 21, 2021

▨ Evaporated
▨ Surface
▨ Naturally dispersed

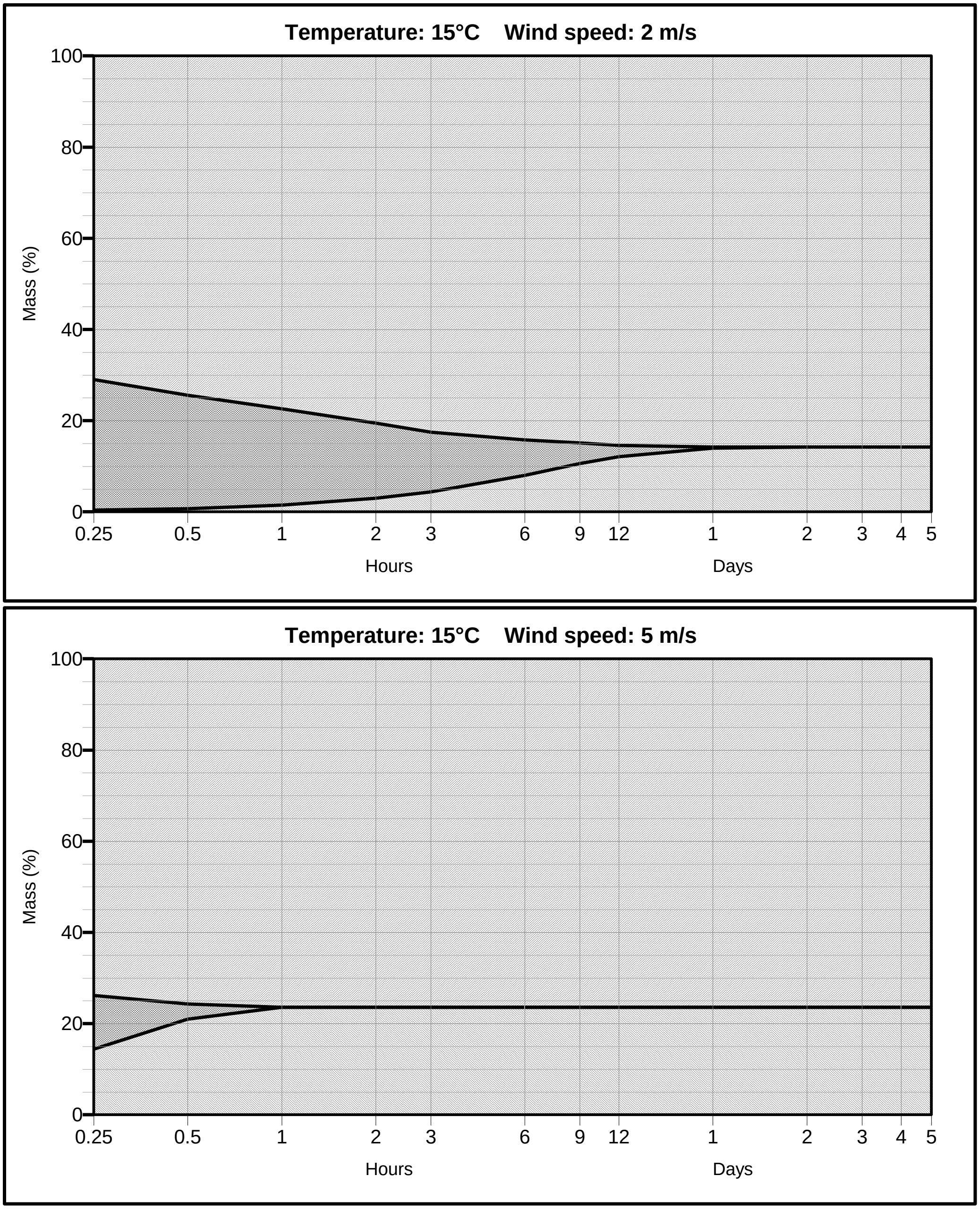
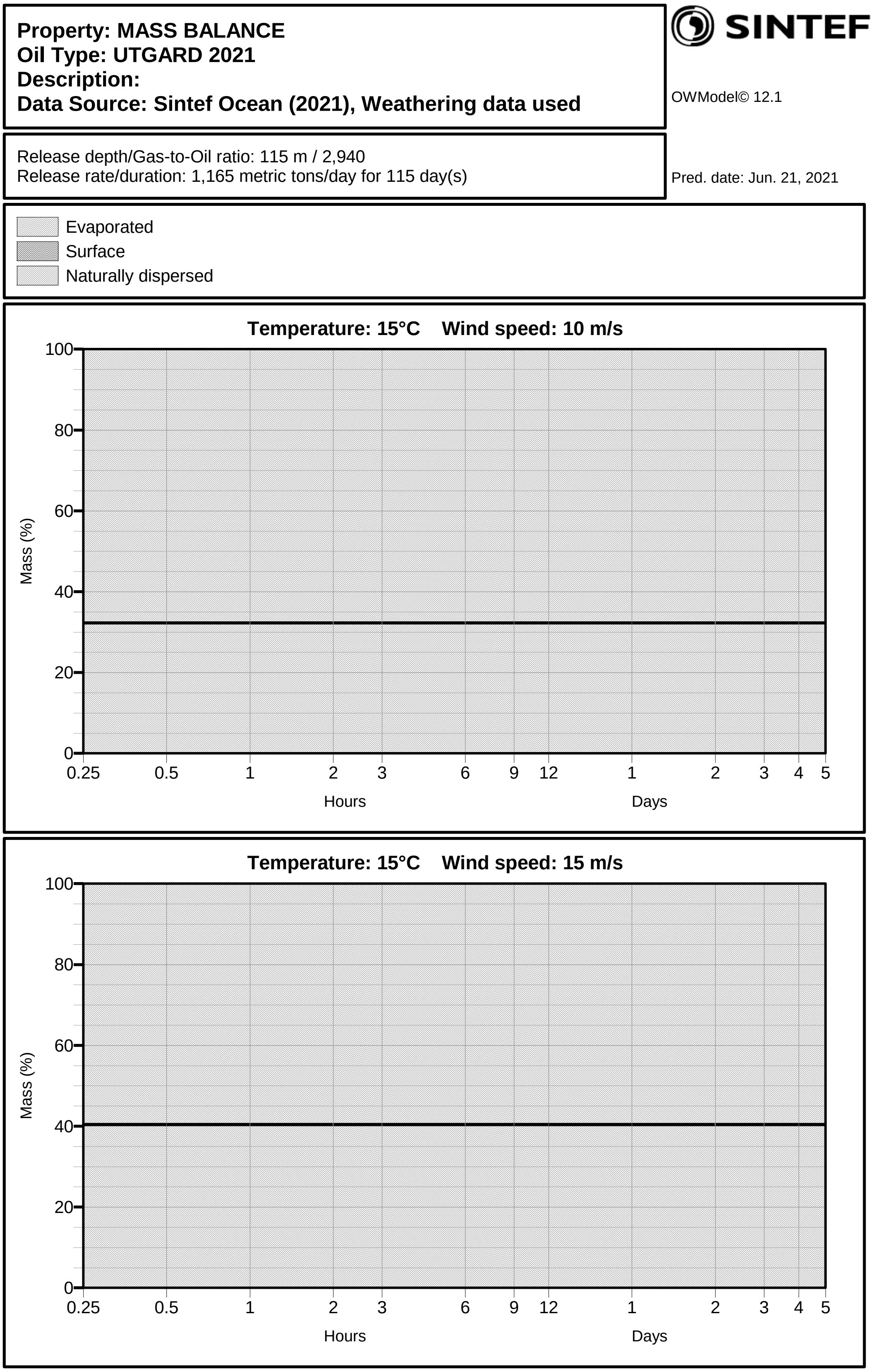
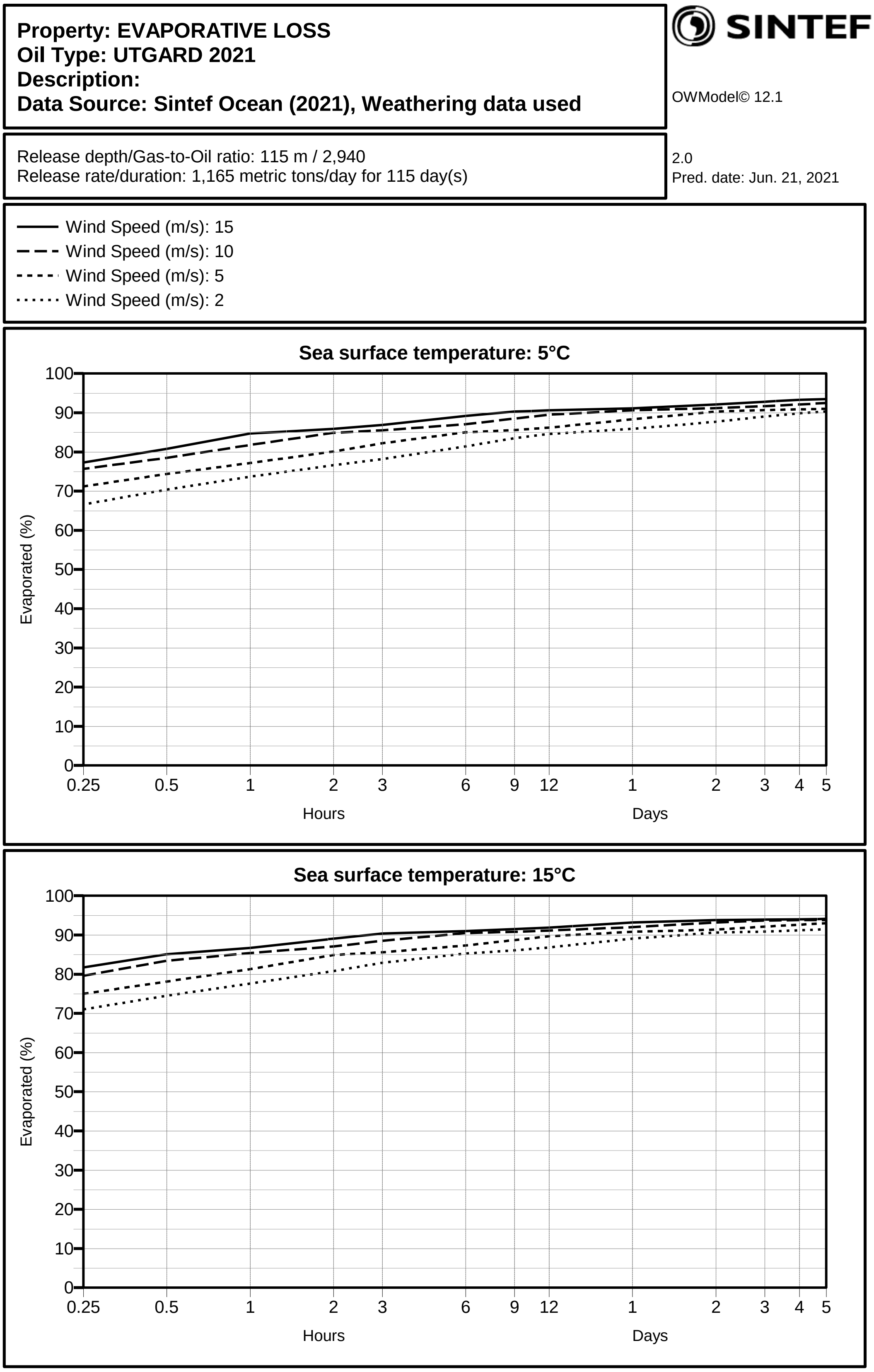


