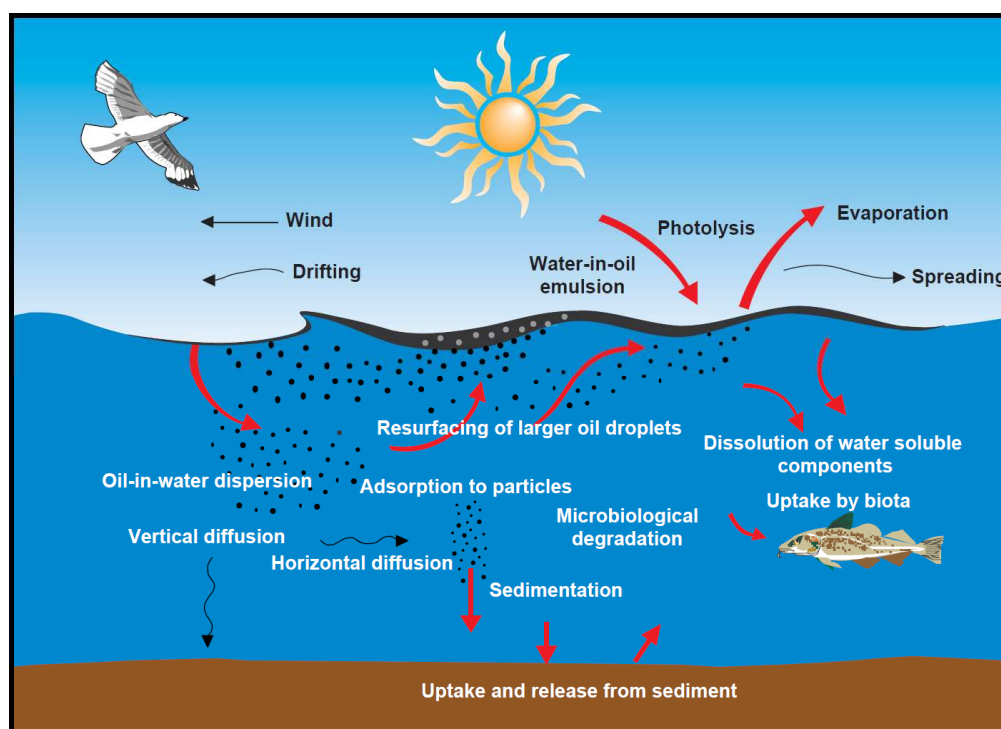# Report

Sigyn condensate – properties and behaviour at sea

In relation to oil spill response

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Report

Sigyn condensate – properties and behaviour at sea

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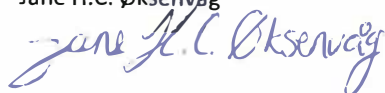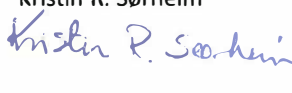| CLASSIFICATION	CLASSIFICATION THIS PAGE	ISBN
Unrestricted	Unrestricted	978-82-7174-305-5

ABSTRACT
A weathering study on Sigyn condensate has been performed at 13°C, in small-scale laboratory. The obtained weathering data were used as input to the SINTEF`s Oil Weathering model (OWM) to predict the Sigyn condensate behaviour at different weather conditions in a spill situation at sea. The weathering properties are discussed related to oil spill response; mechanical recovery, mechanical dispersion by water flushing, and chemical dispersion

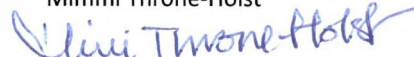MANAGEMENT SYSTEM CERTIFICATION
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1 Executive summary

Spilled oils undergo changes when weathered on the sea surface that affect behaviour and oil spill countermeasures in various ways. Oil weathering varies over time and with different environmental conditions. This summary gives a brief overview of the main changes predicted for Sigyn condensate when weathered on the sea surface. The SINTEF Oil Weathering Model (OWM) has been used to predict the oil weathering properties as a function of time.

The lifetime of an oil spill at sea depends on the oil's composition, the release conditions (e.g. on the surface, underwater) and environmental conditions (temperature, wind, waves). Natural dispersion and evaporation are the main weathering processes that remove an oil spill from the surface. As for all oils and condensates, the lighter compounds will evaporate during an oil spill, causing an increase in the relative amount of wax and asphaltenes, especially in the early stages of weathering. Since the relative concentration of heavy components increases, the physical properties of the oil will change.

The weathering properties of Sigyn condensates was studied at 13 °C, which is regarded to be a typical summer temperature in the North Sea. Sigyn has a density of 0.739 g/mL, and is categorised paraffinic condensate with a relative high wax content (3.14 wt. %) and low content of asphaltenes (0.01 wt. %). The condensate exhibits a high evaporative loss (e.g. 82 vol. % for the 250°C+ residue) that influence the properties of the oil during weathering, resulting in a rapid increase in the relative content of wax, which again will give increased pour points and viscosities.

In general, wax and surface-active compounds such as asphaltenes and resins contribute to the emulsifying properties of an oil as these compounds forms a "skin-layer" that stabilize the water droplets at the water-oil-interface. However, due to the low content of asphaltenes, the relative high wax content is the main contributor to the emulsification observed for the Sigyn condensate. The condensate expressed low water uptake for the 150°C+ and 200°C+ residues (20-30 vol. %), whilst the 250°C+ residue showed high water uptake (~ 77 vol. %). However, the emulsions were loose or unstable, and water was easily released from the emulsion after 24 hours' standstill, and was particularly observed for the 250°C+ residue.

For the emulsions of the 150°C+ and 200°C+ residues, addition of emulsion breaker partially broke and reduced the water content, where the highest concentration (2000 ppm) showed the greatest efficiency. But, for the more heavily weathered condensate, 250°C+ residue, the emulsion breaker showed to have an opposite effect, reducing the emulsion breakup compared to no treatment of Alcopol O 60 %. The results indicated that the use of emulsion breaker has a minimal effect or even stabilized the emulsion, and is therefore not recommended for this condensate.

Sigyn condensate is predicted to pose a fire hazard during the first 2 hours at sea under calm wind conditions (2 m/s) at both summer and winter temperatures, during which time the flash point of the condensate will be below the ambient water temperature. Sigyn condensate has a rapid evaporative loss and the flash point will therefore increase rapidly. Smaller vessels that may be engaged in recovery operations may be limited to recover liquids with flash points of 60 °C or above. For Sigyn, this limit will be surpassed within 7 hours in winter conditions, and 5 hours in summer conditions under conditions with calm wind speeds (2 m/s). The flash point limitations will be reached much faster at higher winds speeds due to higher evaporation.

Sigyn condensate showed low viscosities over time (< 600 mPa.s for the first 5 days), but the relative increase in wax content due to high evaporative loss of lighter components may cause the weathered condensate to solidify. Solidification is not expected to be a likely scenario in a spill situation at summer temperatures under breaking waves conditions (> 5m/s wind speed). The condensate spilled on the sea surface will normally at these conditions start to mix with the seawater, the wax lattice will then be broken up with applied mechanical

stress. At low seawater temperature, the condensate could possible solidify, but was not studies in this project. Solidification on sea surface is known to start typically at pour points 5-15 °C above the sea temperature.

The laboratory testing showed that use of chemical dispersant have potential in summer conditions for the Sigyn condensate. However, the use of chemical dispersant assumes that the condensate film thickness is greater than 0.05 - 0.1 mm. The use of chemical dispersant is also dependent on the lifetime of the slick, which may be short for condensates at increasing wind speeds. Lumps of solidified condensate may be generated on the sea surface in calm weather conditions, especially at low temperatures, and may not be dispersible. Water flushing from high-capacity water flush boom or using Fi-Fi (Firefighting) monitors, either as mechanical dispersion or in combination with chemical dispersants, could have a potential for breaking up oil/emulsion with viscosities < 150-300 mPa.s into smaller droplets. However, in higher sea states the water and oil will normally be mixed and generate a thin oil film on the sea surface for a limited period. This will encourage naturally dispersion of oil into the water column.

The use of traditional mechanical recovery on Sigyn condensate is assumed to have low efficiency due to a thin oil film (< 0.1 mm) and limited lifetime of the slick. In addition, a high degree of boom leakage is particularly pronounced if the viscosity of the oil or the emulsion is lower than 1000 mPa.s. The Sigyn condensate have viscosities < 600 mPa.s for the first days at sea under summer and winter conditions, and reduced efficiency for mechanical recovery with use of booms should be expected. In cases where low viscosity of the oil/emulsion is a limiting factor for use of booms, the high pour point could cause solidification after a time on the sea surface, generating lumps with higher thicknesses, and confinement in a boom could after all be feasible. However, if spread over large areas this could be challenging.

The laboratory studies for Sigyn condensate has shown a relatively high increase in the wax content, from 3.14 wt. % for fresh to 15.5 wt. % for the 250°C+ residue. This might cause the weathered condensate to solidify at the sea surface at low temperatures and may have an impact on the condensate fate and lifetime. Additional experimental emulsification and dispersibility studies at low temperature (5 °C) would therefore have given a more robust data for predicting the fate of the Sigyn oil at winter temperature using the OWM.

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 oils can be when spilled on the sea surface. For that reason, having good knowledge about the expected behaviour of oil at sea in case of an accidental spill is highly valuable.

Recent dispersibility studies of the oil spilled after the Deepwater Horizon incident in the Gulf of Mexico (2010) clearly showed how dispersant application efficiency may change as the oil is weathered and emulsified on the sea surface over a longer period. This may form important support for refining operative strategies in terms of where, when and how dispersants could be effectively applied during a response operation.

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.

The Sigyn field is located in the Sleipner area in the North Sea and commenced production in 2002. The field consists of two gas/condensate producers and one oil producer that are connected to the Sleipner A platform via a subsea template, see Figure 2.1. The gas is then exported via the dry gas system from Sleipner Riser, while the condensate is exported through the dedicated pipeline to Kårstø north of Stavanger. ExxonMobil is the operator with 40 % ownership, the other participant is Statoil (60 %) (http://www.exxonmobil.no).

Figure 2.1 The location of the Sigyn field and the subsea template.

Exxon requested a small-scale weathering study of the Sigyn condensate. The obtained data were used to predict Sigyns's fate and behaviour when spilled at sea under different weathering conditions using the SINTEF`s Oil Weathering model (OWM). The effect of oil weathering related to oil spill response is also discussed.

3 Experimental results and discussion

The weathering study was performed at 13°C, which are regarded to be typical sea temperature in the North Sea during summertime. Sigyn fresh and the residues of 150°C+, 200°C+ and 250°C+ are shown in Figure 3.1. The Sigyn condensate was given SINTEF ID: 2017-113-C1.

Figure 3.1 Sigyn fresh and the residues 150°C +, 200°C + and 250°C +.

The small-scale weathering results of Sigyn are compared with similar data of other Norwegian condensates and crude oils. Kristin is located in the Norwegian Sea, and the light crude oil has earlier been used as a reference oil for the Sigyn condensate, and used in environmental risk assessment (MRA) for the Sleipner field. The Sleipner condensate and Gudrun crude oil are located in the same area as Sigyn in the North Sea. The presented Sleipner data is based on laboratory data from 1993, and the true boiling point (TBP) curve is from 2000. The OWM simulations for the Sleipner condensate were performed in 2002. The Alve condensate was also used as a test oil in the Petromaks 2 "Thin Oil Films" project (Ramstad et al., 2016), located in the Norwegian Sea. The oils for comparison are listed in Figure 3.1. The oils were selected in agreement with ExxonMobil and Statoil, since Statoil will take over as operating company for the Sigyn field from January 2018.

Table 3.1 Condensates and oil compared with Sigyn in this report

Oil	SINTEF ID	SINTEF report no.	Reference (SINTEF report)
Kristin light oil (2006)	2006-0256	STF80MK A06221	Leirvik, 2006
Sleipner condensate (1993)	No SINTEF ID	No SINTEF report no.	Knudsen et al., 1993
Alve condensate (2010)	2009-0552	SINTEF A16808	Sørheim et al., 2010
Gudrun crude oil (2012)	2012-0056	SINTEF A23435	Andreassen et al., 2012

3.1 Chemical composition and physical properties

Gas chromatographic flame ionization detector (GC/FID) characterization

The chemical composition of Sigyn condensate, as characterized by gas chromatography (GC/FID), is shown in Figure 3.2. The same figure also present the gas chromatographic characterization of the corresponding residues (150°C+, 200°C+, and 250°C+), and verify the artificial evaporation of the oil by use of distillation

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(topping) in the laboratory. Gas chromatograms for fresh Sigyn condensate in comparison with Kristin light oil, Sleipner condensate, Alve condensate and Gudrun crude oil are shown in Figure 3.3.

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 not as easily separated as n-alkanes and are shown as a broad and poorly defined bump below the sharp peaks. The bump is often described as "Unseparated Complex Mixture" (UCM). Heavier compounds such as asphaltenes ($> nC_{40}$) are not possible to analyse with this technique. For Sigyn, the GC/FID chromatograms show high peaks of the lighter hydrocarbon (n-alkanes) $< nC_{10}$, and n-alkanes peaks from nC_{20} indicates that the condensates exhibit a wax content. The GC/FID characterization indicates that Sigyn is a paraffinic oil related to its hydrocarbon distribution. However, this batch of Sigyn has a characteristic feature where the peak ratio between the pristane and phytane is relative high compared to other oils from the North Sea, as shown in Figure 3.2.

Appendix C shows the results of the GC/MS chemical characterization of the fresh oil.

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SINTEF ID: 2017-113-C1 Fresh
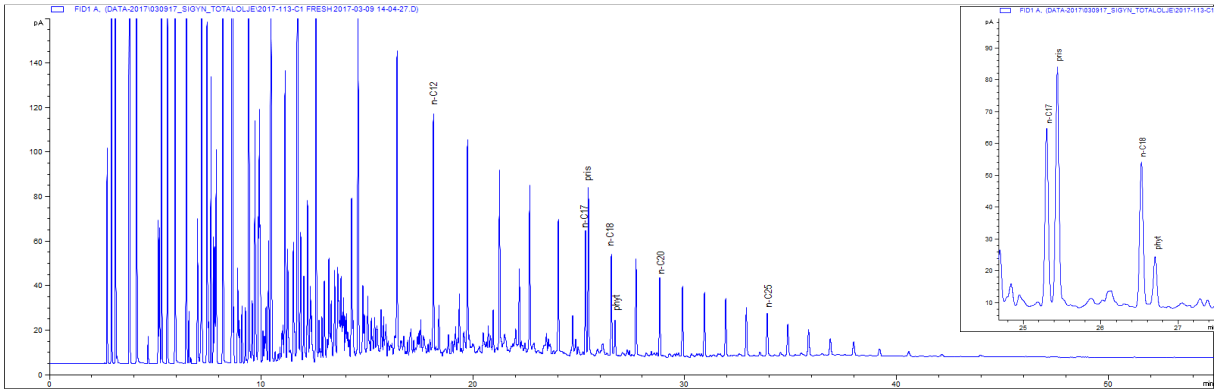
SINTEF ID: 2017-113-C1-C1-S1 150°C+
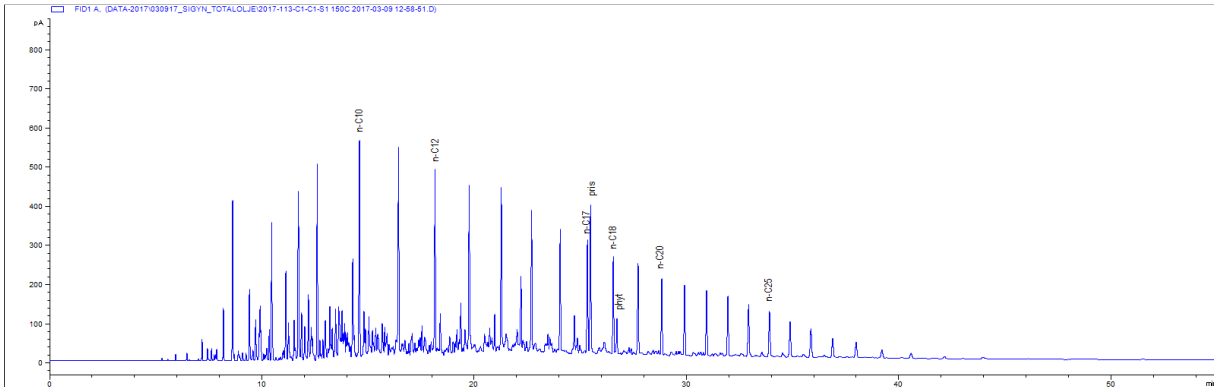
SINTEF ID: 2017-113-C1-C3-S1 200°C+
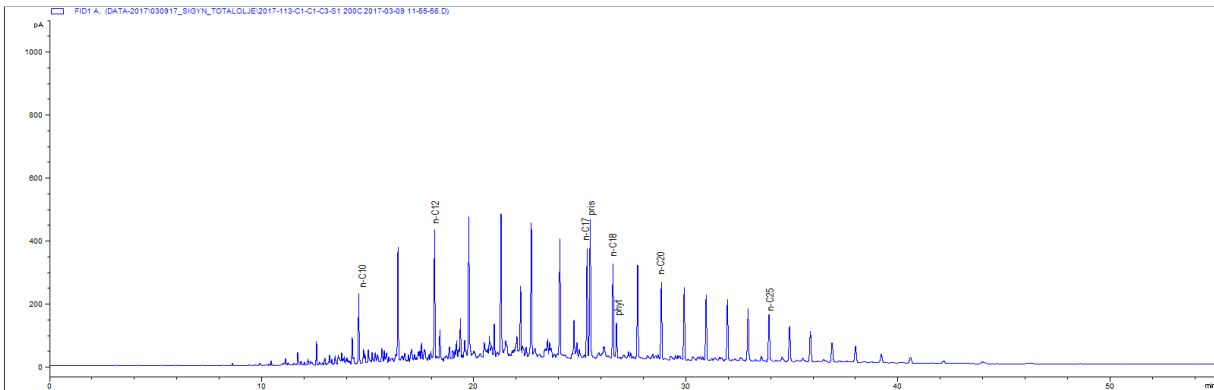
SINTEF ID: 2017-113-C1-C2-S1 250°C+
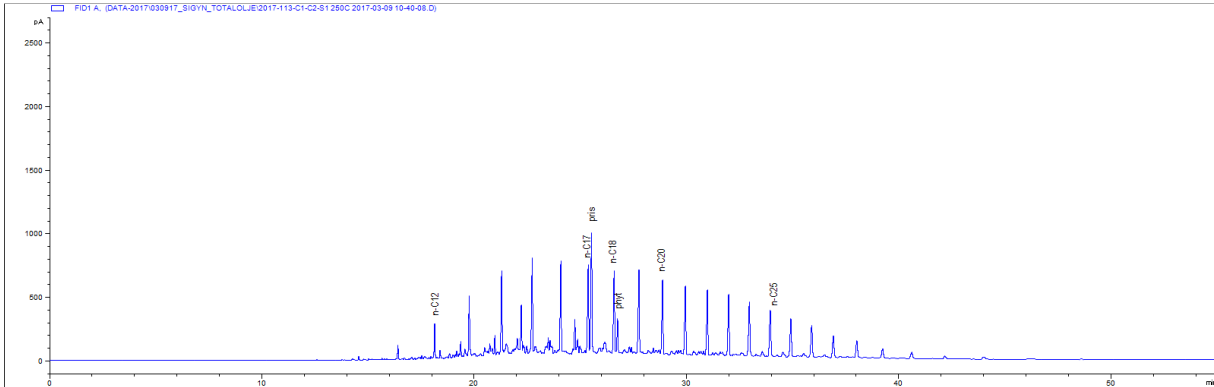
Figure 3.2 GC/FID chromatograms of fresh sample and evaporated residues of Sigyn condensate.