Figure 7-3 Mass balance of Utgard from a subsea release at 15 °C and wind speeds of 2 and 5 m/s



7-4 Mass balance of Utgard from a subsea release at 5 °C and wind speeds of 2 and 5 m/s



Property: EVAPORATIVE LOSS
Oil Type: UTGARD 2021
Description:
Data Source: Sintef Ocean (2021), Weathering data used

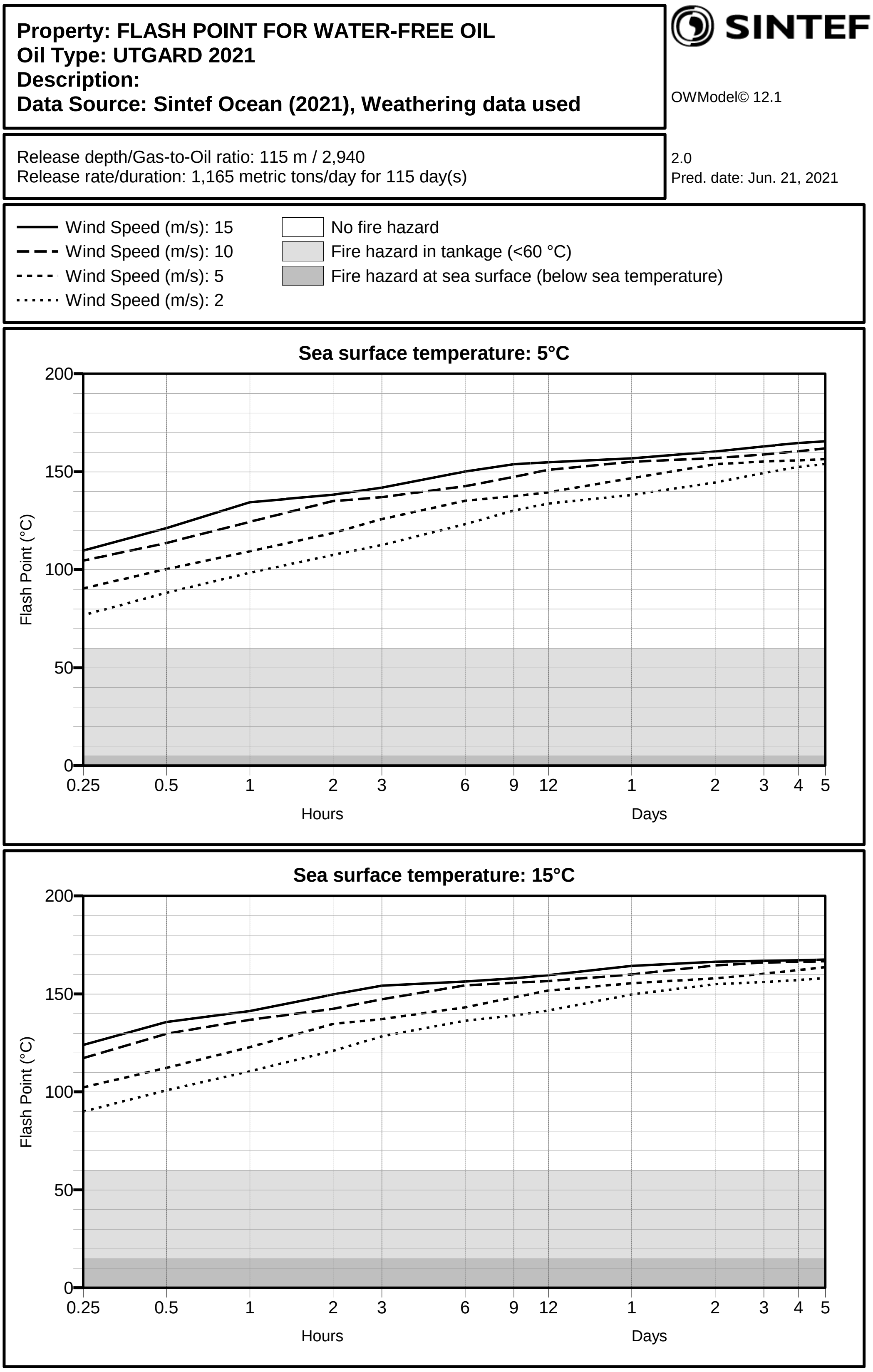
SINTEF

OWModel© 12.1

Release depth/Gas-to-Oil ratio: 115 m / 2,940
Release rate/duration: 1,165 metric tons/day for 115 day(s)

2.0
Pred. date: Jun. 21, 2021

7-5 Evaporative loss of Utgard from a subsea release at sea temperatures of 5 and 15 °C



Property: FLASH POINT FOR WATER-FREE OIL
Oil Type: UTGARD 2021
Description:
Data Source: Sintef Ocean (2021), Weathering data used

OWModel© 12.1

Release depth/Gas-to-Oil ratio: 115 m / 2,940
Release rate/duration: 1,165 metric tons/day for 115 day(s)

2.0
Pred. date: Jun. 21, 2021

7-6 Flash point of Utgard from a subsea release at sea temperatures of 5 and 15 °C

8 Summary of response options

Surface release

For a surface release of Utgard with oil film thickness > 0.1 mm, this condensate has a potential to form (loose) emulsions if spilled at sea with low emulsion viscosities. The high pour point of the waterfree residue may cause solidification at sea, particularly in low temperature.

Mechanical recovery:

- The low emulsion viscosity (< 1000 mPa.s) may reduce the efficacy of mechanical response due to risk of boom leakage.
- Risk of boom leakage and reduced recovery are expected for Utgard, that should be considered during mechanical recovery operations.

Use of chemical dispersants*:*

- Use of dispersants were not tested for Utgard in the laboratory. It is assuming a high degree of natural dispersion in breaking waves (>5 m/s wind speeds), but use of dispersant could be used in combination with water-flushing in an early stage after a release if the film thickness is > 0.05-0.1 mm.

High-capacity water flushing (mechanical dispersion):

- Water flushing may be a strategy for thin oil film < 0.2-0.3 mm, but could be used in combination with dispersant application in an early phase after a release if the film thickness is >0.2-0.3 mm.

Monitoring and remote sensing:

- Monitoring and remote sensing should be used a support in a response operations for Utgard.

Subsea release

For the specified subsea release of Utgard the predicted initial film thickness (5-10 micron) is to too low for emulsification and neither mechanical recovery nor dispersant application are therefore not considered to be an efficient response option. However, high-capacity water flushing can be suitable in spill situations with calm sea conditions (non-breaking waves < 2-5 m/s wind speed) to enhance the naturally dispersion in an early phase.

9 References

Brakstad, O.G., and Faksness, L.-G., (2000). Biodegradation of water-accommodated fractions and dispersed oil in the seawater column. Proceedings for the International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, Stavanger, 26-28 June 2000

Brakstad, O-G and A.G.G Lødeng 2005. Microbial diversity during micro biodegradation of crude oil in seawater from the North Sea. Microbial Ecology 49:94-104

Brandvik, P.J., Hellstøm, K.C., Sørheim, K.R. 2015. Modernisation and updating of SINTEF Oil Weathering Model (OWM) - Extending and recalibration of the Crude Assay (CA) module in SINTEF OWM. SINTEF report: OC2018 A-040.

Bridié, A.L., Wanders, T. H., Zegweld, W. V. and den Heijde, H. B., 1980. Formation, Prevention and Breaking of Seawater in Crude Oil Emulsions, Chocolate Mousse. Marine Poll. Bull., vol. 11, pp. 343-348. Commission Internationale De L'Eclairage (CIE), No. 85, ISBN No. 3 900 734 22 4, 1989.

Daling, P. S., Brandvik, P. J., Mackay, D. and Johansen, Ø. (1990): "Characterisation of crude oils for environmental purposes." Oil & Chemical Pollution 7, 1990, pp. 199-224.

Daling, P.S., Lewis, A., Sørheim, K.R., Gjesteland, I. 2017. Full-scale field testing of thin oil films from releases of light crude oil at sea. NOFO Oil-on-Water field trial in 2016. SINTEF report 2017:00030 Unrestricted. ISBN:978-82-21-40670-8.

Hellstrøm, K.C. 2018. Gudrun crude oil-Weathering properties and behaviour at sea. SINTEF report OC2019 A-59. ISBN: 9788271743567

Hokstad, J. N., Daling, P. S., Lewis, A. and Strøm-Kristiansen, T. 1993: "Methodology for testing water-in-oil emulsions and demulsifiers. Description of laboratory procedures." Proceedings Workshop on Formation and Breaking of W/O Emulsions. MSRC, Alberta June 14-15, 24 p.

Johansen, Ø. 1991. "Numerical modelling of physical properties of weathered North Sea crude oils." DIWO-report no. 15. IKU-report 02.0786.00/15/91. Open.

Leirvik, F., Moldestad, M. and Johansen, Ø., 2001. Kartlegging av voksrike råoljers tilflytsevne til skimmere

McAuliffe, C.D. (1987). Organism exposure to volatile/soluble hydrocarbons from crude oil spills - a field and laboratory comparison. In: Proc. 1987 Oil Spill Conference. Washington, D.C., American Petroleum Institute. pp. 555-566.

Mackay, D. and Zagorski, W. 1982. "Studies of W/o Emulsions". Report EE-34: Environment Canada, Ottawa, Ontario.

Mackay, D. and Szeto, F. 1980. "Effectiveness of oil spill dispersants - development of a laboratory method and results for selected commercial products." Institute of Environmental Studies, University of Toronto, Publ. no. EE-16.

McDonagh, M., Hokstad, J. N. and Nordvik, A. B. 1995. “Standard procedure for viscosity measurement of water-in-oil emulsions”. Marine Spill Response Corporation, Washington, D.C. MRSC Technical Report Series 95-030, 36 p.

Nordvik, A. B., Daling, P. and Engelhardt, F. R. 1992. "Problems in the interpretation of spill response technology studies." In: Proceedings of the 15th AMOP Technical Seminar, June 10-12, Edmonton, Alberta, Canada, pp. 211-217.

Perry JJ (1984). Microbial metabolism of cyclic alkanes: Atlas RM (Ed) Petroleum Microbiology Macmillan Publ Co New York pp 61-98

Ramstad S., Sørheim K.R., Daling, P.S. 2017. Thin Oil Films – Properties and behaviour at sea. Laboratory studies and oil weathering predictions. SINTEF report OC2017 A-207. ISBN: 978-82-7174-321-3

Reed M., and C. Turner, 1991: Field Tests of Satellite tracked buoys to simulate oil drift. In Proceeding of the IOSC, SanDiego, CA. US., pp. 619 – 628

Reed, M., Turner, C. and Odulo, A. 1994. "The role of wind and emulsification in modelling oil spill and surface drifter trajectories." Spill Science and Technology, Pergamon Press (2): .143-157.

Singsaas, I., Daling, P.S., Moldestad M. Ø and Jensen, H. 2000.Samle rapport: Effektivitet av Foxtail skimmer på IF-30 bunkersolje og forvitret Ula, Balder, Jotun og Troll råoljer. SINTEF report. STF66 A00082

Stiver, W. and Mackay. D. 1984. "Evaporation rate of spills of hydrocarbons and petroleum mixtures." Environ, Sci. Technol., vol. 18 (11), pp. 834-840.

Singsaas, I., Sørheim, K. R. and Daling, P.S., 2017. Project recommendations for response to oil spills from condensates and light crude oils. SINTEF report no.: OC2017A-205. ISBN: 9788271743208.

Sørheim, K.R., Daling, P.S., and F., Leirvik., 2017: "Mekanisk dispergering av tynne oljefilmer. Oljevern 2015". WP048. SINTEF rapport: OC2017 A-125, ISBN: 978-82-7174-300-0.

Øksenvåg J.H, Daling, P.S., Hellstrøm K.C, Bakken, O.M., Johnsen, M.2017. Sigyn condensate – properties and behaviour at sea. SINTEF report OC2017 A-137. ISBN:978-82-7174-305-5.

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

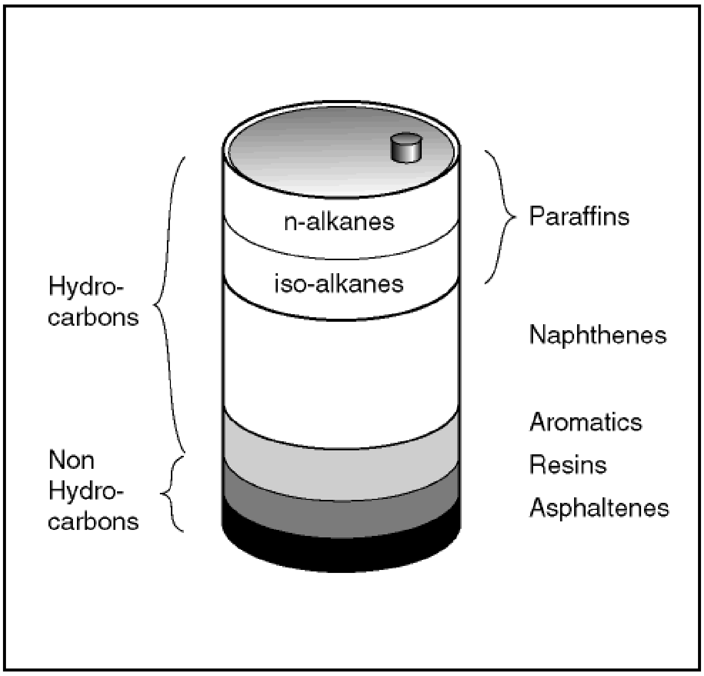


Figure A-1 The chemical composition of crude oils.

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.1.1 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 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.2Main 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.3Physical 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:

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

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.htmlThe 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.

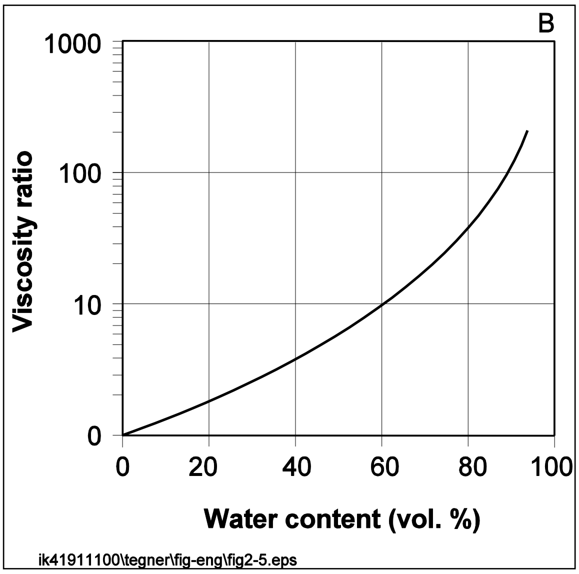


Figure A-2 Example of viscosity ratio as a function of water content

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^{o}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.4The 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.