Sigyn - Fresh (SINTEF ID: 2017-113-C1)
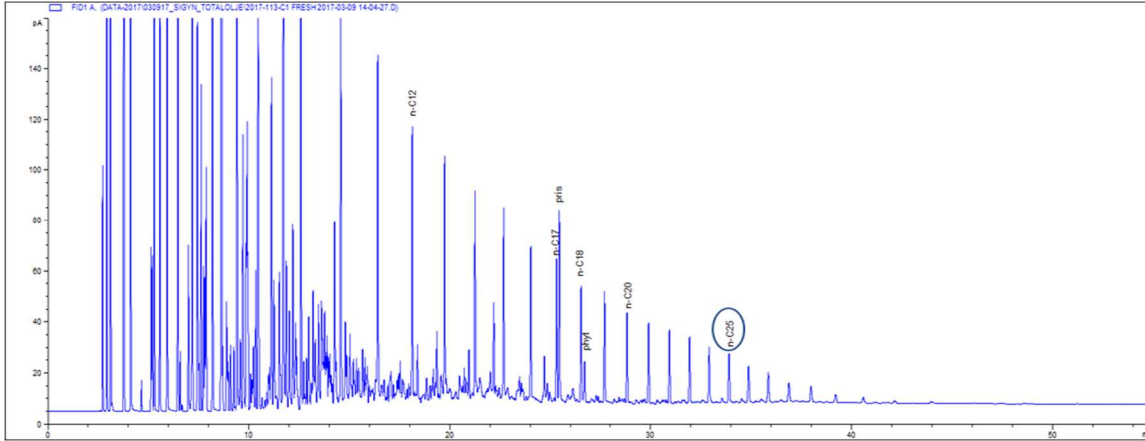
Kristin light oil – Fresh- (SINTEF ID: 2006-0256)
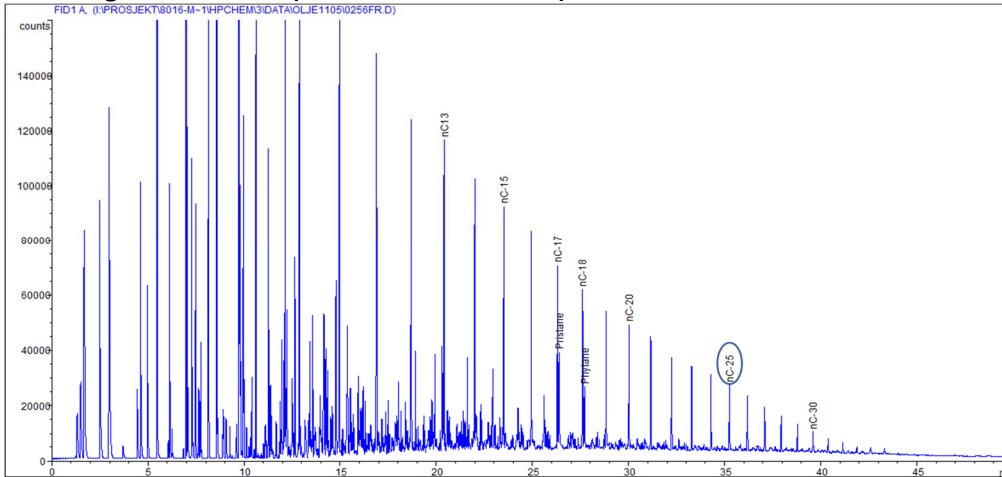
Sleipner condensate – Fresh (99-021) – (Faksness et al., 2002, Nordtest – Sintef report no. STF66 A02028)
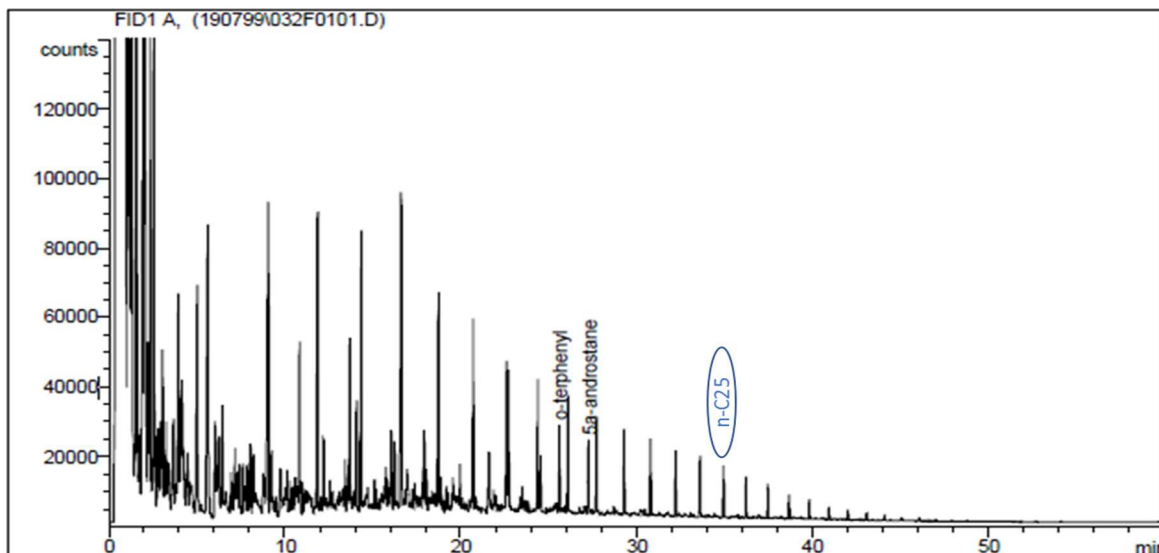
Alve condensate – Fresh - (SINTEF ID: 2009-0552)
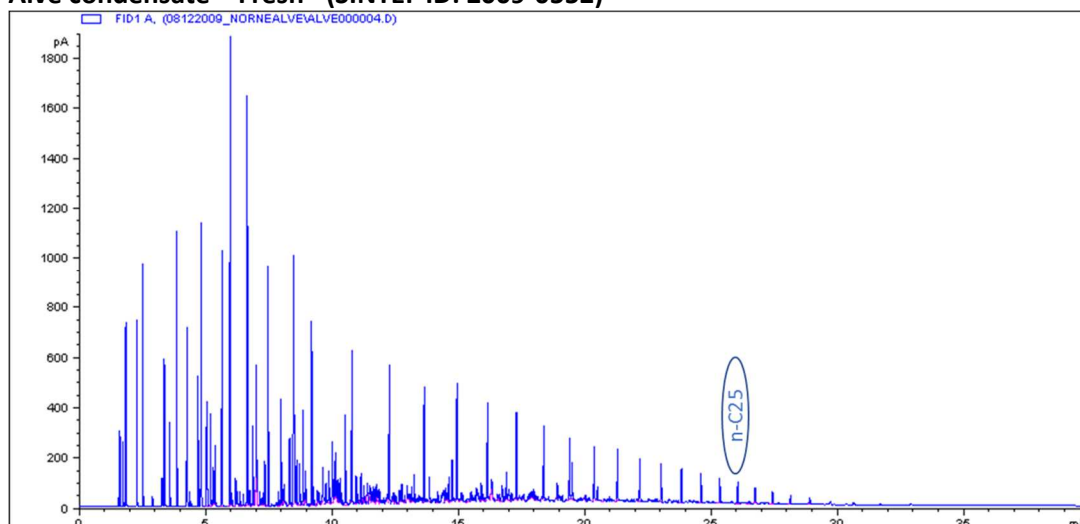
Gudrun – Fresh - (SINTEF ID: 2012-0056)
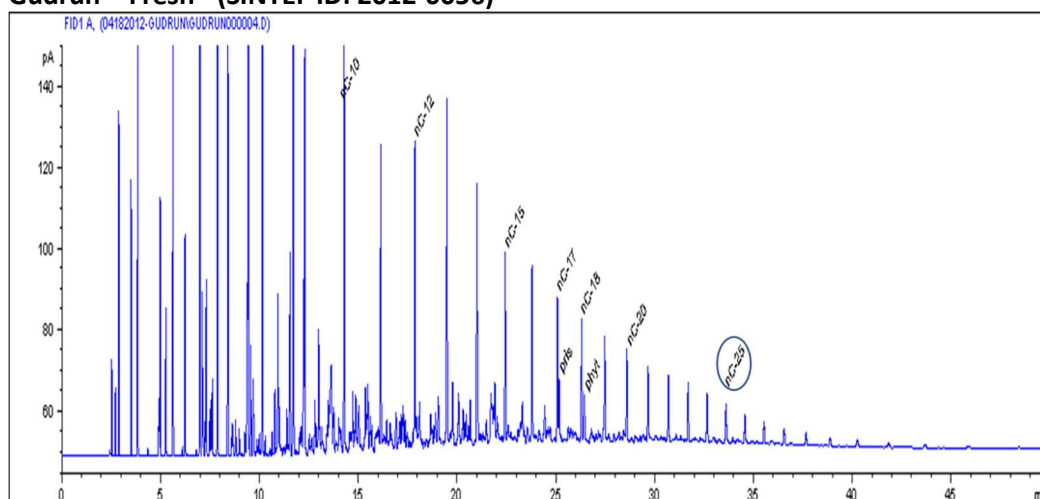
Figure 3.3 GD/FID chromatograms for fresh residue of Sigyn condensate and the selected oils used for comparison.

The use of gas chromatography (GC/FID) is often an important tool for oil spill identification. Common screening parameters used for identification, as well as for the degree of biodegradation, are the nC_{17}/Pristane and nC_{18}/Phytane ratios. These ratios give the relation between the n-alkanes and the corresponding isoprenoids (pristane and phytane) based on their peak heights from the GC/FID-chromatogram. The ratios for the fresh Sigyn condensate and the comparison condensates and oils are given in Table 3.2.

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Table 3.2 nC$_{17}$/Pristane and nC$_{18}$/Phytane ratios for Sigyn fresh condensate and other Norwegian oils

Oil	nC$_{17}$/Pristane	nC$_{18}$/Phytane
Sigyn condensate (2017)	0.74	2.91
Kristin light oil (2006)	1.91	2.56
Sleipner condensate (2002)	1	2.10
Alve condensate (2010)	-	-
Gudrun (2012)	2.55	2.70

-: No data available

Asphaltenes and wax content

The content of asphaltenes and wax for Sigyn fresh and corresponding residues, in comparison to selected oils/condensates, are given in Table 3.3. All the fresh oils in comparison have relatively high content of wax (in the range of 3-7 wt. %), expect the Sleipner condensate with low wax content (0.85 wt. %). Gudrun has a tenfold higher content of asphaltenes compared with the other oils.

Table 3.3 Asphaltenes ("hard") and wax content for the chosen oils for comparison and their residues.

Oil	Residue	Asphaltenes "hard" (wt.%)	Wax (wt.%)
Sigyn condensate (2017)	Fresh	0.01	3.14
	150°C+	0.03	7.44
	200°C+	0.05	10.6
	250°C+	0.07	15.5
Kristin light oil (2006)	Fresh	0.02	6.8
	150°C+	0.03	9.7
	200°C+	0.04	12.0
	250°C+	0.05	15.0
Sleipner condensate (2002) Lab. data from 1993	Fresh	-	0.85
	150°C+	-	2.1
	200°C+	-	3.4
	250°C+	<0.1	5.3
Alve condensate (2010)	Fresh	0.03	5.0
	150°C+	0.05	7.8
	200°C+	0.06	9.8
	250°C+	0.08	12.5
Gudrun (2012)	Fresh	0.1	5
	150°C+	0.2	6
	200°C+	0.2	8
	250°C+	0.3	9

-: Not quantified

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Physical properties of fresh and weathered residues

Physical properties of Sigyn and the oils in comparison are listed in Table 3.4.

Table 3.4 Physical parameters for Sigyn, compared with a selection of oils/condensate.

Oil type	Residue	Evap. (vol.%)	Residue (wt.%)	Density (g/mL)	Flash point (°C)	Pour point (°C)	Viscosity 13°C (mPa.s)		IFT (mN/m)
							(10 s1)	(100 s1)	
Sigyn condensate (2017)	Fresh	0	100	0.739	-	-3	1	1	-
	150°C+	62	42	0.817	35	18	53	11	5.1
	200°C+	74	30	0.834	76	21	266	61	3.7
	250°C+	82	20	0.841	111	27	1120	232	-
Kristin light oil (2006)	Fresh	0	100	0.793	-	-39	2	2	-
	150°C+	32	70	0.830	36	0	26	12	-
	200°C+	46	57	0.846	72	12	539	113	-
	250°C+	57	45	0.860	114	27	7730	826	-
Sleipner condensate (2002)	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	-
Alve condensate (2010)	Fresh	-	100	0.796	-	0	-	-	10.7**
	150°C+	37	64	0.837	35	12	9*	-	4.6**
	200°C+	51	51	0.849	68	18	78*	-	4.4**
	250°C+	61	40	0.859	102	21	-	-	5.8**
Gudrun (2012)	Fresh	0	100	0.824	-	-6	15	8	21.8
	150°C+	23	79	0.850	37	0	43	22	19.6
	200°C+	38	65	0.867	77	12	332	106	20.8
	250°C+	50	53	0,881	112	24	2497	594	16.4

–: no data available

*Data from the Petromaks 2 Thin Oil Films (Ramstad et al., 2016)

** IFT at equilibrium

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3.2 Emulsifying properties

The emulsifying properties of Sigyn were studied by use of the rotating cylinders (Hokstad et al., 1993). Figure 3.4 show the Sigyn emulsions for the three residues 150°C+, 200°C+ and 250°C+, four cylinder of each, after 24 hours of rotation.

Figure 3.4 The rotating cylinders showing the emulsification of seawater in oil after 24 hours at 13 °C.

Viscosity of water free residues and the w/o emulsions

The viscosity expresses the oils ability to resist gradually deformation by increasing shear, where viscosities of so-called *Newtonian* oils remains constant independent on the applied shear rate (s^{-1}) at a given temperature. When shear applies on so-called *non-Newtonian* oils, the viscosity of such oils decreases. The yield stress is the force that must be applied to make the oil to begin to flow.

The fresh Sigyn condensate has Newtonian properties. Table 3.5 shows the measured viscosities and yield stress of water free residues and the residues emulsified with 50%, 75% and maximum water content, respectively at 13°C. The evaporated and emulsified Sigyn condensate showed to be a non-Newtonian fluid, hence the viscosities are dependent on the shear rate. The studies showed higher viscosities at a lower share rate ($10 \ s^{-1}$) compared to higher shear rate ($100 \ s^{-1}$). This decrease in viscosity with increasing mechanical force (shear rate) is likely caused by a breakup of the wax lattice structure. The fresh Sigyn condensate has Newtonian properties.

Table 3.5 Viscosity and yield stress of the Sigyn water free residues and emulsified residues at 13 ºC.

Oil	Residue	Water content (vol. %)	Viscosity (mPa.s)		Yield stress (Pa)
			10 s⁻¹	100 s⁻¹	
	Fresh	0	1	1	-
	150°C+	0	53	11	1.82
	200°C+	0	266	61	0.57
	250°C+	0	1120	232	0.94
Waterfree	150°C+	50	10	3	1.20
50% wio	200°C+	50	52	11	0.10
75% wio	250°C+	50	330	89	0.24
	150°C+	27* (75)	9	4	1.81
	200°C+	62* (75)	113	45	0.16
	250°C+	75	225	54	0.88
Maximum	150°C+	67	18	6	1.81
water	200°C+	27	65	33	0.78
uptake	250°C+	77	374	82	0.66

*: The residues did not emulsify 75% water

wio: water in oil

Water uptake and maximum water content

The rate of water uptake and maximum water uptake were studied by use of the rotation cylinders, see Appendix B, similar to the emulsifying properties. The water content in the emulsion as a function of time (nine measurements during 24 hours rotating time), was evaluated. $T_{1/2}$, is defined as the consumed time (hours) to incorporate half the maximum water uptake, and is usually derived from the tabulated data for each residue. Since the Sigyn condensate did not produce stable emulsions, the $T_{1/2}$ value was estimated from the emulsification of the 150°C+ residue, see Table C3.

Stability and efficiency of emulsion breaker

The stability of the emulsions from the weathered residues of Sigyn condensate was tested by quantifying the amount of water released from the emulsion during 24 hours of settling, i.e. after 24 hours of rotation. In addition, the efficiency of emulsion breaker (Alcopol O 60 %) was evaluated. The results are given in Table 3.6.

The 150°C+ and 200°C+ residue of Sigyn formed emulsions containing only 20-33 vol.% seawater, while the 250°C+ residue incorporated up to 90 vol. % seawater. Similar for the residues was the formation of loose or unstable emulsions. For the heavy weathered residue (250°C+), the analyses showed that when the energy that makes the seawater incorporate in to the oil stops, the emulsions started to break, reducing the water content from 90 vol.% seawater to 29 vol.%.

For the 150°C+ and 200°C+ residues, addition of emulsion breaker only partially breaks and reduces the water content in the emulsions, the highest concentration showing the greatest efficiency. However, for the heavily weathered condensate, 250°C+ residue, the emulsion breaker showed to have an opposite effect, reducing the

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emulsion breakup compared to no treatment of Alcopol O 60 %. A similar effect has also been observed previously for the Skarv condensate (Øksenvåg, 2014). The results indicate that the use of emulsion breaker has a minimal effect or even stabilize the emulsion, and is therefore not recommended for this condensate.

Table 3.6 Stability of Sigyn emulsions and efficiency of emulsion breaker at 13ºC.

Residue	Emulsion breaker (Alcopol O 60%),	Water in emulsion (vol.%)		
		Reference*	24 hours **	24 hours + rot ***
150ºC+	none	20	19	19
200ºC+	none	33	27	27
250ºC+	none	90****	29	38
150ºC+	Alc. O 60 % 500 ppm	20	0	17
200ºC+	Alc. O 60 % 500 ppm	33	25	35
250ºC+	Alc. O 60 % 500 ppm	90****	90****	90****
150ºC+	Alc. O 60 % 2000 ppm	20	0	6
200ºC+	Alc. O 60 % 2000 ppm	33	9	14
250ºC+	Alc. O 60 % 2000 ppm	90****	70	68

ppm: parts per million

*w/o emulsion after 24 hours of rotation

**w/o emulsion after 24 hours' rotation and 24 hours settling

*** w/o emulsion after 24 hours' rotation and 24 hours settling and 10 rotations

**** 90 vol.% due to supersaturation, will not likely happen at sea.

3.3 Chemical dispersibility

The dispersibility testing included:

- Screening of four different dispersants to find the most appropriate and relevant dispersant for the Sigyn condensate
- Dosage testing of the relevant dispersant
- Systematic testing on weathered condensate samples as a basis to predict the time-window for effective use of dispersant at the optimal dosage rate Dispersant to Oil Ratio (DOR)

Screening study of dispersants

The screening testing was performed using the low energy test (IFP), reflecting non-breaking waves (< 5 m/s wind speed). The test was performed according to the Norwegian dispersant testing regulations. The screening test was performed at a standard temperature of 13°C, using a 200°C+ residue emulsified with 50 vol. % seawater with DOR of 1:25. In addition, the high-energy test (MNS) was also tested with use of Corexit 9500 and Dasic NS.