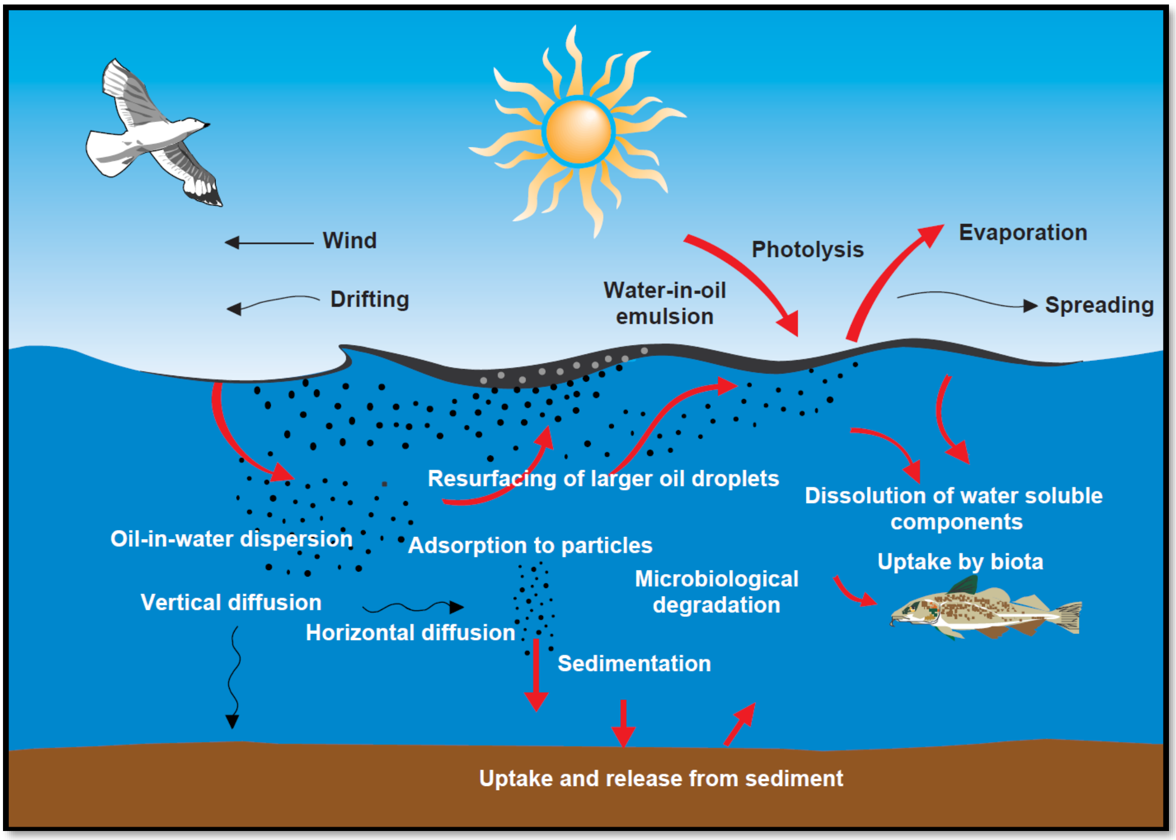


Figure A-3 Illustrating the weathering processes that take place when oil is spilled on the sea surface

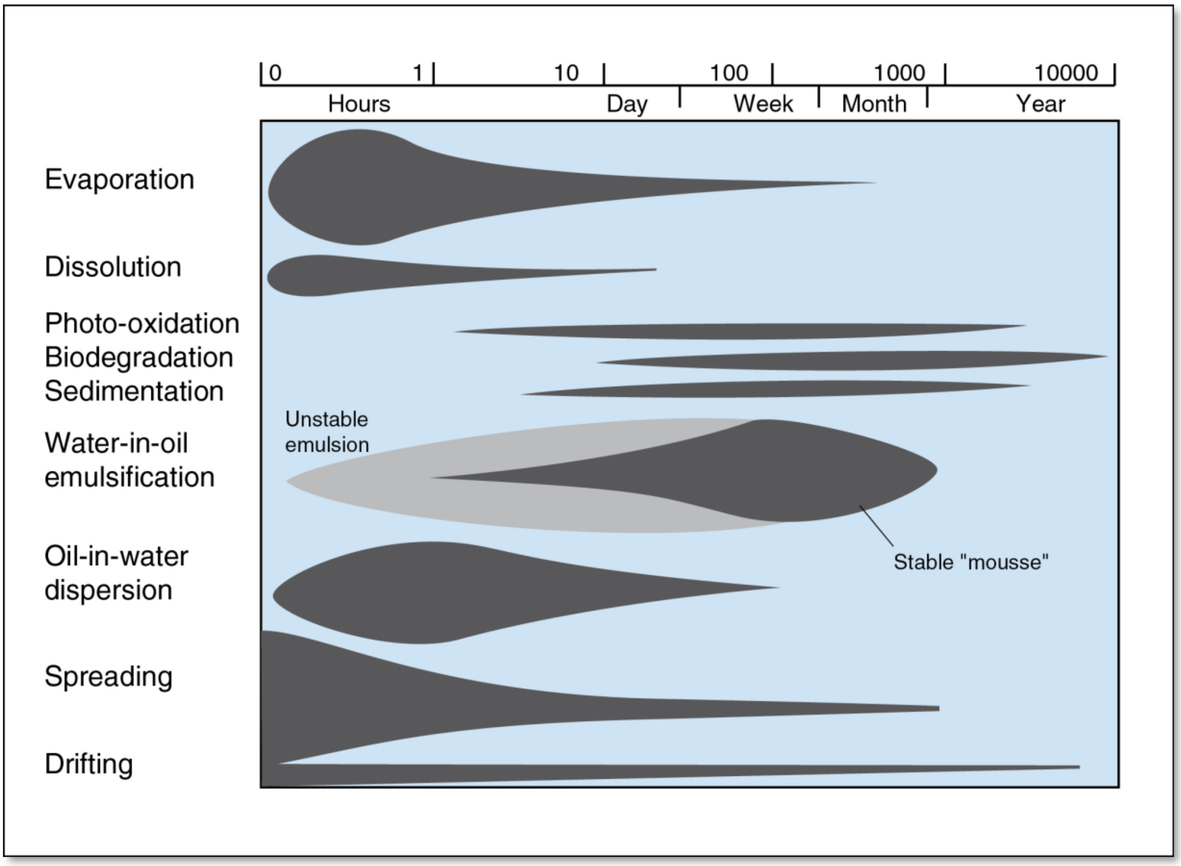


Figure A-4 Weathering processes' relative importance over time. Note: logarithmic scale

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 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.

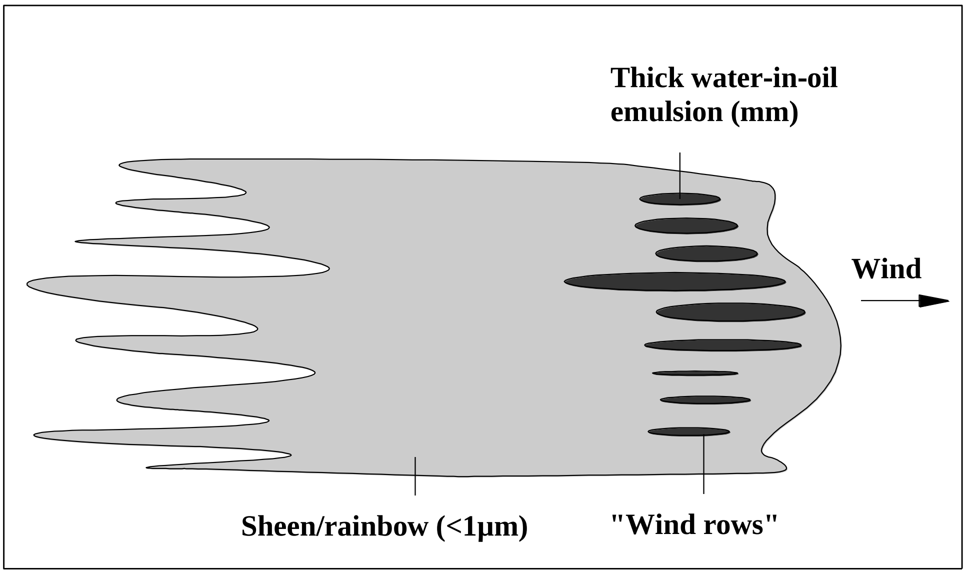


Figure A-5 The spreading of oil spilled on the sea surface and the distribution within the oil slick

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.

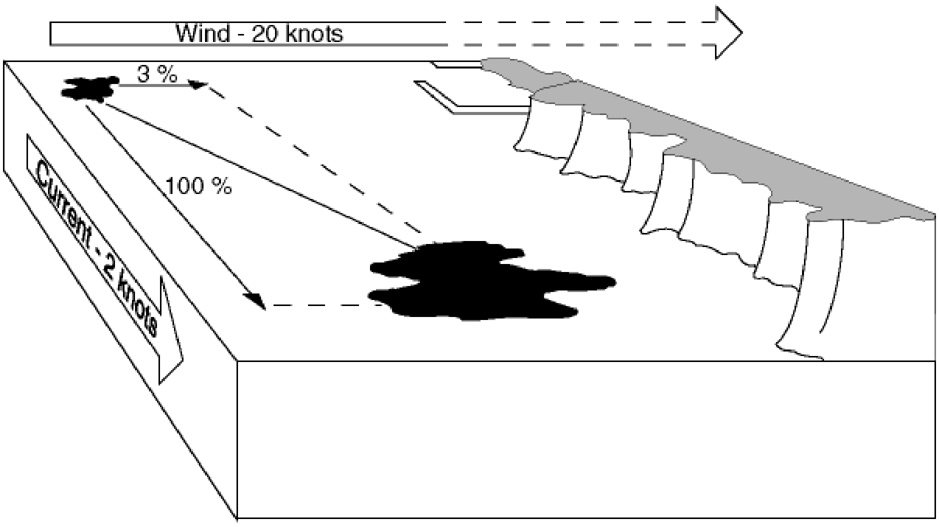


Figure A-6 An illustration showing how wind and current can influence the drifting of an oil slick

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.

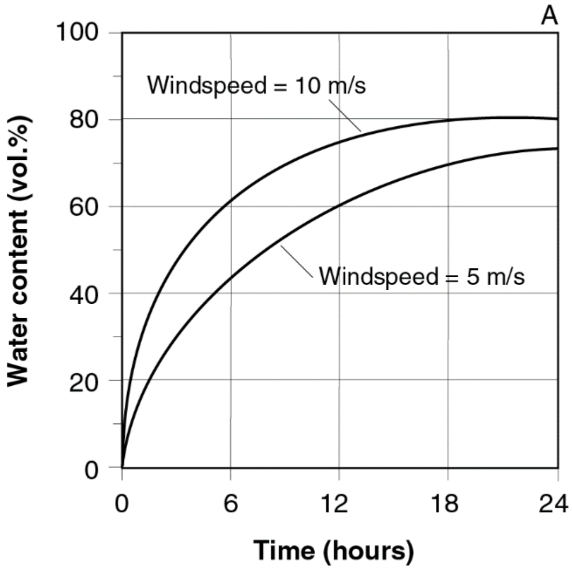


Figure A-7 Example of how weather conditions influence the w/o emulsion formation for typical oils

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.

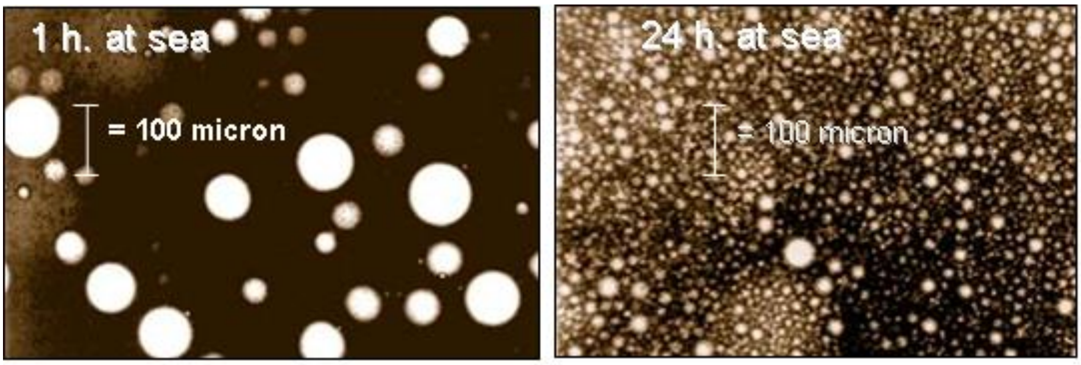


Figure A-8 *Microscope pictures of w/o emulsion after (A) 1 h. and (B) 24 h. in a rotating cylinder*

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.

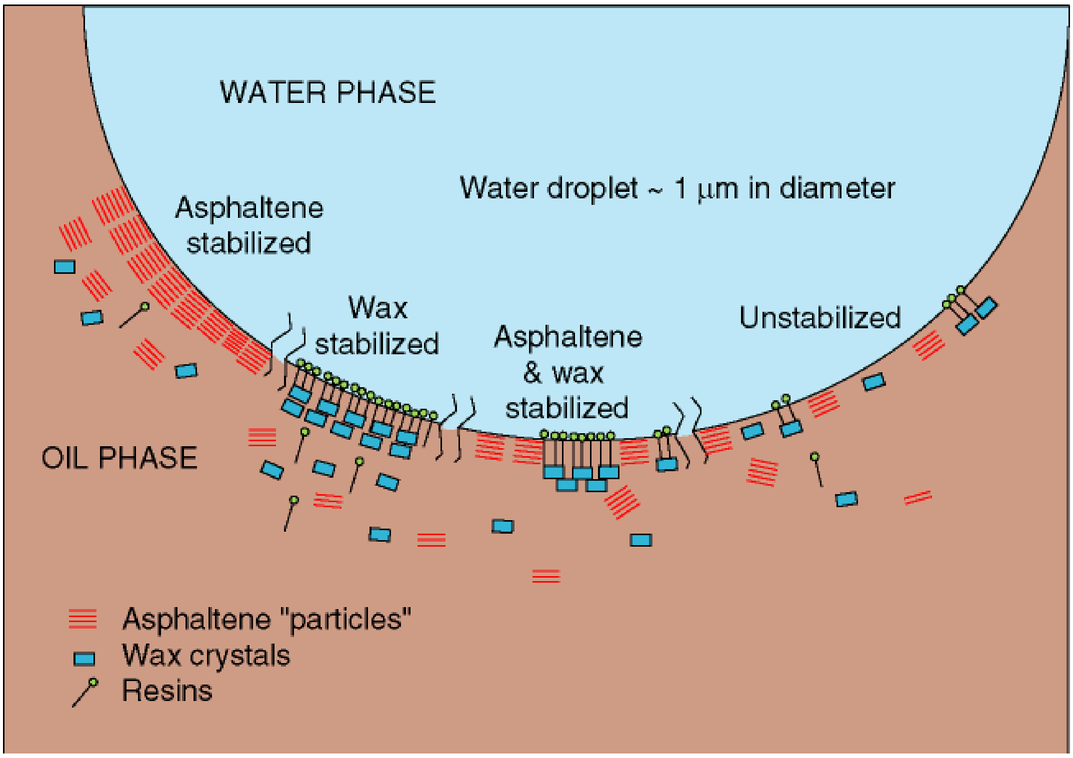


Figure A-9 *Interfacial layer stabilized by wax and asphaltenes in w/o emulsion*

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 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 Lødeng, 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.

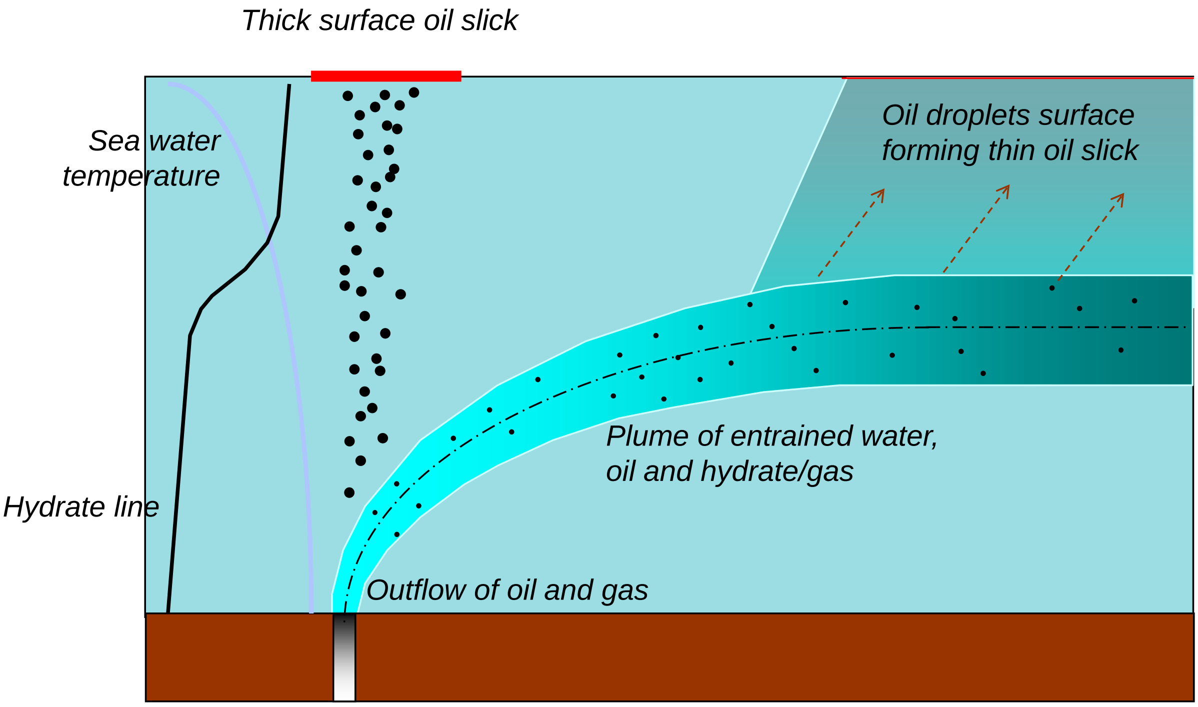


Figure A-10 Illustration of possible creation of thick surface oil slick (> 200 µm) from deep-water release of oil

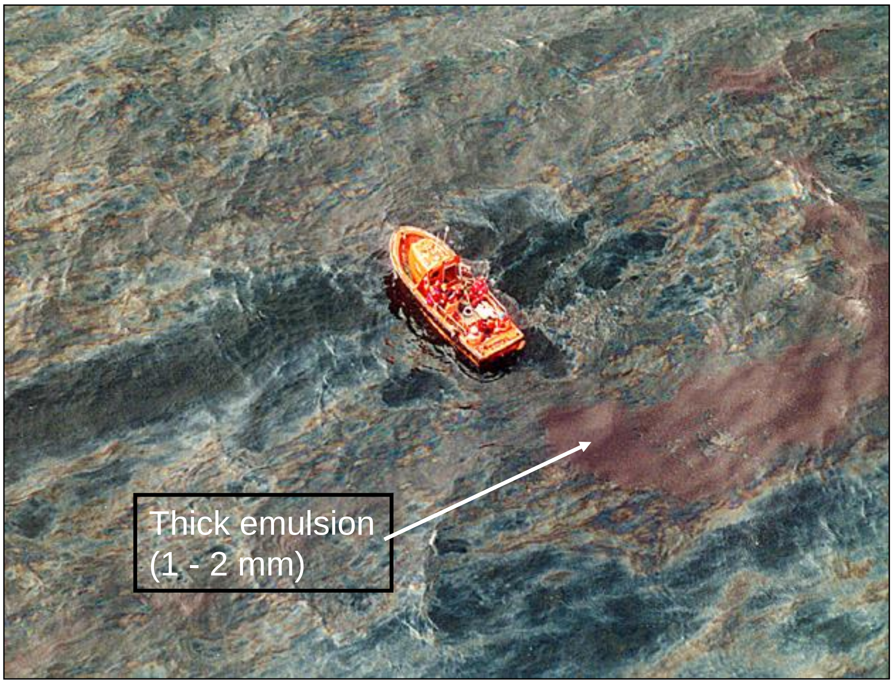


Figure A-11 Surface oil slick (initial thickness > 200 µm) from the experimental deep-water release "DeepSpill" in 2000. Surface oil is emulsifying like an oil slick from a surface batch release (from Leirvik et al., 2011)