Results from the screening study are listed in Table 3.7. The study show a good dispersing effectiveness (67-74% on IFP and 100% on MNS) using both Dasic NS and Corexit 9500 on the Sigyn condensate.

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Table 3.7 Screening test of dispersants on Sigyn 200°C+ emulsified with 50 vol.% seawater at 13 ºC.

Dispersant (DOR 1:25)	Effectiveness dispersant		Viscosity (mPa.s) shear rate 10 s⁻¹
	IFP	MNS	
Corexit 9500	74	100	52
Dasic NS	67	100	52
Finasol OSR-52	31	-	52
Radiagreen	20	-	52

Based on the fact that Dasic NS is the dispersant agent in NOFO's stockpile, it was decided to use Dasic NS in the dosage rate study as well as to establish the time window for effective use of dispersants.

Dosage rate study of dispersants

The dosage rate study was performed to find the optimal dosage rate for the Sigyn condensate at 13ºC. The study was performed using a 200°C+ residue emulsified with 50 vol. % water, as for the screening study.

Results from the dosage rate study are listed in Table 3.8 and show an increasing effectiveness for the IFP-test with an increase in dosage rate. The MNS results were all high (effectiveness of 82-100%) at all the dosages rates tested, indicating high dispersibility in breaking waves conditions (> 5 m/s wind speed). Based on the high effectiveness results for the MNS dispersibility test, a dosage study without adding dispersant agents would have been beneficial.

Table 3.8 Dosage rate testing of Dasic NS on Sigyn 200°C+, 50 % emulsified with 50 vol.% seawater at 13ºC.

Dispersant (dosage rate)	Effectiveness dispersant		Viscosity (mPa.s) 10 s⁻¹
	IFP	MNS	
Dasic NS (1:200)	23	82	63
Dasic NS (1:100)	58	91	63
Dasic NS (1:50)	78	85	63
Dasic NS (1:25)	67	100	52

Window of opportunity for use of dispersant on Sigyn condensate

A dosage rate of 1:25 (4 wt.%), was used for the continued testing of Sigyn to predict the time window for dispersant use, which is standard procedure to establish the time window for dispersant application. The same dosage rate is usually used as the operational target when applying dispersant on a marine oil spill by vessel or air application.

Results from the systematic dispersibility study are listed in Table 3.9. The results show a quite high dispersing effectiveness for the high-energy test (MNS), for all the residues /emulsions tested. Since Sigyn produce quite unstable emulsions, the water content in the emulsions might vary, and could influence on the effectiveness results from the dispersibility studies.

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Table 3.9 Efficiency of Dasic NS on Sigyn weathered oil at 13°C.

Residue	Water content (vol.%)	Viscosity (mPa.s) 10 s⁻¹	IFP Effectiveness (%)	MNS Effectiveness (%)
150°C+	0	11*	26	100
200°C+	0	61*	37	100
250°C+	0	232*	32	96
150°C+	50	10	67	100
200°C+	50	52	67	100
250°C+	50	330	64	88
150°C+	27 (75)	9	-	-
200°C+	62 (75)	113	-	-
250°C+	75	225	61	89
150°C+	20** (Max. water uptake)	18	47	80
200°C+	27 (Max. water uptake)	65	56	90
250°C+	77 (Max. water uptake)	374	49	100

Viscosity is given for shear 100 s⁻¹ for the fresh oil samples

** For calculation of the effectiveness, water content results from the emulsion stability study was used

-: not analysed

The Sigyn condensate was found to be dispersible with use of both the low-energy test (IFP) and the high-energy test (MNS), for all the emulsified residues tested at 13 °C (summer conditions).

As the condensate incorporate water (emulsify), the wax structure in the condensate breaks up, the viscosity of the oil will then decrease and no longer be a limiting factor for dispersibility and the oil will be more receptive for dispersion. However, if the oil/residue solidify on the sea surface due to high pour points, e.g. at low wind speeds (< 5 m/s) and cold temperatures, one can expect reduced dispersibility since the dispersants droplets could have a reduced ability to diffuse into the oil or and may appear as droplet on the surface of the solidified condensate and be washed of by wave activity.

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4 Predictions with SINTEF Oil Weathering Model (OWM)

The SINTEF OWM relates oil properties to a chosen set of conditions (oil/emulsion film thickness, sea state and sea temperature) and predicts the change rate of the oil's properties and behaviour on the sea surface.

4.1 Input to the SINTEF OWM

Laboratory studies of the weathering properties of Sigyn condensate at 13°C have been conducted. The data are used as input to the SINTEF OWM (version 4.0 beta). Input to the OWM for Sigyn condensate is given in Table 4.1. Basic information about the SINTEF OWM is given in Appendix C.

Table 4.1 Input to the OWM.

Input to the oil weathering model (OWM)	
Oil type	Condensate
Geographical area	The North Sea
Terminal oil film thickness	0.05 mm
Release rate	1.33 metric tons/minute for 15 min., a total of 20 metric tons*
Spill scenario	Surface release
Sea temperature	5°C and 15°C
Wind speed	2 m/s, 5 m/s, 10 m/s and 15 m/s

The weathering properties are normally not significantly influenced on the release rate in OWM.

Oil film thickness

In the SINTEF OWM, the oils are categorized into condensate, emulsifying crude, low emulsifying crude, heavy bunker fuel or refined distillate, based on experimental results obtained in small-scale testing. The terminal film thickness varies among these categories, based on experimental field experience. Sigyn is categorized as a condensate.

Spill scenario

In this project, a surface release at a standard rate of 1.33 metric tonnes per minute was chosen as the spill scenario.

Sea temperature

The prevailing weather conditions may influence the weathering rate of oil on the sea surface. Two sets of predictions are given in this report, one for a typical summer temperature in the North Sea given as prediction at 15°C, and one for average winter temperature, 5°C, both being based on 13°C laboratory data.

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 4.2.

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Table 4.2 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 Sigyn condensate weathering properties

How to use the prediction charts: an example

If Sigyn has drifted on the sea surface, the following prediction charts can be used to determine the remaining oil/emulsion's chemical, physical and emulsifying properties.

Table 4.3 gives an example for the following scenario:

- Drift time: 12 hours
- Sea temperature: 5 °C/15 °C
- Wind speed: 10 m/s

Table 4.3 Weathering properties for Sigyn condensate after 24 hours, obtained from the prediction charts.

Property	Winter temperature (5 °C, 10 m/s)	Summer temperature (15 °C, 10 m/s)
Evaporation, vol.%	81	85
Flash point, °C	115	130
Pour point, °C	27	28
Viscosity of the emulsion, mPa.s	300	150
Water content, vol.%	65	77

mPa.s = cP (mPa.s: SI-standard, cP: Industrial denotation

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Property: EVAPORATIVE LOSS
Oil Type: SIGYN (2017)
Description:
Data Source: Sintef Ocean (2017), Weathering data used

SINTEF

OWModel

Surface release - Terminal Oil film thickness: 0.05 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Jun. 08, 2017

Wind Speed (m/s): 15
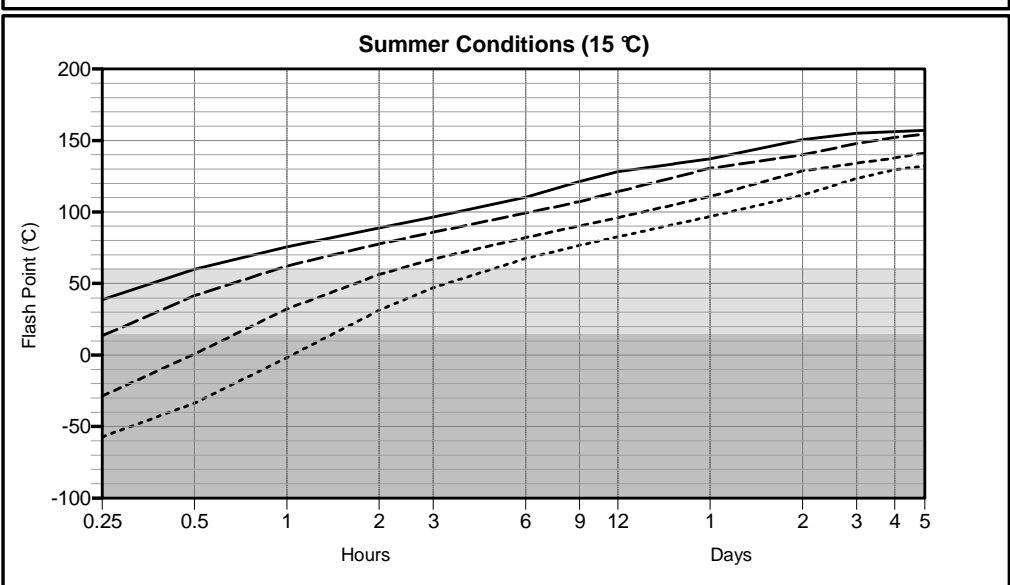Wind Speed (m/s): 10
Wind Speed (m/s): 5
Wind Speed (m/s): 2
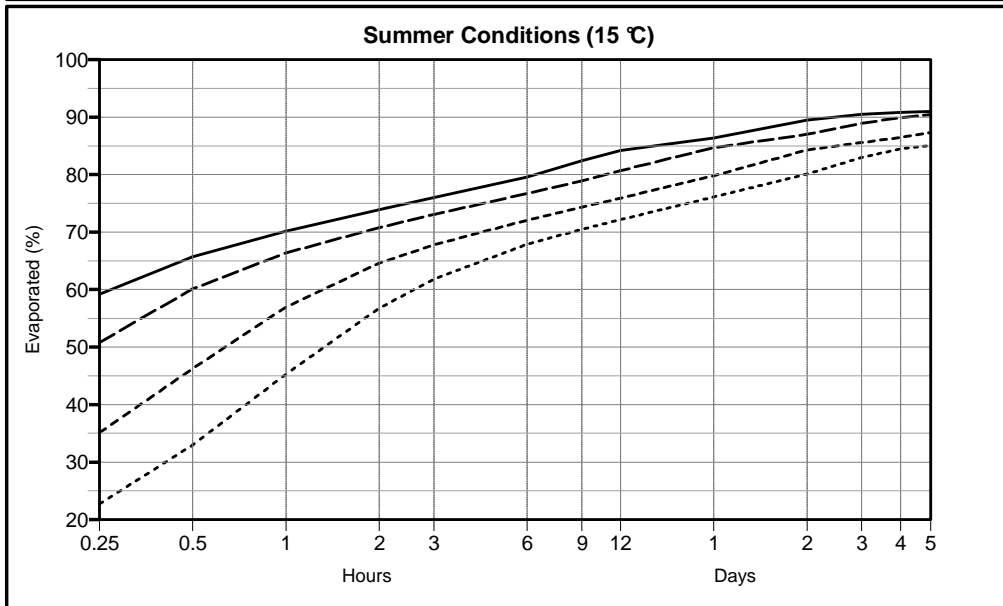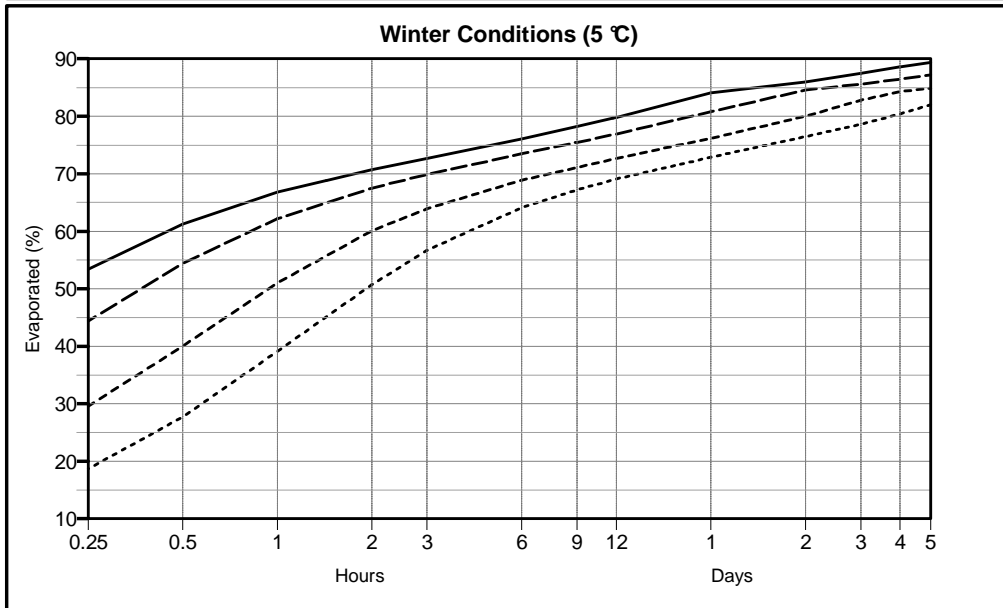
Figure 4.1 Evaporative loss of Sigyn condensate predicted at sea temperatures 5 °C and 15 °C.

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Figure 4.2 Flash point of Sigyn predicted at sea temperatures 5 °C and 15 °C.

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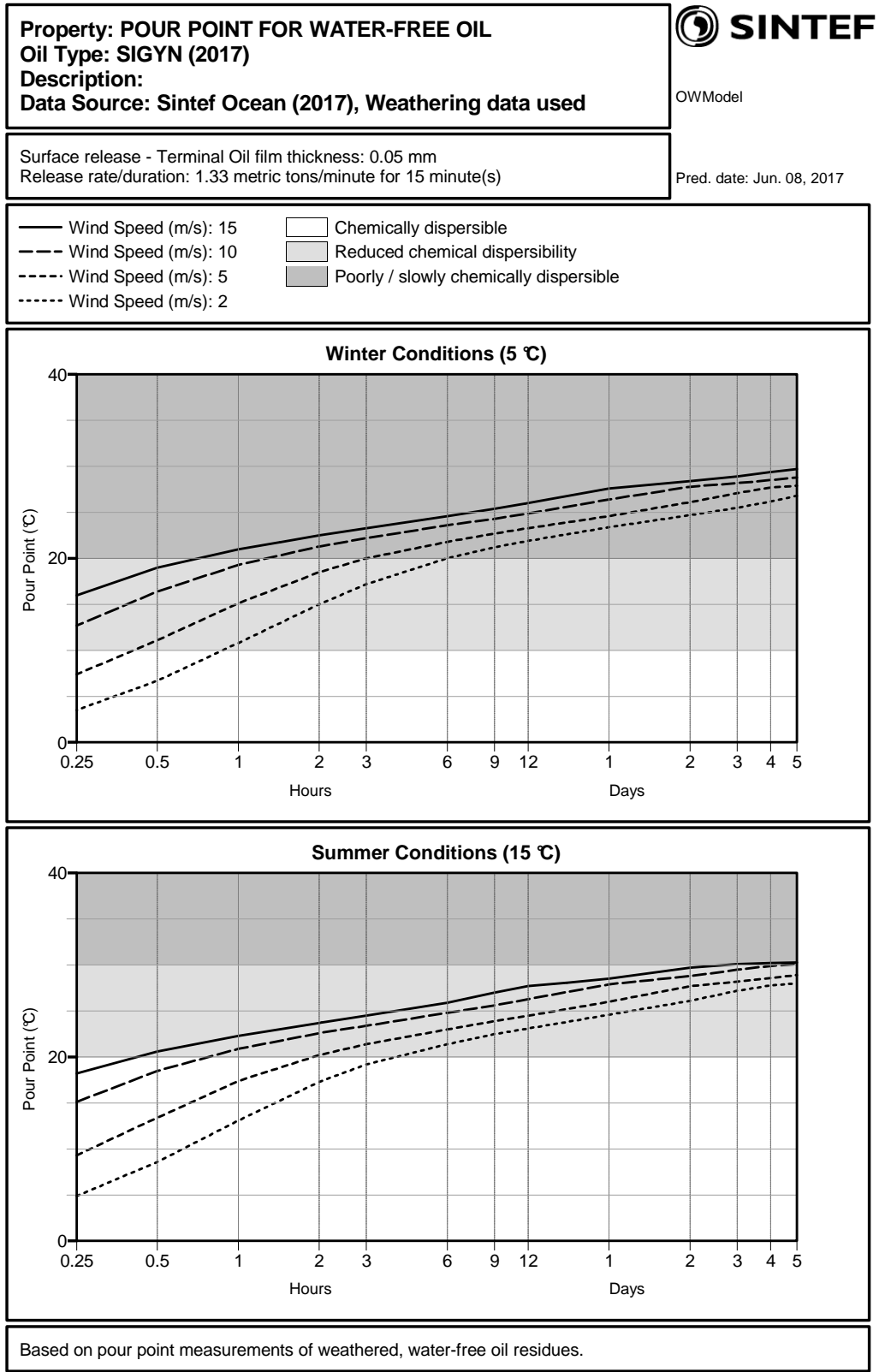
Figure 4.3 Pour point of Sigyn predicted at sea temperatures 5 °C and 15 °C.

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Property: VISCOSITY OF EMULSION
Oil Type: SIGYN (2017)
Description:
Data Source: Sintef Ocean (2017), Weathering data used

SINTEF

OWModel

Surface release - Terminal Oil film thickness: 0.05 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Jun. 08, 2017

——— Wind Speed (m/s): 15
— — — Wind Speed (m/s): 10
– – – Wind Speed (m/s): 5
········· Wind Speed (m/s): 2
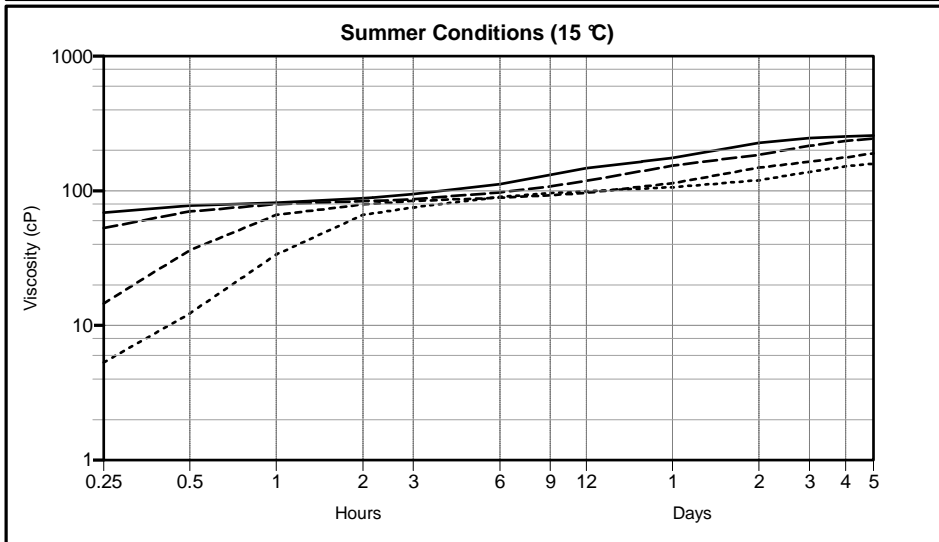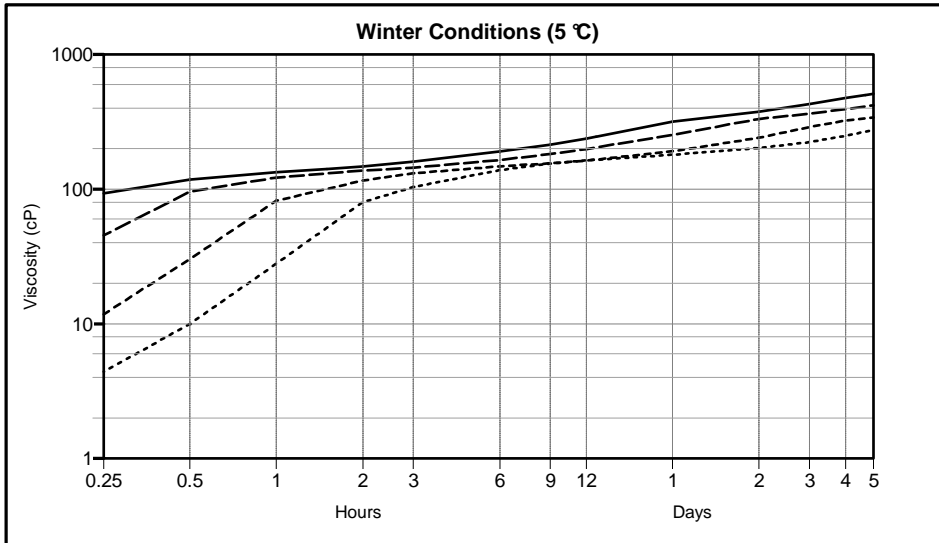
Based on viscosity measurements carried out at a shear rate of 10 reciprocal seconds.