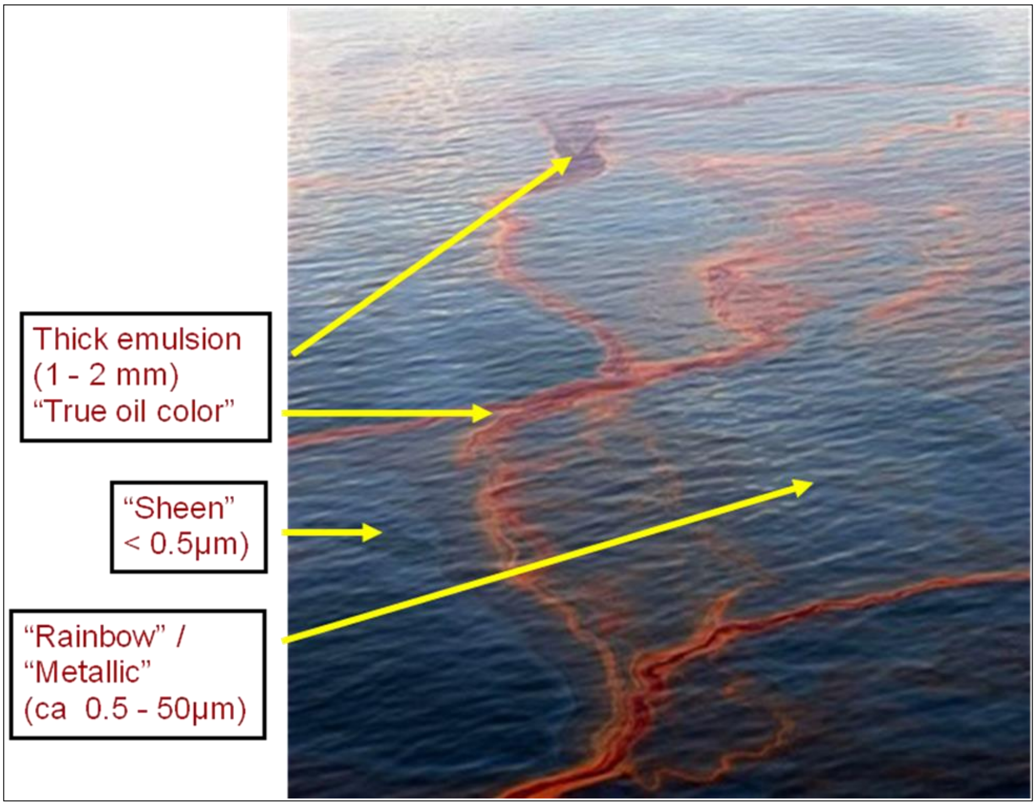


Figure A-12 Surface oil slick (initial thickness > 200 µm) from the DWH deep-water release. Surface oil is emulsifying like an oil slick from a surface batch release

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 and Figure A-14, 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.

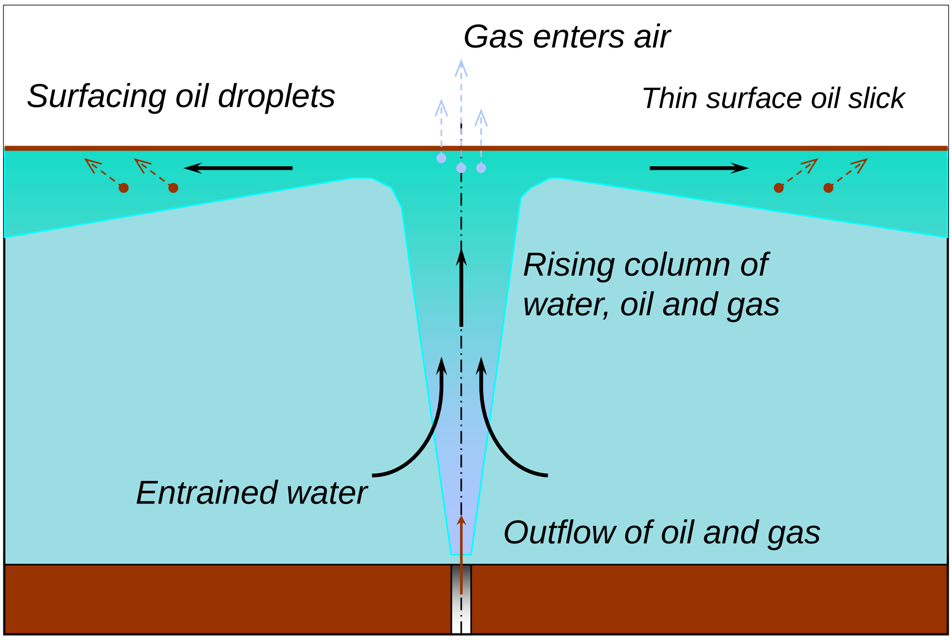


Figure A-13 Illustration of possible creation of thin surface oil slick (< 200 µm) from a shallow subsurface release (<500 m)

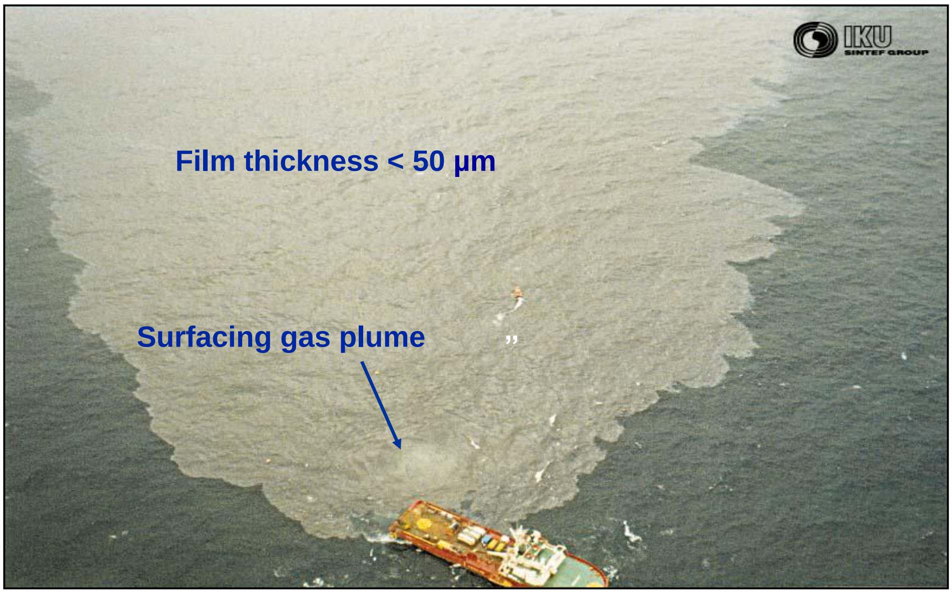


Figure A-14 Surface oil slick (< 50 µm) from experimental subsurface release at 106 m in 1996. The surface oil did not emulsify and had a very limited lifetime (hours) due to the low film thickness and high rate of natural dispersion (even at < 10 m/s wind)

B Experimental setup

B.1 Oil samples and test temperature

SINTEF Ocean received 3x20 litres of pressurized cylinders with Utgard condensate 2021-02-23. Safety job analysis (SJA) was performed when transferring the liquid (condensate) to separate cans for further handling and homogenization. Information of handling of the pressurized cylinders was given by Equinor.

The oil was given the unique SINTEF ID 2021-879. The weathering study (small-scale) were performed at 13 °C.

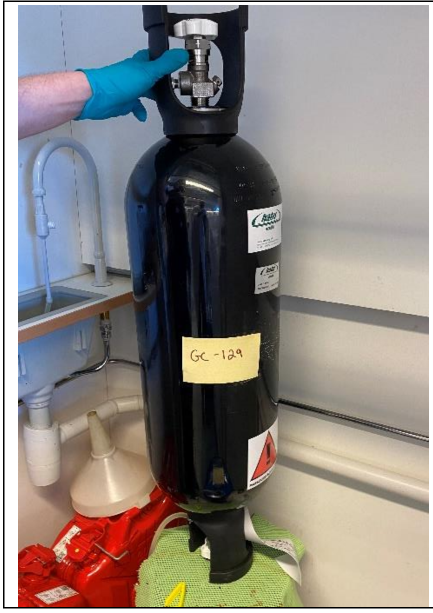
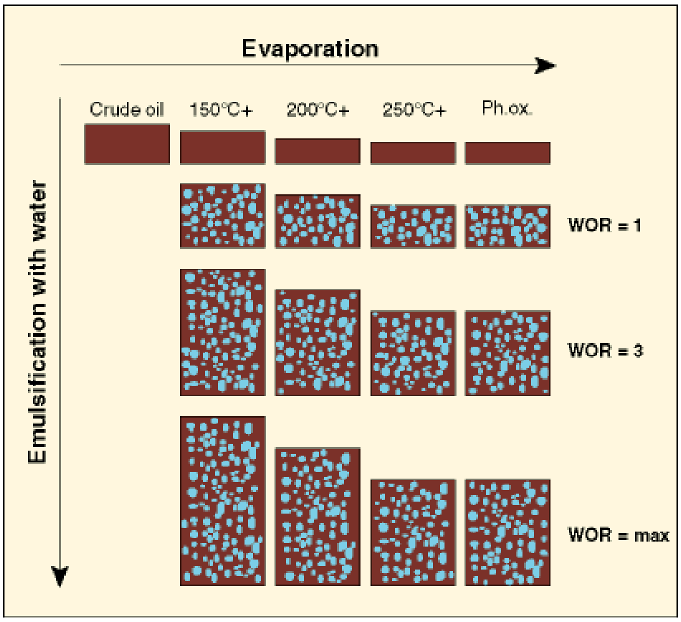
	Delivery: 142410951 Ship to 1070 Dusavik-Sleipn. Ø.O046C Shipping point: 1140 Sleipmer A platform Description: Olje fra Utgard til Sintef Quantity: 3 Comments SINTEF: Free water in the cylinders: 18-40 mL. The cylinders were heated to 30-35°C prior to homogenization (rolled the cylinders on the floor).