Figure 4.4 Viscosities of Sigyn emulsions predicted at sea temperatures 5 °C and 15 °C. The predictions are based on measurements performed at a shear rate of 10 s^{-1}, but 100s^{-1} for the water free residues.

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Property: WATER CONTENT	SINTEF
Oil Type: SIGYN (2017)	
Description:	
Data Source: Sintef Ocean (2017), Weathering data used	OWModel

| Surface release - Terminal Oil film thickness: 0.05 mm | |
| Release rate/duration: 1.33 metric tons/minute for 15 minute(s) | Pred. date: Jun. 08, 2017 |

——— Wind Speed (m/s): 15
– – – Wind Speed (m/s): 10
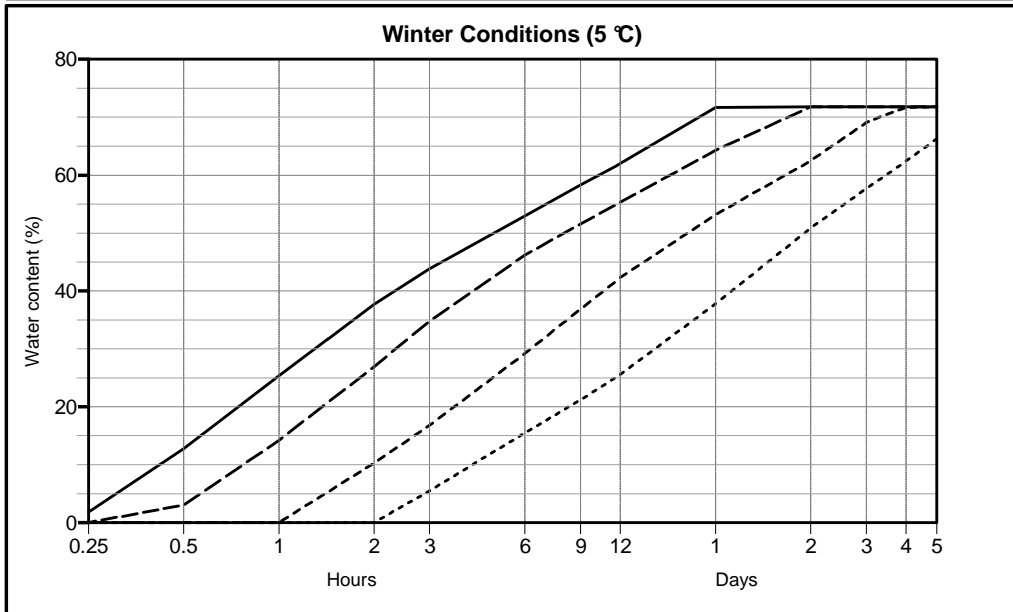----- Wind Speed (m/s): 5
········ Wind Speed (m/s): 2

Winter Conditions (5 ℃)

Summer Conditions (15 ℃)
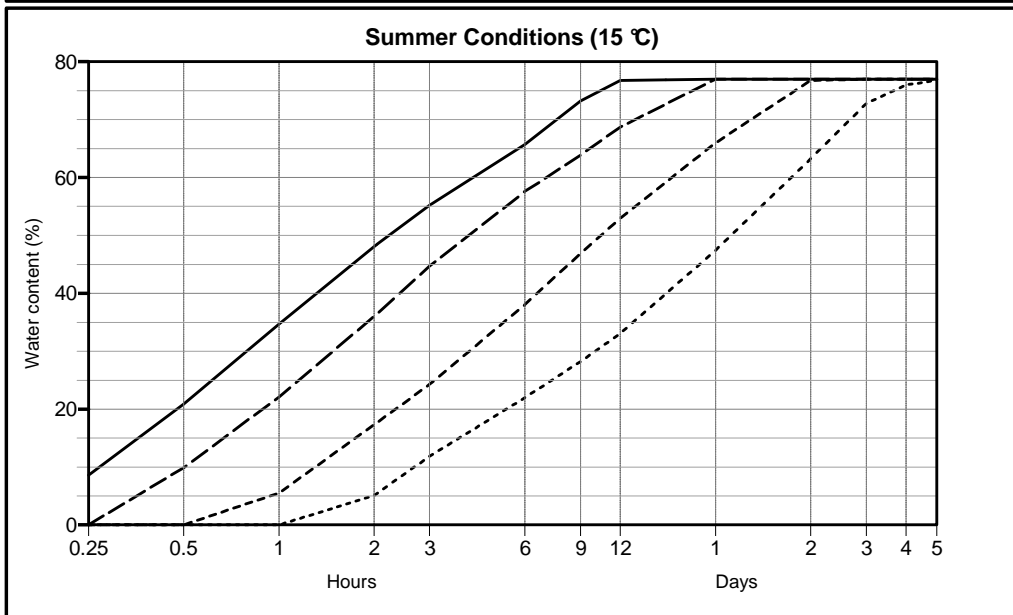
Figure 4.5 Water content of Sigyn predicted at sea temperatures of 5 °C and 15 °C.

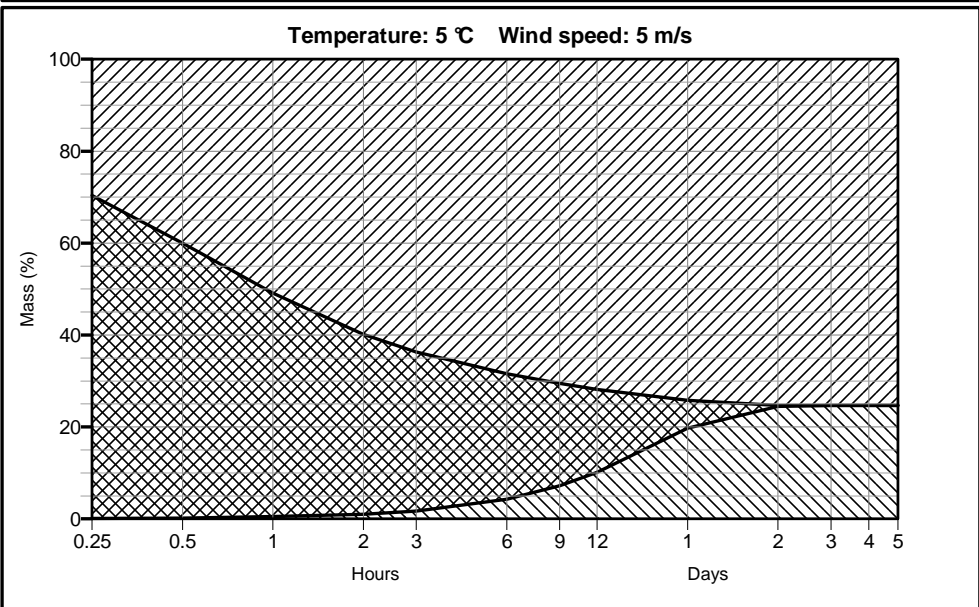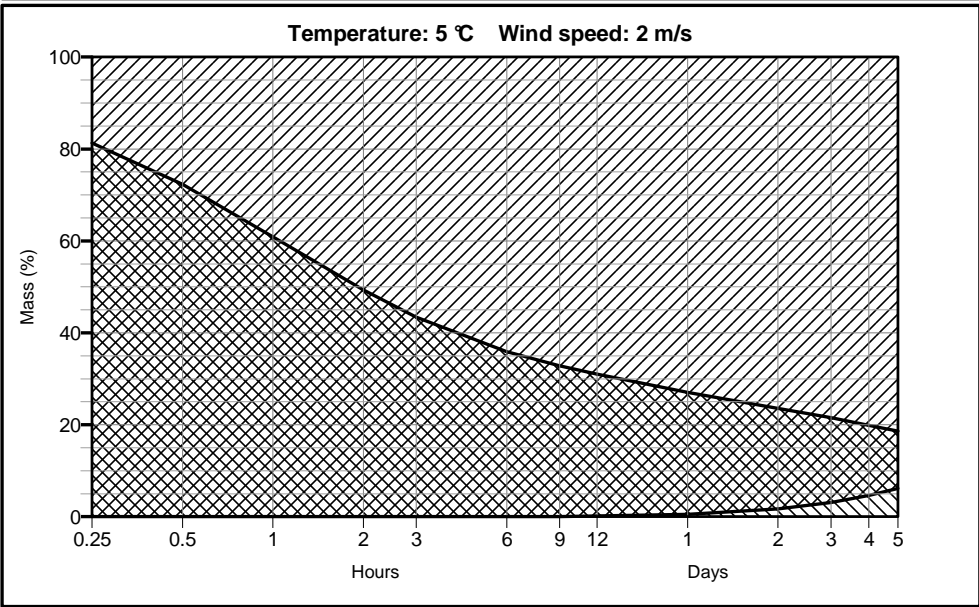| Property: MASS BALANCE Oil Type: SIGYN (2017) Description: Data Source: Sintef Ocean (2017), Weathering data used	**SINTEF** OWModel
Surface release - Terminal Oil film thickness: 0.05 mm Release rate/duration: 1.33 metric tons/minute for 15 minute(s)	Pred. date: Jun. 08, 2017

Evaporated
Surface
Naturally dispersed

Figure 4.6 Predicted mass balance for Sigyn at 5°C and wind speeds of 2 and 5 m/s.

Property: MASS BALANCE	**SINTEF**
Oil Type: SIGYN (2017)	
Description:	
Data Source: Sintef Ocean (2017), Weathering data used	OWModel

| Surface release - Terminal Oil film thickness: 0.05 mm | |
| Release rate/duration: 1.33 metric tons/minute for 15 minute(s) | Pred. date: Jun. 08, 2017 |

Evaporated
Surface
Naturally dispersed

Figure 4.7 Predicted mass balance for Sigyn at 5°C and wind speeds of 10 and 15 m/s.

Property: MASS BALANCE
Oil Type: SIGYN (2017)
Description:
Data Source: Sintef Ocean (2017), Weathering data used

SINTEF

OWModel

Surface release - Terminal Oil film thickness: 0.05 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

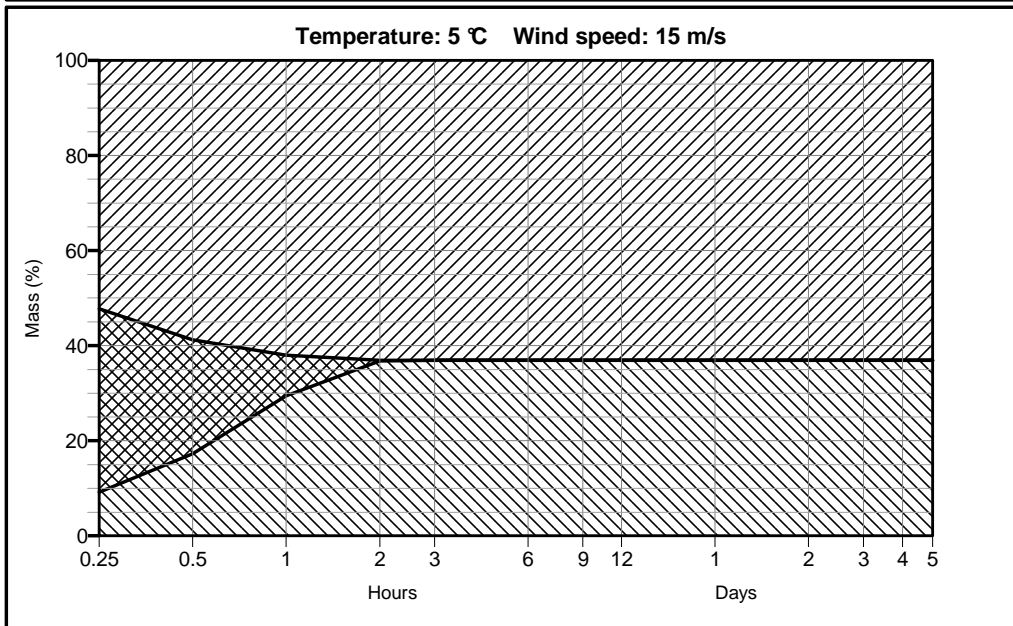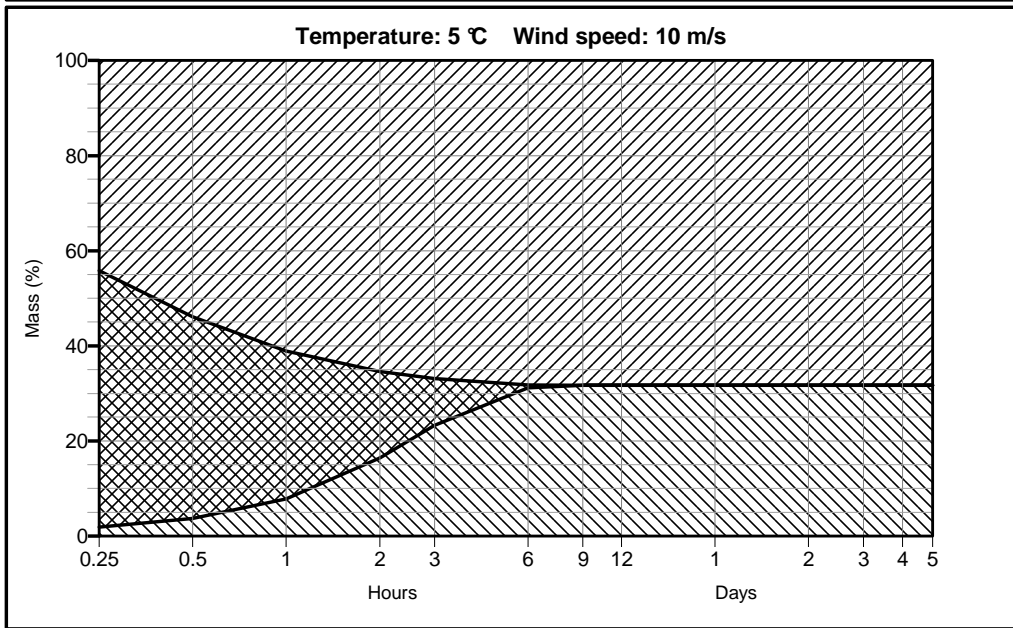Pred. date: Jun. 08, 2017

Evaporated
Surface
Naturally dispersed

Temperature: 15 ℃   Wind speed: 2 m/s

Temperature: 15 ℃   Wind speed: 5 m/s

Figure 4.8 Predicted mass balance for Sigyn at 15 °C and wind speeds of 2 and 5 m/s.

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SINTEF

Property: MASS BALANCE
Oil Type: SIGYN (2017)
Description:
Data Source: Sintef Ocean (2017), Weathering data used

OWModel

Surface release - Terminal Oil film thickness: 0.05 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Jun. 08, 2017

Evaporated
Surface
Naturally dispersed

Temperature: 15 ℃   Wind speed: 10 m/s

Temperature: 15 ℃   Wind speed: 15 m/s

The algorithm for prediction of natural dispersion is preliminary and is currently under improvement. Model predictions have been field-verified up to 4-5 days.

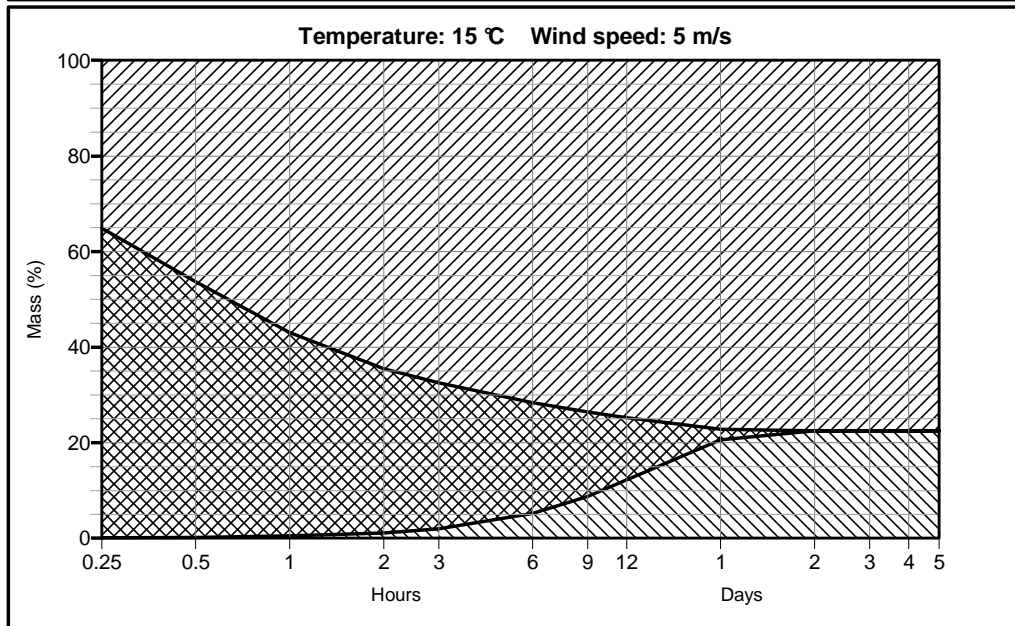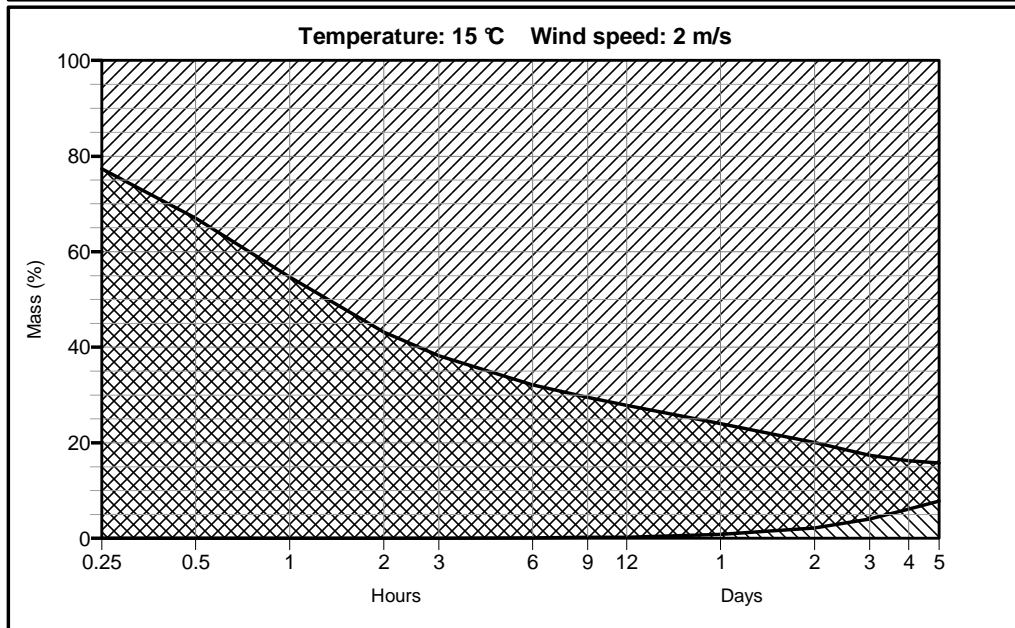**Figure 4.9 Predicted mass balance for Sigyn at 15°C and wind speeds of 10 and 15 m/s.**

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4.3 Comparison with other condensates and oil

The weathering predictions of Sigyn condensate are compared to Kristin light oil, Sleipner condensate, Alve condensate and Gudrun crude oil at 15 °C and 10 m/s, see Table 4.4.

Table 4.4 Predictions for comparison to Sigyn, as given in OWM.

Predictions in OWM
Kristin 2006, 13°C
Sleipner 2002
Alve kondensat petromaks TOF
Gudrun, 13°

Evaporative loss

Figure 4.10 shows that Sigyn contains light components approximately in the same range as Sleipner, but much less than Alve. Kristin and Gudrun (both crude oils) show the lowest evaporative loss.

Figure 4.10 Predicted evaporative loss at 15°C and 10 m/s for Sigyn condensate, compared with other Norwegian condensates and crude oils.

Flash point

When oil is spilled on the sea surface, the temperature of the oil will be cooled to the ambient water temperature within a short period of time. The fire hazard is based on the volatile components from the oil, and will be at its greatest as long as the flash point of the oil is below the sea temperature.

The fire hazard is over within a few minutes of weathering at sea due to rapid evaporation of the light components. As shown in Figure 4.11, there is a potential fire/explosion hazard for Alve condensate and Kristin light oil within the first 30 minutes as the flash point is below the sea temperature of 15°C at a wind speed of 10 m/s.
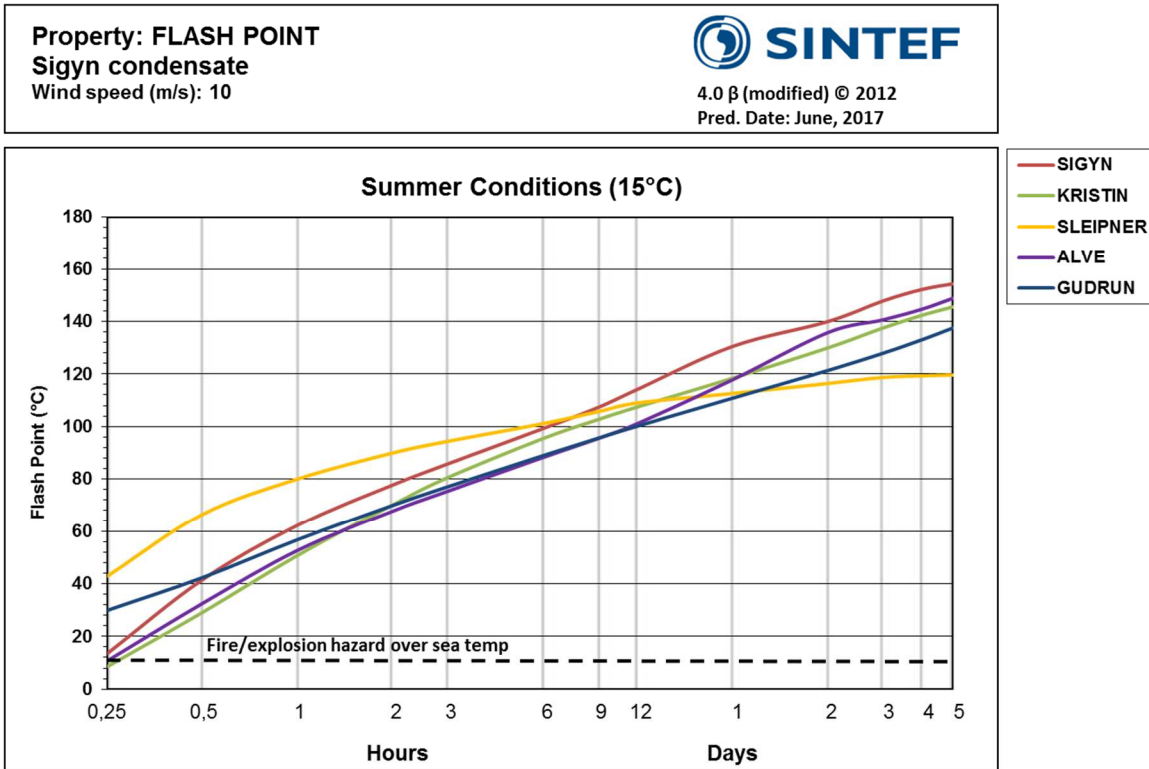
Figure 4.11 Predicted flash point at 15°C and 10 m/s for Sigyn, compared with other Norwegian condensates and crude oils.

Pour point

Pour point depends on the condensates/oils wax content and the content of light components that are able to keep the waxes dissolved in the oil. Solidification typically arises at 5-15°C above sea temperature (see dotted line in Figure 4.12). Water free residues has a potential to solidify, and high pour points of Sigyn might cause solidification quite rapidly after an oil release at sea (approx. after 6 hours). The same accounts for the Kristin, which also contain a large content of wax.

Property: POUR POINT
Sigyn condensate
Wind speed (m/s): 10

SINTEF

4.0 β (modified) © 2012
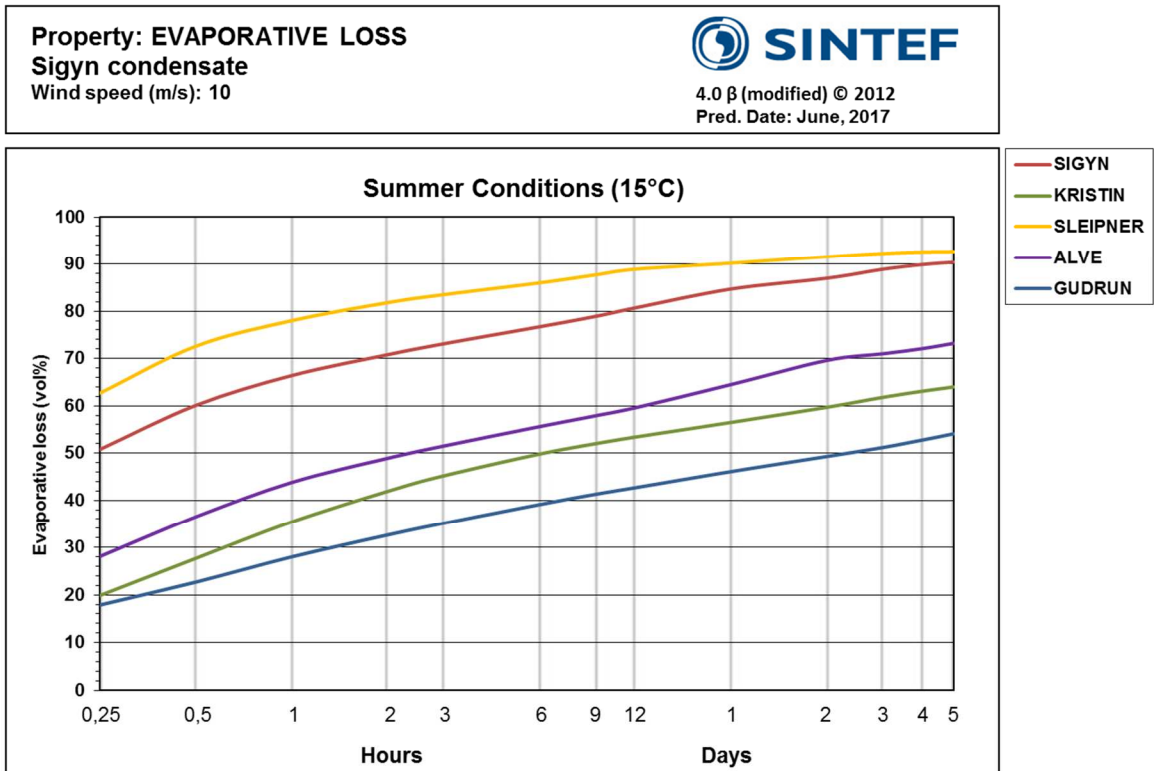Pred. Date: June, 2017

Summary Conditions (15°C)
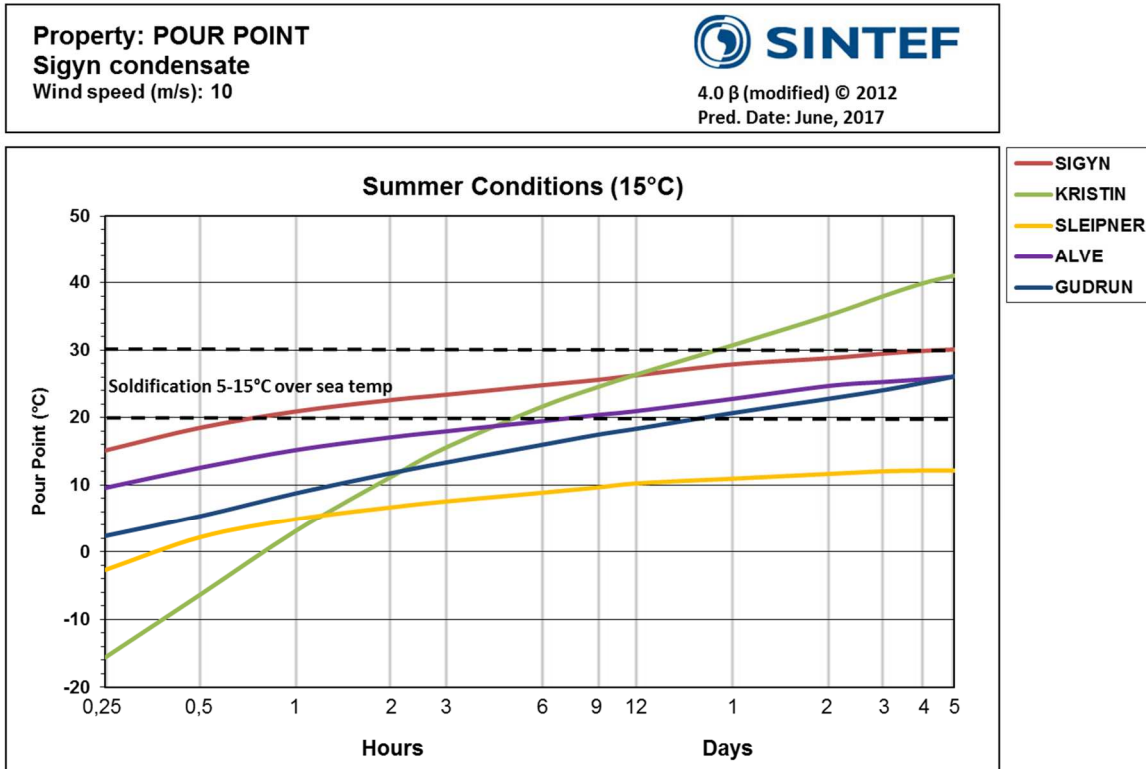
Figure 4.12 Predicted pour point at 15°C and 10 m/s for Sigyn condensate, compared with other Norwegian condensates and crude oils.

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Water content

Sigyn has the property to emulsify giving a maximum water uptake of (~ 77 vol. %), but the emulsions formed were quite loose or unstable and broke quite easily, resulting in low viscosities, see Figure 4.13 and Figure 4.14. Sleipner and Alve show no emulsification at all during the time scale predicted.
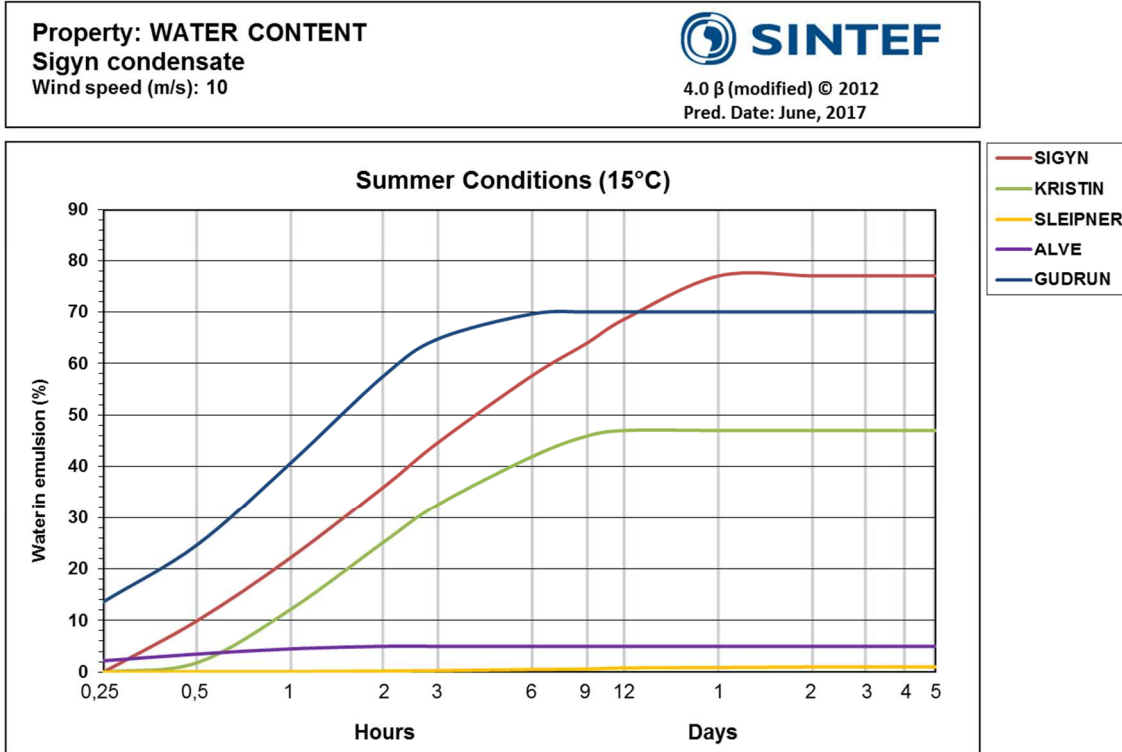
Figure 4.13 Predicted water content at 15 °C and 10 m/s for Sigyn condensate, compared with other Norwegian condensates and crude oils.

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Emulsion viscosity

Figure 4.14 shows a limited increase in viscosity as a function of time, which gives the same results as the other condensates of Sleipner and Alve. Kristin light oil and Gudrun crude oil have a greater ability to form stable emulsions and the viscosities increases with time, primarily as a function of emulsification.
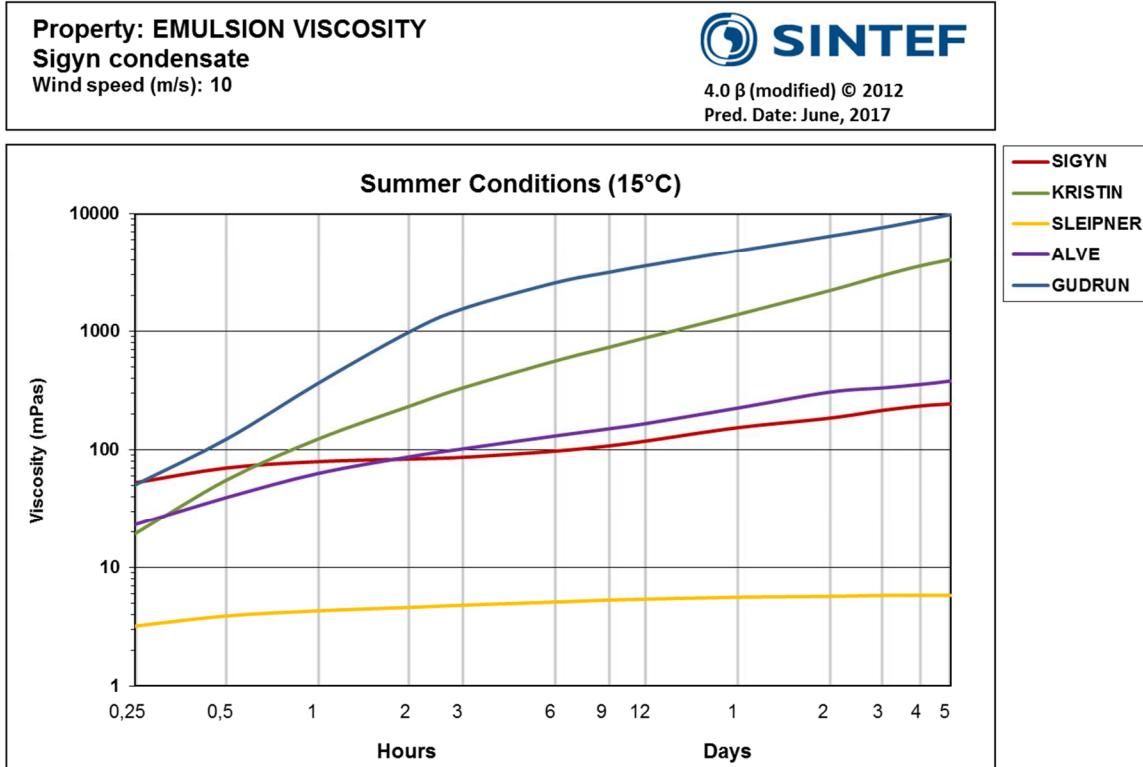
Figure 4.14 Predicted viscosity of the emulsions at 15 °C and 10 m/s for Sigyn, compared with other Norwegian condensates and crude oil.