Figure B-1 Utgard condensate (pressurized cylinder).

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.3 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.4 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)

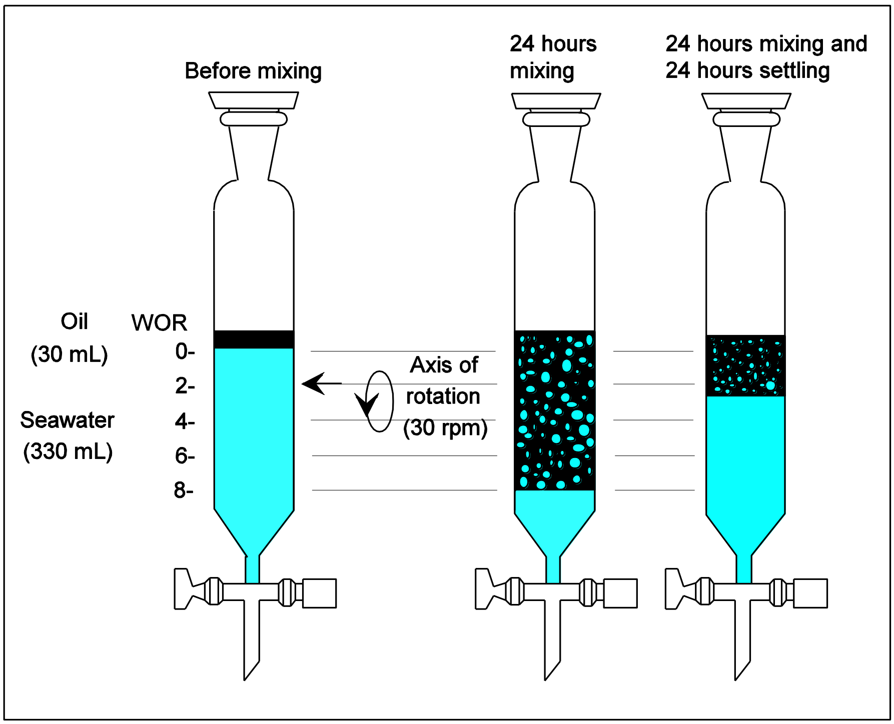
The volatile components were in the range of nC_5-nC_{10} and were quantified by use of PT-GC-MS (Purge and Trap Gas chromatograph Mass Spectrometer operating in full-scan mode and using a modified version of the EPA 8260 analysis method).

B.5 Emulsification properties

The w/o emulsification studies were performed by the rotating cylinders method developed by Mackay and Zagorski (1982), which is described in detail by Hokstad et al.,1993. The method includes the measuring of the following parameters:

- Relative water uptake (kinetics)
- Maximum water uptake
- Stability of the emulsion
- Effectiveness of emulsion breaker (Alcopol 60%)

The principle of the rotating cylinders method is illustrated in Figure B-3. Oil (30 mL) and seawater (300 mL) are mixed and rotated with a rotation speed of 30 rpm in separating funnels (0.5 L). The emulsification kinetics is mapped by measuring the water content at fixed rotation times. The maximum water content is determined after 24 hours of rotation.



6621/handbøker/grafisk/fig-eng/3skilletrakter.eps

Figure B-3 Principle of the rotating cylinder method

C Input data to SINTEF Oil Weathering Model (OWM)

The laboratory data used as input to the SINTEF OWM for Utgard are given in Table C-1 to Table C-3. The oil weathering predictions were based on the laboratory data at 13 °C.

Table C-1 Physical and chemical properties Utgard

Properties of fresh oil	**Utgard condensate**
Density (g/mL)	0.7718
Pour point (°C)	-27
Reference temperature (°C)	13
Viscosity at ref. temp. (mPa·s = cP) *	1
Flash point (°C)	-
Asphaltenes (wt. %)	0.02
Wax Content (wt. %)	0.89
Dispersible for visc. <	-
Not dispersible for visc. >	-

** Measured at shear rate 100 s^{-1}*

*** Conservative estimate*

-: Not analyzed or tested

Table C-2 True boiling point (TBP) curve of Utgard condensate
**TBP based on Simdist. Intertek Sunbury, UK. 2021-SUNB-000489.*

Temp. °C	**Utgard* Vol. %**
28	6
60	14
80	22
98	30
118	43
139	53
165	62
212	73
260	82
290	87
326	92
383	96
440	98
475	99
508	100

Table C-3 Lab weathering data for Utgard, 13 °C

Properties	**Fresh**	**150°C+**	**200°C+**	**250°C+**
Boiling Point Temp. (°C)	-	183.0	239.4	290.5
Vol. Topped (%)	0	56.4	70.0	80.3
Weight Residue (wt. %)	100	47.6	33.4	22.3
Density (g/mL)	0.77182	0.84316	0.86047	0.8751
Pour point (°C)	-27	6	15	21
Flash Point (°C)	-	38	75	112
*Viscosity of water-free residue (mPa.s =cP)	1	3	36	269
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*

D Chemical characterization – OSCAR composition file

The method for generating oil profile as input for OSCAR 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 of Utgard (fresh oil) from GC-MS analysis and TBP oil fraction

Wt.%	Comp. group no.	Utgard SINTEF ID 2021-879
6.000	1	C1-C4 gasses (dissolved in oil)
8.000	2	C5-saturates (n-/iso-/cyclo)
6.086	3	C6-saturates (n-/iso-/cyclo)
1.914	4	Benzene
9.000	5	C7-saturates (n-/iso-/cyclo)
4.082	6	C1-Benzene (Toluene) et. B
14.918	7	C8-saturates (n-/iso-/cyclo)
4.219	8	C2-Benzene (xylenes; using O-xylene)
4.463	9	C9-saturates (n-/iso-/cyclo)
2.318	10	C3-Benzene
4.000	11	C10-saturates (n-/iso-/cyclo)
0.157	12	C4 and C4 Benzenes
6.332	13	C11-C12 (total sat + aro)
0.011	14	Phenols (C0-C4 alkylated)
0.834	15	Naphthalenes 1 (C0-C1-alkylated)
7.666	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
0.981	18	Naphthalenes 2 (C2-C3-alkylated)
4.019	19	C15-C16 (total sat + aro)
0.415	20	PAH 1 (Medium soluble Polyaromatic hydrocarbons (3 rings-non-alkylated;<4 rings)
3.585	21	C17-C18 (total sat + aro)
3.000	22	C19-C20 (total sat + aro)
3.808	23	C21-C25 (total sat + aro)
0.192	24	PAH 2 (Low soluble polyaromatic hydrocarbons (3 rings-alkylated; 4-5+ rings)
4.000	25	C25+ (total)

The SINTEF OSCAR model is a 3-dimensional Oil Spill Contingency And Response 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.

E Find model oil

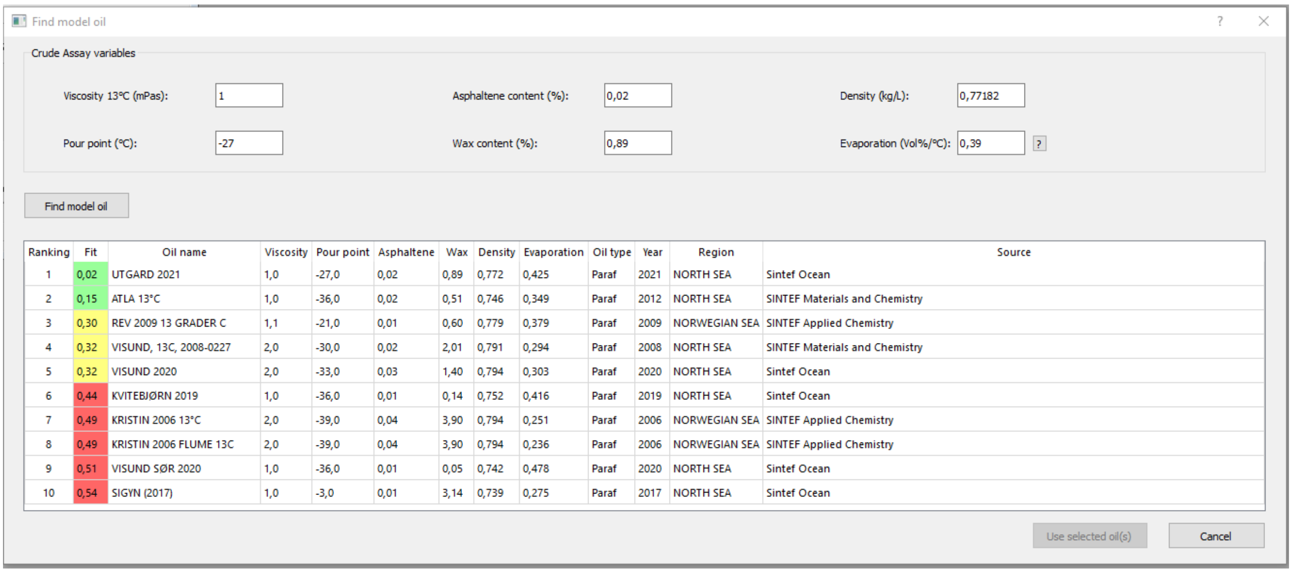
The "Find model oil" module in SINTEF OWM correlates Crude Assay (CA) variables for the fresh oil to weathering behaviour to search for a surrogate or a model oil in the SINTEF oil database. The approach for comparing fresh oil properties identifying a model oil is based on calculating a parameter describing the *fit factor* (Figure E-1) (Brandvik et al., 2015) between the new oil and the characterised oil present in the oil database.