Mass balance of surface slick

The mass balance of the total surface oil is shown in Figure 4.15 as a function of weathering. The total surface slick is reduced due to evaporation and natural dispersion. However, water mixed into the oil might increase the volume. Sigyn is predicted to have a limited lifetime at sea at high wind speeds, where the condensate is evaporated and naturally dispersed /entrained within the first 6 hours. The Sleipner condensate is predicted to be even less persistent on the sea surface. The crude oils, Kristin and Gudrun, show longest lifetime at sea, but also Kristin will be totally evaporated and/or dispersed after a day or two.
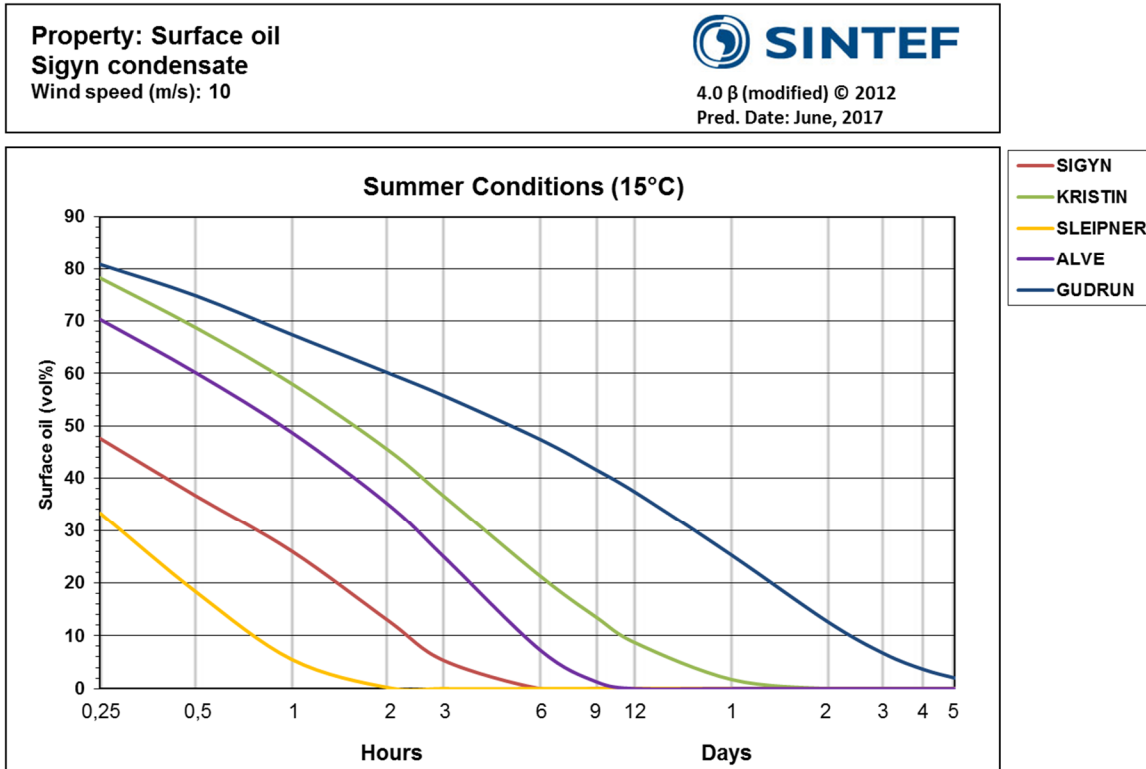

Figure 4.15 Predicted surface oil as a function of time at 15 °C and 10 m/s for Sigyn, compared with other Norwegian condensates and crude oils.

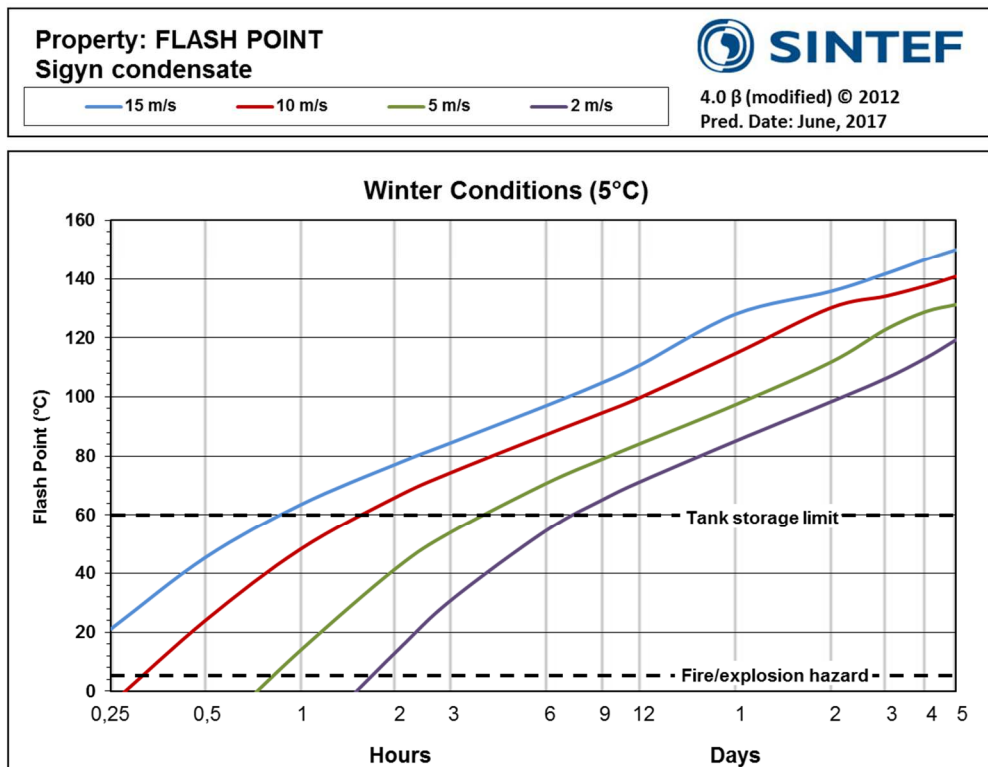# 5 Weathering properties of Sigyn condensate related to oil spill response

In general, the lighter compounds will evaporate during an oil spill, causing an increase in the relative amount of wax and asphaltenes, especially in the early stages of weathering. Knowledge about how the oil properties change during weathering is important in an oil spill response.

Sigyn condensate has a density of 0.740 g/mL, low asphaltene content (0.01 wt. %) and high wax content of 3.14 wt.%. Sigyn has a high evaporative loss, 82% for 250°C+ and lacks the ability to form stable w/o-emulsions. Based on the GC/FID analyses (Figure 3.2), and the mentioned properties, the oil is categorized as a paraffinic condensate, with systematic n-alkanes (nC_5-nC_{30}). The categorization of crude oils, light oils and condensates are described in Appendix A. The evaporated residues have high pour points that may result in solidification. The fate of the solidified oil film is dependent on the environmental conditions. Under calm conditions and low temperature, the evaporation will probably be slowed down due to the solidification, and spreading of the oil may be restricted. The residue from the Sigyn condensate is categorised as a "class 3 - solidifying oil", according to the recommendations from the TOF project (Thin Oil Films) by Singsaas et al., 2017.

5.1 Flash point - fire/explosion hazard

As oil is spilled on the sea surface, the temperature of the oil will be cooled to the ambient water temperature within a short period of time. The fire hazard will be at its greatest as long as the flash point of the oil is below the sea temperature. For Sigyn, the flash point will be above the sea temperature within the first 2 hours for both summer and winter temperature.

Some vessels engaged in oil recovery operations may not be classified to carry liquids with flash point lower than 60°C (e.g. towing vessels, smaller cargo or vessels available in a spill situation). At low wind speed (2 m/s) this limit will be reached within approximately 7 hours in winter conditions and 5 hours at summer conditions. The flash point limitations will be reached much faster at higher winds speeds due to higher evaporation, see Figure 5.1

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Figure 5.1 Flash point at different sea states of Sigyn condensate at 5 ᵒC and 15 ᵒC.

5.2 Pour point - solidification

The water free residue of Sigyn have the potential to solidify. However, when the condensate is spilled on the sea surface it normally starts to mix with the seawater, and the wax lattice will then be disturbed with applied mechanical stress. The emulsion formed is not expected to be stable, and the viscosities decreases compared with the water free residues. Therefore, solidification is not expected to be a likely scenario in a spill situation at summer temperatures, under breaking waves conditions (> 5 m/s wind speed). However, Sigyn may solidify after a release at winter conditions and form lumps/flakes of solidified residue, especially at calm weather conditions, see Figure 5.2. Solidification on sea surface is known to start at pour points 5-15 °C above the sea temperature.
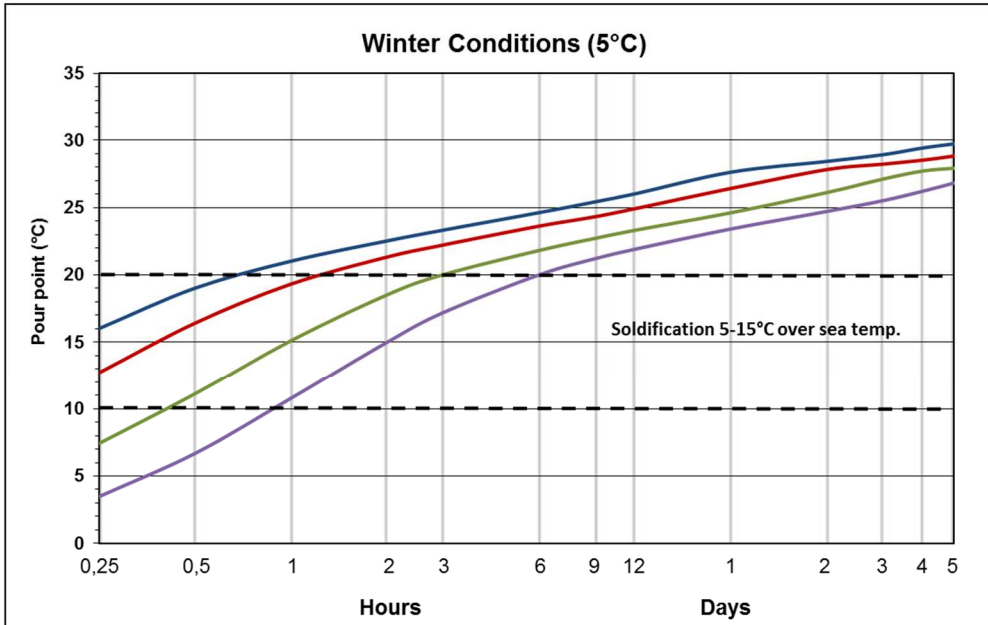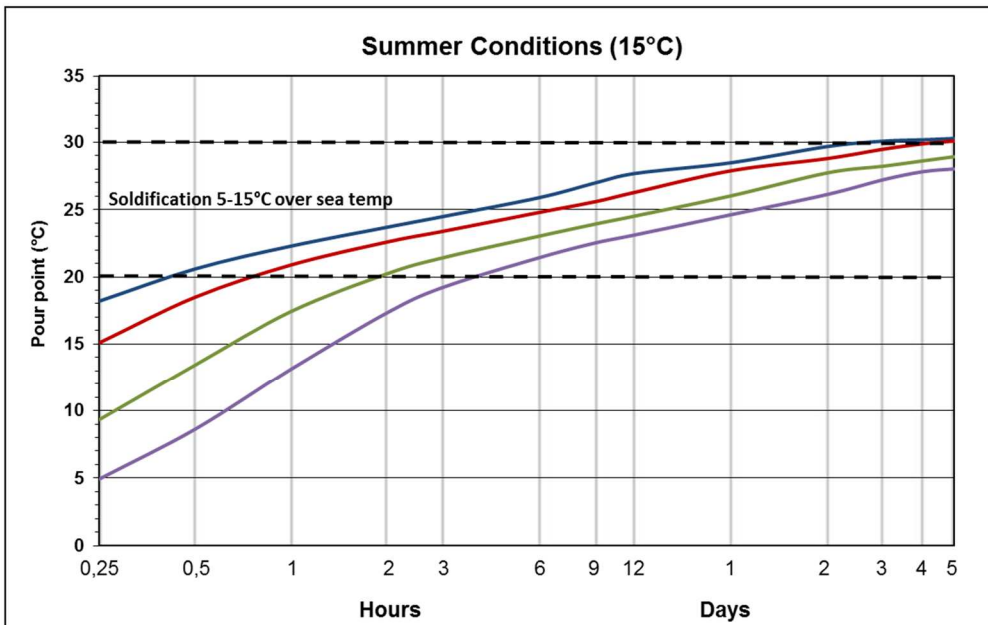
Figure 5.2 Pour point at different sea states of Sigyn condensate at 5 °C and 15 °C.

5.3 Lifetime at sea

The lifetime of an oil spill at sea depends on the oil's composition, the release conditions (e.g. on the surface, underwater) and environmental conditions (temperature, wind, waves). Natural dispersion and evaporation are the main weathering processes that remove an oil spill from the surface. It is expected that Sigyn rapidly will spread on the sea surface with high degree of evaporation loss and natural dispersion. Figure 5.3 shows that the amount surface oil (%) is dependent on the wind speeds. In high wind speeds (10-15 m/s), Sigyn is predicted to have a low lifetime on the sea surface, less than 6 hours. However, at calmer sea conditions (2-5 m/s), the oil is predicted to be more persistent.
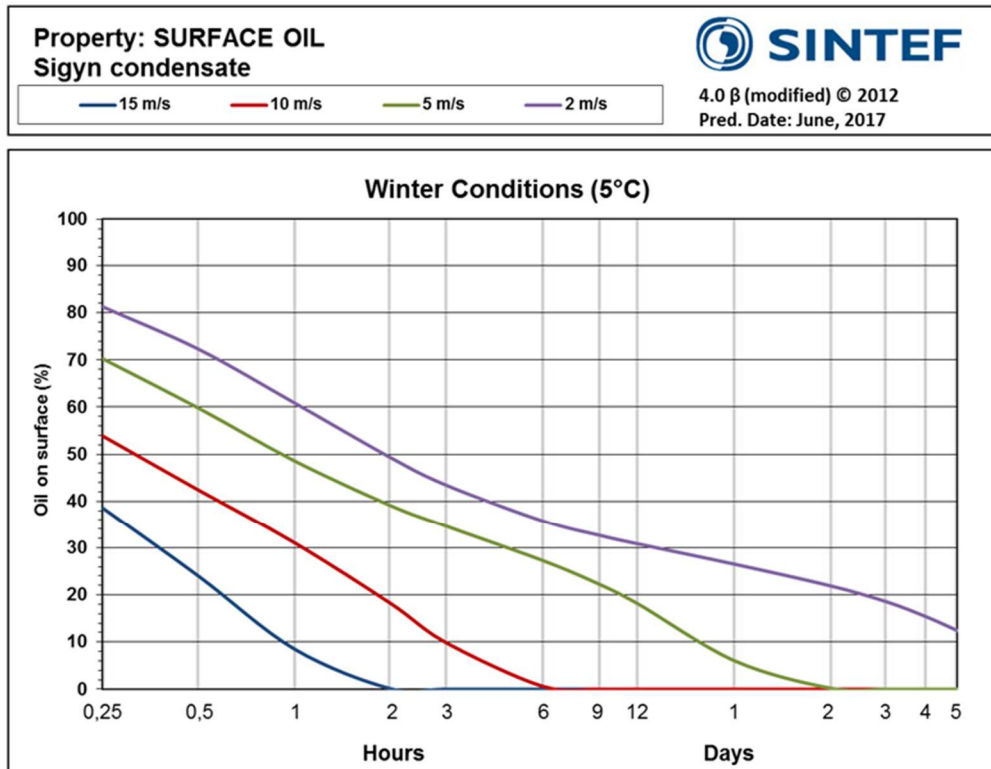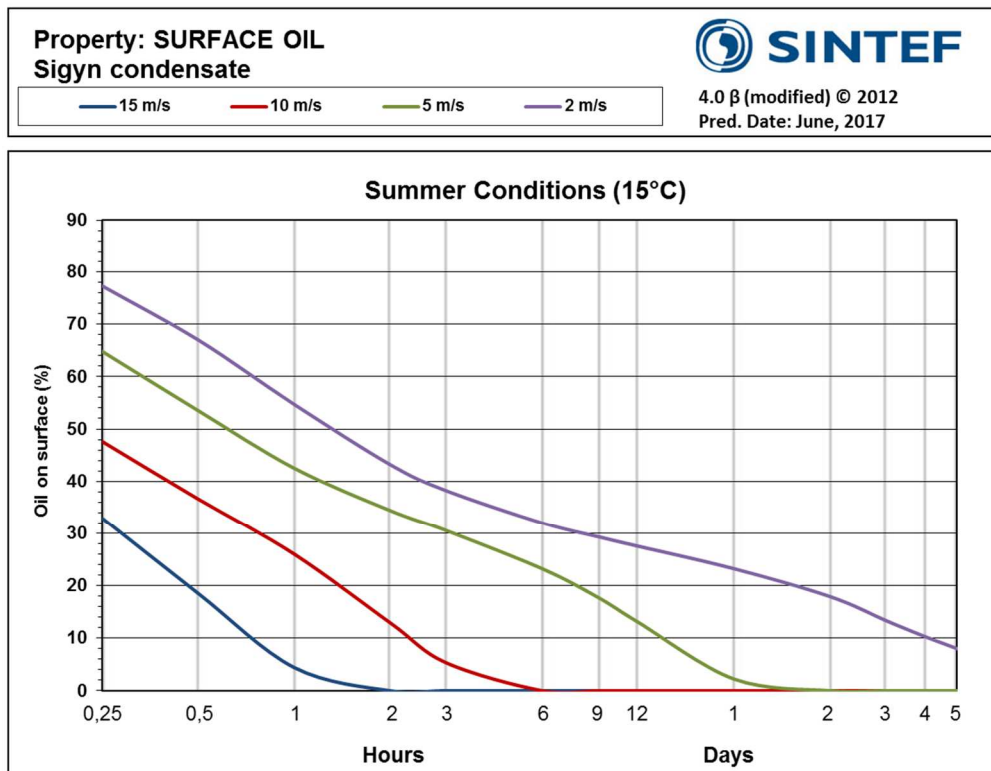
Figure 5.3 Surface oil under different wind speeds for Sigyn condensate at 5 °C and 15 °C.

5.4 Emulsion film thickness

A minimum film thickness requirement for mechanical recovery is 0.1 mm – 0.2 mm, while film thicknesses > 0.05 mm – 0.1 mm can be considered for application of oil spill dispersants. With a surface release at sea, both chemical dispersion and mechanical recovery could be applied for the Sigyn condensate, both under summer and winter conditions. The emulsion film thickness will hence not be a limiting factor. Up to 0.2 mm film thickness, mechanical dispersion by water flushing (e.g. by using FiFi monitors or high capacity water flushing boom) should be considered. It should be emphasized that that a subsea release is expected to give lower initial film thickness, but this would also be dependent on the spill scenario and other factors as gas-oil ratio, water depth etc.

Property: Emulsion film thickness
Sigyn condensate

| — 15 m/s | — 10 m/s | — 5 m/s | — 2 m/s |

SINTEF

4.0 β (modified) © 2012
Pred. Date: June, 2017

Winter Conditions (5°C)

Reduced mechanical recovery < 0.1-0.2 mm

Reduced effectiveness of dispersants < 0.05-0.1 mm

Emulsion film thickness (mm)

Hours   Days

Property: Emulsion film thickness
Sigyn condensate

| — 15 m/s | — 10 m/s | — 5 m/s | — 2 m/s |

SINTEF

4.0 β (modified) © 2012
Pred. Date: June, 2017

Summer Conditions (15°C)

Reduced mechanical recovery < 0.1-0.2 mm

Reduced effectiveness of dispersants < 0.05-0.1 mm

Emulsion film thickness (mm)

Hours   Days

Figure 5.4 Expected time window for effective use by mechanical recovery and dispersants, as a function of emulsion film thickness for Sigyn at 5 °C and 15 °C, surface release. The emulsion film thickness graphs are stopped according to the lifetime of the surface oil, as presented in Figure 5.3.Figure 5.3 Surface oil under different wind speeds for Sigyn condensate at 5 °C and 15 °C.

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5.5 Mechanical recovery

After a spill, the Sigyn condensate will probably spread and form a thin oil film on the sea surface, having a limited lifetime on the sea surface. The use of traditional mechanical recovery systems is assumed to have low efficiency on thin oil films (< 0.1 mm). Other limitations for effective mechanically recovery is related to the oil/emulsion viscosity. For instance, low viscosities (< 1000 mPa.s) may result in boom leakage (Nordvik et al., 1992), while high viscosity oils (>15 000 - 20 000 mPa.s) may be difficult to collect when using weir skimmers due to low flowability. The Sigyn condensate is predicted to have viscosities < 600 mPa.s for the first days at sea under summer and winter conditions, and reduced efficiency for mechanical recovery with use of booms should be expected, see Figure 5.5.

In cases where low viscosity of the oil/emulsion is a limiting factor for use of booms, the high pour point could cause solidification after some time on the sea surface, generating lumps with higher thicknesses, and confinement in a boom could after all be feasible. However, if spread over large areas this could be challenging.

Limits for mechanical dispersion by water flushing is presented in Figure 5.5, and will be discussed in Chapter 5.6.
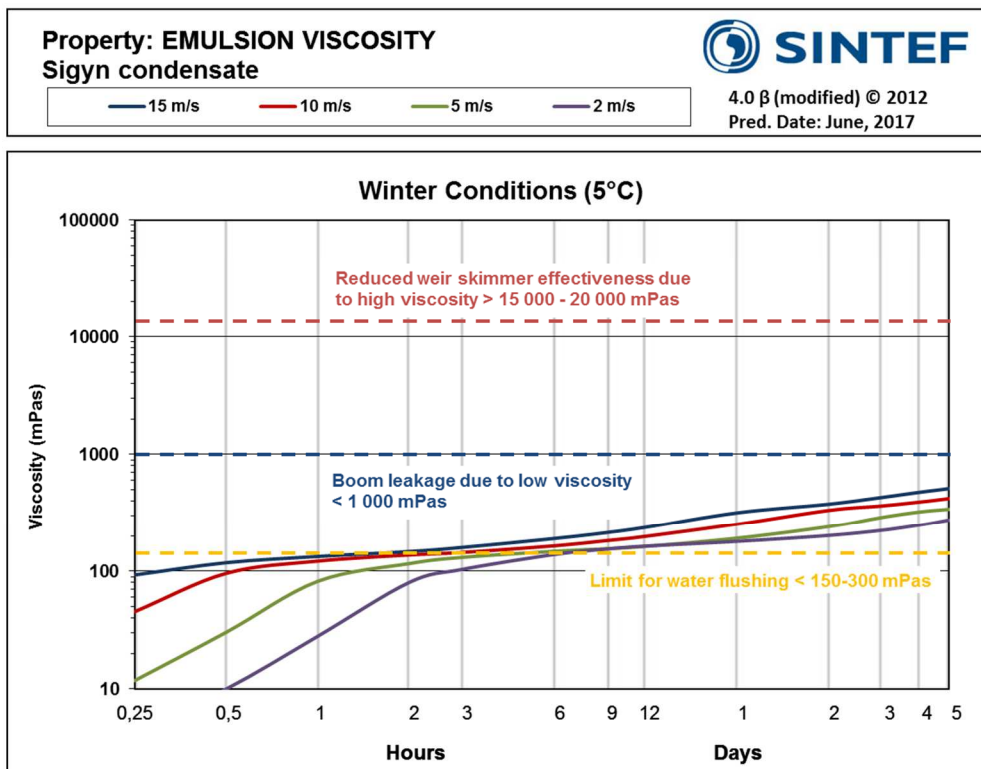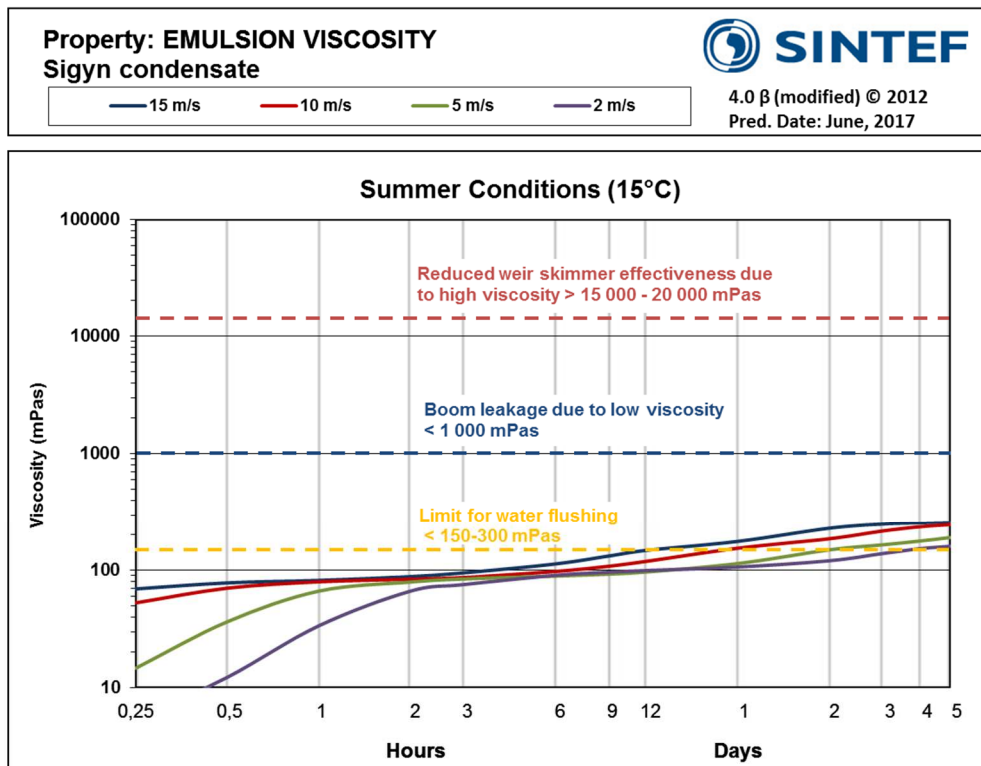
Figure 5.5 Expected time window for effective use of booms, skimmers and water flushing as a function of viscosity for Sigyn at 5 ºC and 15 ºC.

5.6 Mechanical dispersion by water flushing

In spill scenarios with thin initial film thickness 0.2-0.3 mm (e.g. subsea release), mechanical dispersion by water flushing could have a potential. Water flushing from high-capacity water flush boom or by using the Fi-Fi monitors could have a potential for breaking up oil/emulsion with viscosities < 150-300 mPa.s into smaller droplets, particularly at summer conditions, see Figure 5.5. This technology was tested in a full-scale trial (NOFO Oil-on-Water trial) in 2016, and is described by Daling et al., 2017 and Sørheim et al., 2017. Mechanical dispersion by water flushing could also be used in combination with chemical dispersant (see Chapter 5.7). It should be emphasized that this technology by water flushing has not been implemented as a part of the oil spill response in Norway, today.

5.7 Dispersibility with use of chemical dispersants

The use of chemical dispersants assumes film thicknesses > 0.05 - 0.1 mm, and also depends on the lifetime of the slick. The emulsion film thickness has shown to not be a limiting factor for chemical dispersion, at neither summer nor winter conditions for the time window predicted, see Figure 5.4. However, it is expected that Sigyn will have a limited lifetime at sea at high wind speeds (>10 m/s), this due to spreading on the sea surface, with high degree of evaporation loss and natural dispersion, as shown in Figure 5.3. The laboratory testing showed that use of chemical dispersant has a potential in summer conditions. It could nevertheless be beneficial to add some extra artificial energy to enhance the dispersion rate, particularly in calm sea conditions, to increase the dispersant efficiency.

In calm weather conditions and winter temperature, the residue of Sigyn may solidify on the sea surface resulting in reduced dispersibility. The dispersant droplets could then have a reduced ability to diffuse into the oil and may appear as droplets on the surface of the solidified condensate and be washed of by wave activity. The use of dispersant should preferably be used before solidification, but when the oil has reduced dispersant

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efficacy, chemical dispersion in combination with mechanical dispersion by water flushing could enhance the dispersion effectiveness of the oil. However, in higher sea states the water and oil will normally be mixed and generate a thin oil film on the sea surface with a limited lifetime, and hence enhance the natural dispersion into the water column.

In a spill situation, the use of a dispersibility testing kit is recommended to assess the potential for chemical dispersion of the oil/emulsion both in summer and winter conditions.

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Appendices

A The behaviour of crude oil on the sea surface

The Sigyn condensate was given the SINTEF ID 2017-113. The laboratory results were registered in the laboratory information management system (LIMS).

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 heteroatomic organics see Figure A 1.
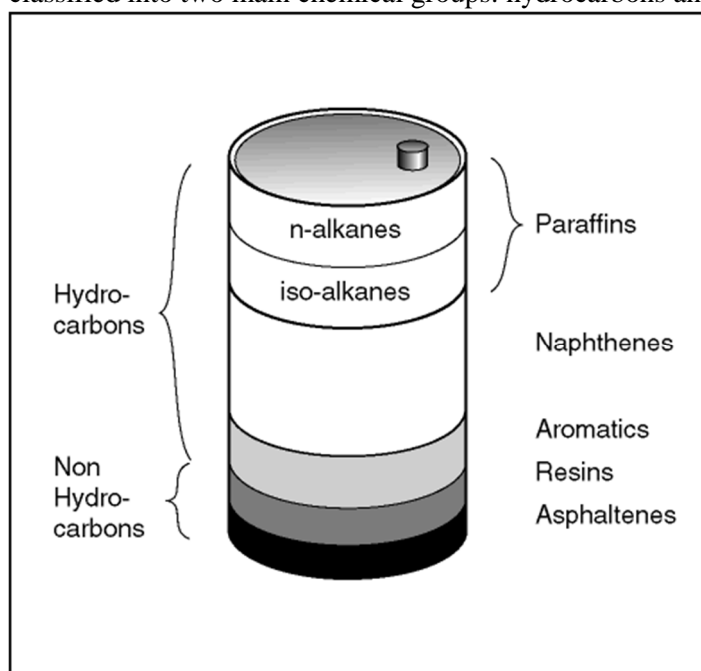
Figure A 1 The chemical composition of crude oils.

A.1.1 Hydrocarbons

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

Naphthenes

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

Aromatics

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

A.1.2 Heteroatomic organics

In addition to pure hydrocarbons, 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. The two most important groups of heteroatomic organic compounds are resins and asphaltenes.

Resins

Resins are relatively polar compared to the hydrocarbons, 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

This is a complex group of poorly characterized chemical compounds that consist of condensed polycyclic aromatic compounds. They are large molecules with 6-20 aromatic rings and side chains (molecular weight 1000-10000). Asphaltenes may be classified as "hard" or "soft" on the basis of the method of determination. Crude oils may contain up to 6 wt. % "hard" and 10 wt. % "soft" asphaltenes.

A.2 Main oil categories – Related to weathering

The relative composition of oils will differ extremely, resulting in great variations in physical properties and following, behaviour after a spill at sea. Related to weathering oils can roughly be divided into 3 main categories:
- Crude oils
- Light oils
- Condensates

Crude oils contain relatively more of the heavier components than the other two categories, and the 250˚C+ residue (corresponds to 0.5 to 1 week after a spill at sea) evaporates less than 50 vol. %. The heavier components make possible formation of stable water-in-oil (w/o) emulsions, which reduces the 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 differentiated in the reservoir terminology. However, related to weathering studies, it is suitable to deal with the light oils as a separate category. Light oils have a high content of light components, and the 250˚C+ residue evaporates less than 50 - 70 vol. %. In contrast to condensates light oils also contain heavier components. The content of these heavier, emulsion-stabilizing components cause that light crudes may emulsify water. These w/o emulsions are, however, very unstable. A light oil will spread less than a condensate, and a final film thickness of 0.5 mm is estimated.

Condensates evaporates typically more than 70 vol. % for the 250˚C+ residue. Condensates will not contain components as asphaltenes and heavier waxes, and will not emulsify significantly amounts of water. The spreading is vast, with a final film thickness in the order of 0.05 mm.

A.2.1 Crude oil categorization

SINTEF has developed a concept for tentative categorization of oils into main groups; paraffinic, waxy, naphthenic, and asphaltenic oils, as described below:
- **Naphtenic oils**, characterized by a disrupted n-alkanes pattern in the gas chromatogram due to biodegradation of the oil in the reservoir. The content of paraffin's is therefore normally low.
- **Paraffinic oils,** often characterized by a low density which reflects a high content of light components (paraffines).
- **Asphaltenic oils,** with a high content of heavier components. The content of lighter components is correspondingly low, reflected by high density and low evaporation.

- **Waxy oils,** often exhibit high pour points due to a large content of wax components. At low temperatures these oils can have a tendency to solidify at the sea surface, especially if the seawater temperature is 5-15°C below the pour point.

A.3 Physical properties of crude oils

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

Density

The density of a crude oil is dependent on the density of all of its components. The density of the hydrocarbons increases with increasing molecular weight. Furthermore, paraffinic oils have lower density than those containing large amounts of high molecular weight aromatics, naphthenes and asphaltenes. Specific gravity is defined as the oil density at 60°F (15.5°C) divided by water density at 60°F. In American literature, the density of the oil is often expressed as °API, where:

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

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

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

A.3.1 Rheological properties

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

Absolute viscosity is: *force distance/area speed* and has the unit: dyn·sec/cm^2. = 1 Poise. The industry is often using the unit mPa·s = centipoise (cP). 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 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 in the area of typically 0.9 – 1 g/ml, the units cSt and cP will often have similar values.

The 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 quite 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 and Zagorski, 1982). The difference in viscosity for crude oils is approximately 3 to 2000 mPa·s for fresh crude oils and several hundred/thousand mPa·s for their residues.

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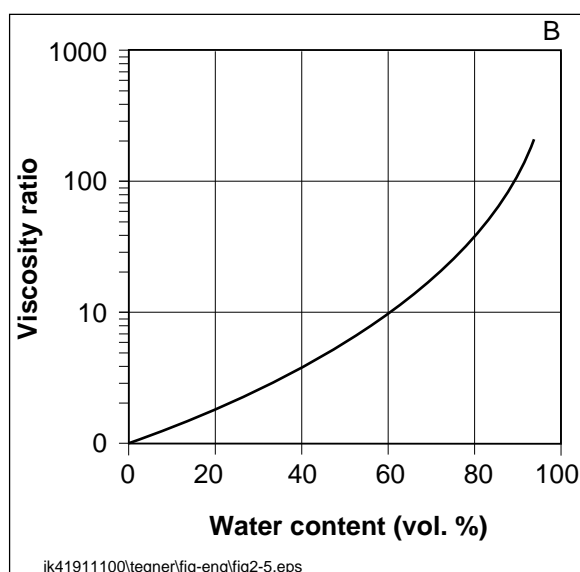
Figure A 2 Example of viscosity ratio as a function of water content

A.3.2 Pour point

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

A.3.3 Distillation curve (True Boiling Point curve – TBP)

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 particular 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 isoalkanes 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.

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

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

A.4 The behaviour of crude oil spilled at sea

There is a number of 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 and the release of oil components into the water column, 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.
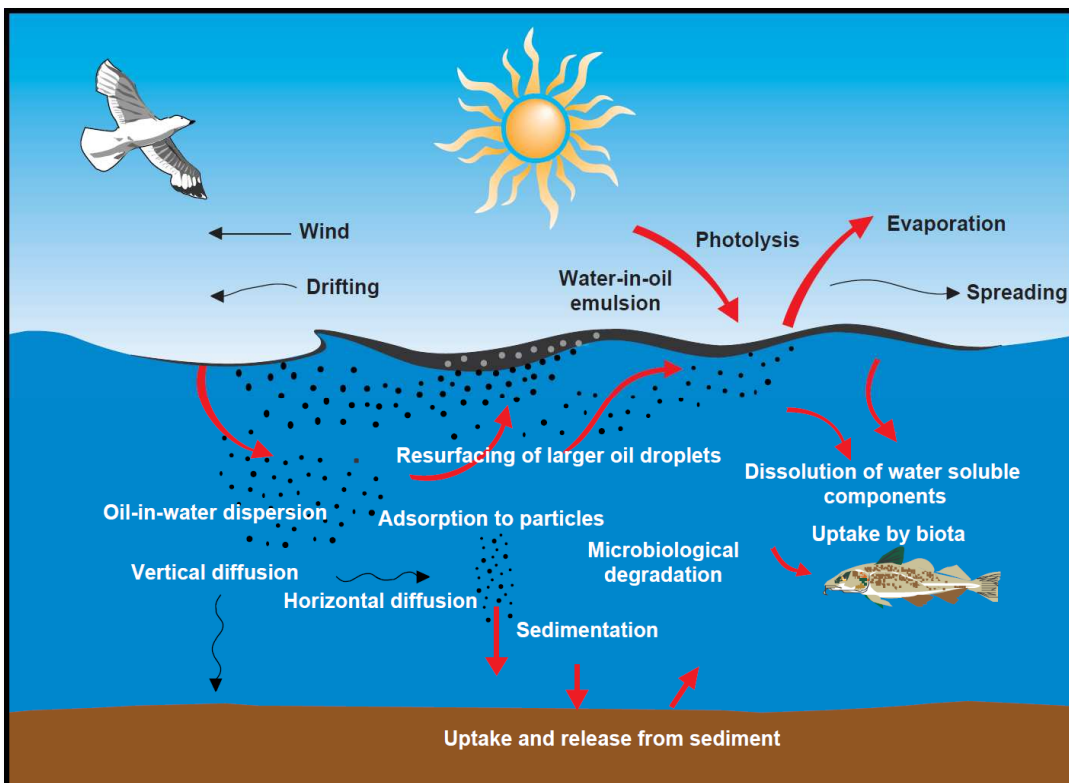