The concept uses the CA variables: viscosity, asphaltene and wax content, density, pour point and the evaporation slope to search in the oil the oil database to find the closest match among the oils with existing weathering data. The evaporation slope (volume% evaporated / °C) is calculated based on the true boiling point curve (TBP) close to the 50 – 250 °C range (corresponds typically up to 5 days of weathering).

Table E-1 Fit factors for Find model oil

Fit factor	Description	Colour code
<0.25	Good fit	Green
0.26 -0.35	Reasonable fit	Yellow
>0.40	Unsatisfactory fit	Red

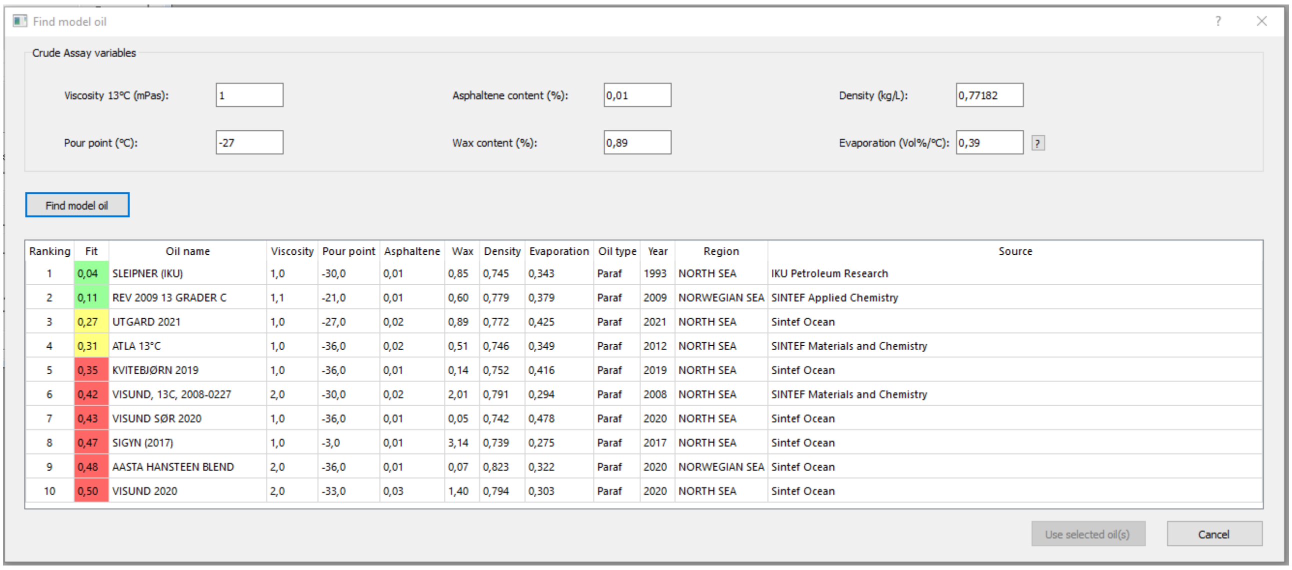
The CA variables (viscosity, pour point, asphaltene, wax, density and evaporation slope) of Utgard was used as input in "Find model oil". The calculated fit to all the oils in the SINTEF oil database given as the 10 oils with the closest fit is shown in Figure E-1. It is assumed that the asphaltene content for Sleipner is too high in the database (0.1 wt.%), and therefore no match with Utgard and Sleipner. A test was done replacing the asphaltene content of Utgard with 0.1 wt.% and then found match with Sleipner. Another test replacing asphaltene of Sleipner with 0.01 wt.% showed match of Utgard with Sleipner and Rev condensate (Figure E-2) which is reasonable .



Viscosity 13°C (mPas): 1
Pour point (°C): -27
Asphaltene content (%): 0,02
Wax content (%): 0,89
Density (kg/L): 0,77182
Evaporation (Vol%/°C): 0,39

Ranking	Fit	Oil name	Viscosity	Pour point	Asphaltene	Wax	Density	Evaporation	Oil type	Year	Region	Source
1	0,02	UTGARD 2021	1,0	-27,0	0,02	0,89	0,772	0,425	Paraf	2021	NORTH SEA	Sintef Ocean
2	0,15	ATLA 13°C	1,0	-36,0	0,02	0,51	0,746	0,349	Paraf	2012	NORTH SEA	SINTEF Materials and Chemistry
3	0,30	REV 2009 13 GRADER C	1,1	-21,0	0,01	0,60	0,779	0,379	Paraf	2009	NORWEGIAN SEA	SINTEF Applied Chemistry
4	0,32	VISUND, 13C, 2008-0227	2,0	-30,0	0,02	2,01	0,791	0,294	Paraf	2008	NORTH SEA	SINTEF Materials and Chemistry
5	0,32	VISUND 2020	2,0	-33,0	0,03	1,40	0,794	0,303	Paraf	2020	NORTH SEA	Sintef Ocean
6	0,44	KVITEBJØRN 2019	1,0	-36,0	0,01	0,14	0,752	0,416	Paraf	2019	NORTH SEA	Sintef Ocean
7	0,49	KRISTIN 2006 13°C	2,0	-39,0	0,04	3,90	0,794	0,251	Paraf	2006	NORWEGIAN SEA	SINTEF Applied Chemistry
8	0,49	KRISTIN 2006 FLUME 13C	2,0	-39,0	0,04	3,90	0,794	0,236	Paraf	2006	NORWEGIAN SEA	SINTEF Applied Chemistry
9	0,51	VISUND SØR 2020	1,0	-36,0	0,01	0,05	0,742	0,478	Paraf	2020	NORTH SEA	Sintef Ocean
10	0,54	SIGYN (2017)	1,0	-3,0	0,01	3,14	0,739	0,275	Paraf	2017	NORTH SEA	Sintef Ocean

Figure E-1 The output crude assay data of Utgard. Match (green value) with Utgard (itself) and Atla from SINTEF oil database.



Crude Assay variables

Viscosity 13°C (mPas): 1

Pour point (°C): -27

Asphaltene content (%): 0,01

Wax content (%): 0,89

Density (kg/L): 0,77182

Evaporation (Vol%/°C): 0,39

Ranking	Fit	Oil name	Viscosity	Pour point	Asphaltene	Wax	Density	Evaporation	Oil type	Year	Region	Source
1	0,04	SLEIPNER (IKU)	1,0	-30,0	0,01	0,85	0,745	0,343	Paraf	1993	NORTH SEA	IKU Petroleum Research
2	0,11	REV 2009 13 GRADER C	1,1	-21,0	0,01	0,60	0,779	0,379	Paraf	2009	NORWEGIAN SEA	SINTEF Applied Chemistry
3	0,27	UTGARD 2021	1,0	-27,0	0,02	0,89	0,772	0,425	Paraf	2021	NORTH SEA	Sintef Ocean
4	0,31	ATLA 13°C	1,0	-36,0	0,02	0,51	0,746	0,349	Paraf	2012	NORTH SEA	SINTEF Materials and Chemistry
5	0,35	KVITEBJØRN 2019	1,0	-36,0	0,01	0,14	0,752	0,416	Paraf	2019	NORTH SEA	Sintef Ocean
6	0,42	VISUND, 13C, 2008-0227	2,0	-30,0	0,02	2,01	0,791	0,294	Paraf	2008	NORTH SEA	SINTEF Materials and Chemistry
7	0,43	VISUND SØR 2020	1,0	-36,0	0,01	0,05	0,742	0,478	Paraf	2020	NORTH SEA	Sintef Ocean
8	0,47	SIGYN (2017)	1,0	-3,0	0,01	3,14	0,739	0,275	Paraf	2017	NORTH SEA	Sintef Ocean
9	0,48	AASTA HANSTEEN BLEND	2,0	-36,0	0,01	0,07	0,823	0,322	Paraf	2020	NORWEGIAN SEA	Sintef Ocean
10	0,50	VISUND 2020	2,0	-33,0	0,03	1,40	0,794	0,303	Paraf	2020	NORTH SEA	Sintef Ocean

Figure E-2 *The output crude assay data of Utgard with 0.01 wt.%. Match (green value) with Sleipner and Rev condensates. Yellow match with itself and Atla from SINTEF oil database*