Figure A 3 Illustrating the weathering processes that take place when oil is spilled on the sea surface.
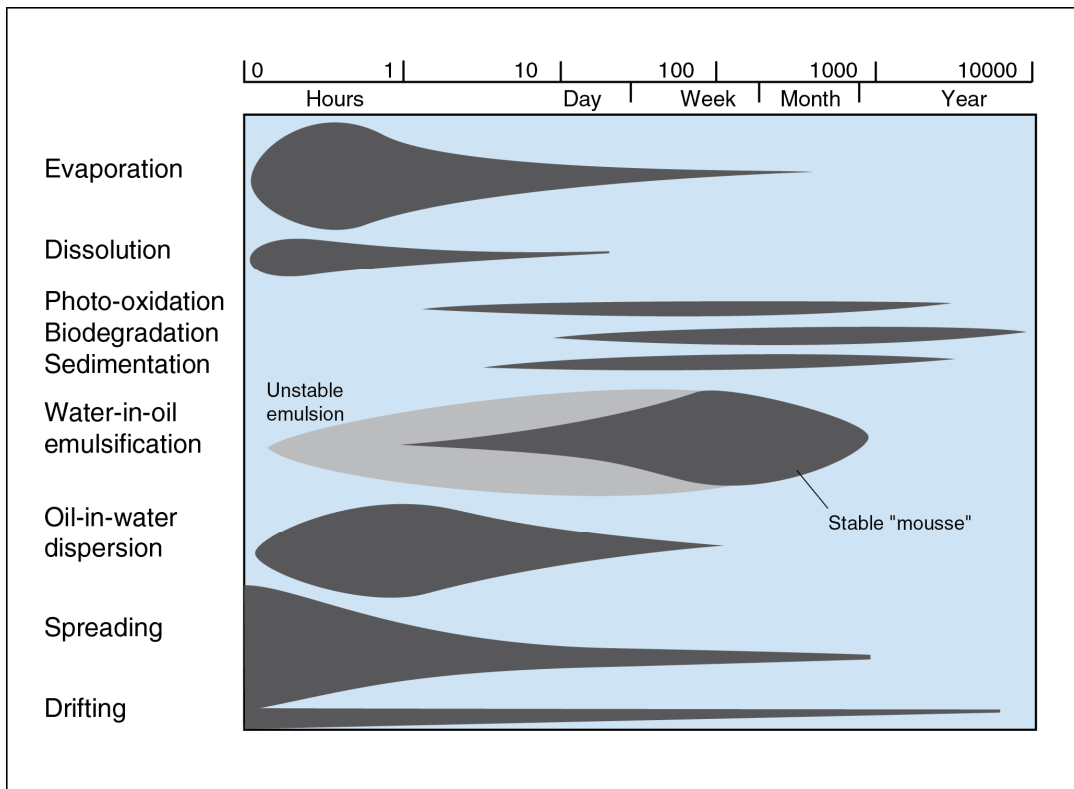
Figure A 4 Weathering processes' relative importance over time. Note: logarithmic scale.
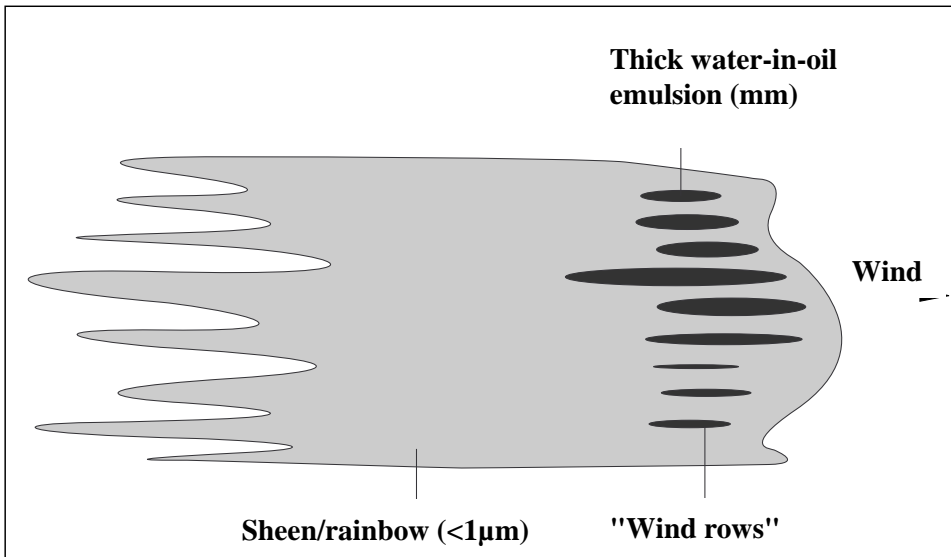
A.4.1 Evaporation

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 retarded 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 windrows 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 e.g. 90 vol.% of the oil spilled may consist of patches of w/o emulsion with a film thickness of 1 to 5 mm, which often constitutes less than 10% of the total oil slick area. The remaining 5-10 vol. % usually covers 90% of the spill area in the form of a sheen (<1 μm oil thickness).

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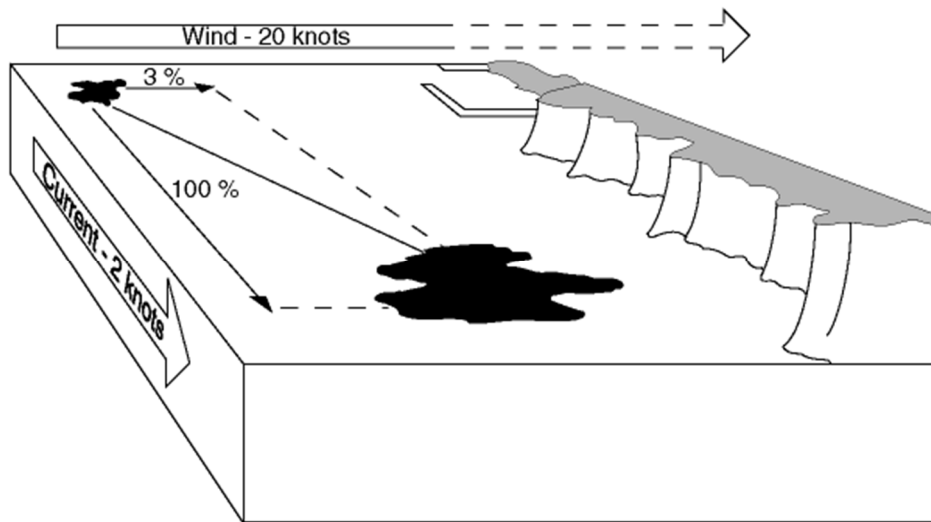
Figure A 6 An illustration showing how wind and current can influence the drifting of an oil slick

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. As a result 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 fairly independent of the prevailing weather conditions as long as 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.
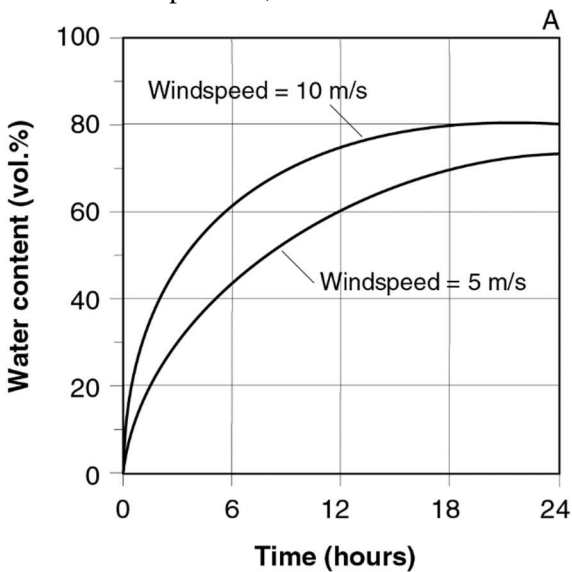
Figure A 7 Example of how weather conditions influence the w/o emulsion formation for typical oils

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 of time, the emulsion may only contain small water droplets with diameters of 1 to 10 μm, yielding a more stable emulsion, see Figure A 9.
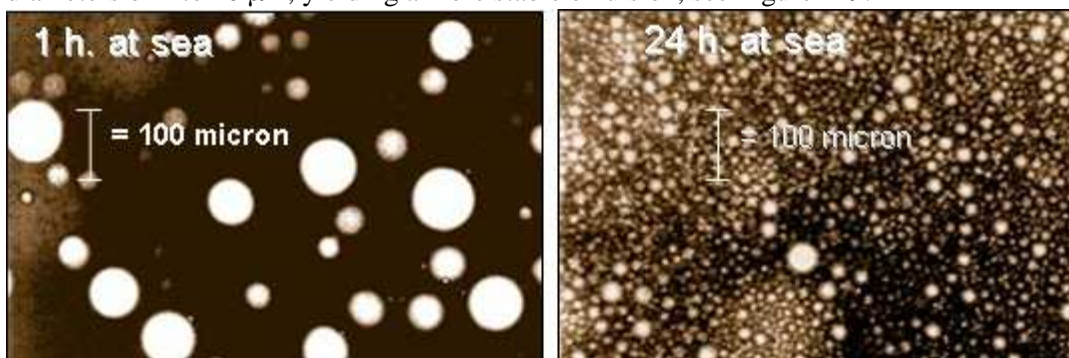
Figure A 8 Microscope pictures of w/o emulsion after (A) 1 h. and (B) 24 h. in a rotating cylinder

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 hydrophobic and hydrophilic properties, which will cause them 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.
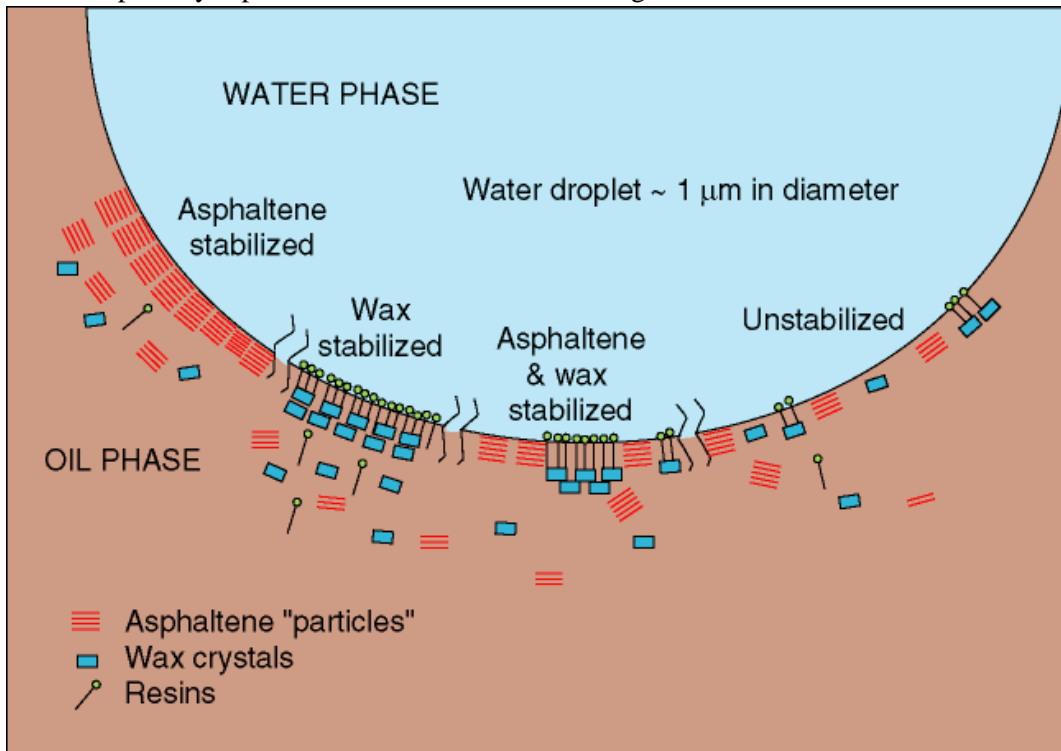
**Figure A 9 Interfacial layer stabilized by wax and asphaltenes in w/o emulsion**

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 seawater interfacial tension (IFT) plays a key role in the process of oil droplet formation. The need to both 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.

At SINTEFs laboratories, there are a possibility to measure the ultra-low interfacial tension (IFT) values of oil/water/surfactant interfaces by the spinning drop apparatus. With our ultra-modern equipment it is possible to measure the IFT in the range from $1 \cdot 10^{-6}$ to $2 \cdot 10^3$ mN/m.

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 droplets of diameters, typically 1 µm - 1 mm, which are then mixed into the water mass. The largest oil droplets will resurface and form a thin oil film (typically <50 µm) behind the oil slick. 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 the 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 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. The dispersant reduces the interfacial tension between water and oil and thus promotes dispersion. When effective chemical dispersion is achieved, small oil droplets are formed with diameters typical 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 isoalkanes 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. This contributes to the stability of w/o emulsions, therefore exerting a large influence on the oil's persistence on the sea surface. The photo-oxidized components will stabilize the w/o emulsions. After a long period of weathering at sea, tar balls, mainly consisting of asphaltenes, may be formed and can break down very slowly, both at sea and on beaches.

A.4.8 Biodegradation

Seawater contains an abundance of micro-organisms that can break down all types of oil components. The various micro-organisms prefer specific oil components as their energy source. Bacteria can only degrade oil in contact with water and depend 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 in the water mass.

Important factors influencing the biodegradation rate are temperature, the nutritive supply that contain nitrogen and phosphorus, the oxygen supply, oil type and the degree of weathering. Low molecular compounds are degraded more rapidly than the heavier compounds in the oil, thus giving the following order for biodegradation: straight-chain *n*-alkanes > branched isoalkanes > cyclic alkanes > cyclic naphthenes > aromatics> resins > asphaltenes (Perry, 1984). PAHs dissolved in water can be degraded within a few days (Brakstad and Faksness, 2000). Degradation of oil in contact with seawater depends highly on the water/oil interface area. The interfacial area increases as the oil is spread over the sea surface as a thin layer or by chemical or natural dispersion of oil into the water column.

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At sea, the formation of oil droplets by natural or chemical enhanced dispersion will increase the biodegradation rate in the water mass by10 to >100 times compared to surface oil due to increased water/oil interfacial area, and it has been shown that n-alkanes are biodegraded within 2-4 weeks at North Sea conditions (Brakstad and Løding, 2005). Other higher molecular-weight oil compounds are biodegraded 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 a particular material 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 particular 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 come in contact with the sea-bed sediment. This can cause some sedimentation of oil droplets to the sea-bed in the vicinity of the release. It is assumed that sub-sea dispersant treatment will reduce the potential for such sedimentation, due to lower adsorption /stickiness to sediment particles.

A.4.10 Deep water releases

Size distribution of the oil droplets formed during a subsurface release strongly influences the subsequent fate of the oil in the environment. Large droplets (typically larger than 5 mm) reach the surface after a couple of hours rise time from a depth of approximately 1000 m, while smaller droplets (down to 0.5 mm) may rise for up to a day before they will come to the surface. Fine droplets (below 100 microns) may stay in the water for weeks or even month before they eventually reach the surface. However, factors like vertical turbulence mixing in the water column, density stratification and cross flows will contribute to keep such fine small droplets submerged for even prolonged periods (Johansen et al., 2003).

In case of deep water releases; large droplets (mm range) will usually rise to the surface and form an oil layer with sufficient thickness to emulsify (form water-in-oil emulsions). This is usually caused by loss of buoyancy and more horizontal entrainment of the gas/oil/water plume due to dissolution of gas, possible hydrate formation, cross currents and density layers. However, large droplets (mm range) will leave the entrained plume and rise to the surface, illustrated in Figure A 10. This was observed both during the DeepSpill experiments in 2000 (Figure A 11) and the DWH oil spill in 2010 (Figure A 12). This emulsification will be dependent on oil properties and environmental conditions, such as temperature and sea state.
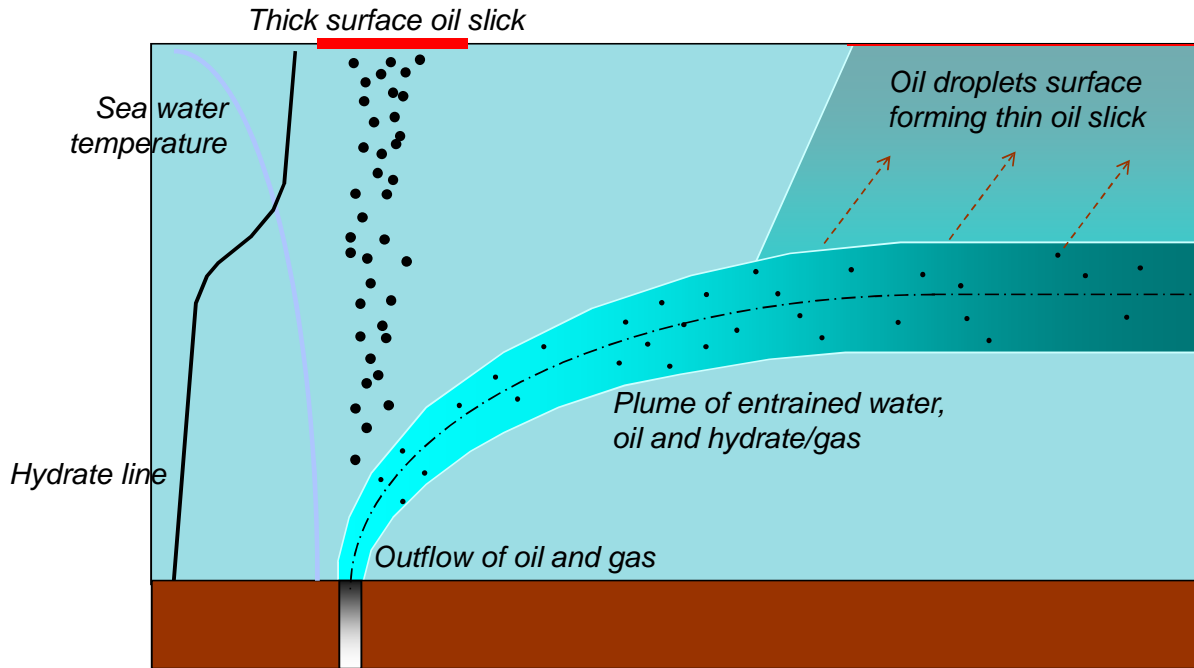
Figure A 10 Illustration of possible creation of thick surface oil slick (> 200 μm) from deep water release of oil.
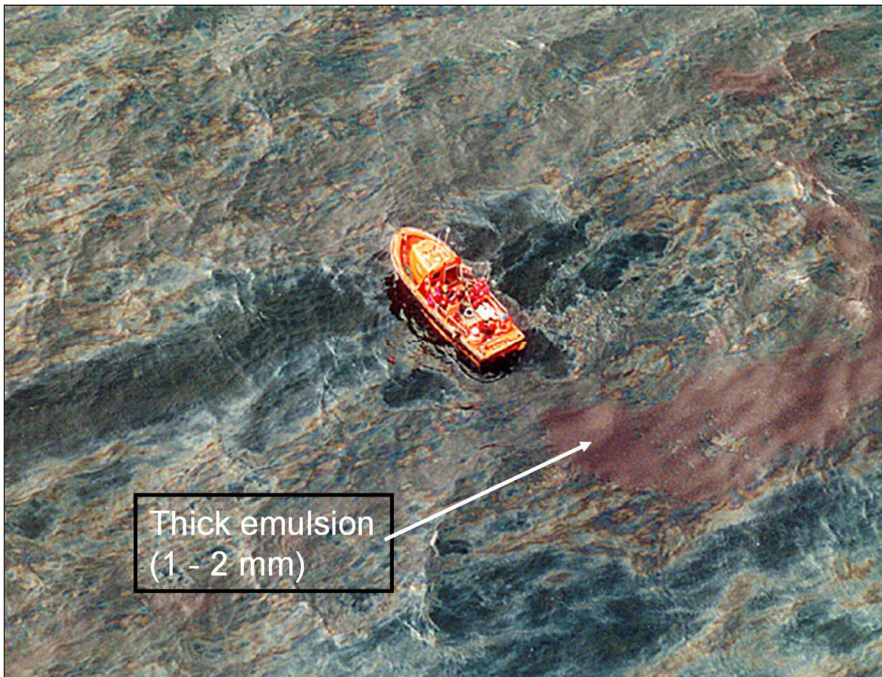
Figure A 11 Surface oil slick (initial thickness > 200 μm) from the experimental deep water release DeepSpill in 2000. Surface oil is emulsifying similar to an oil slick from a surface batch release.
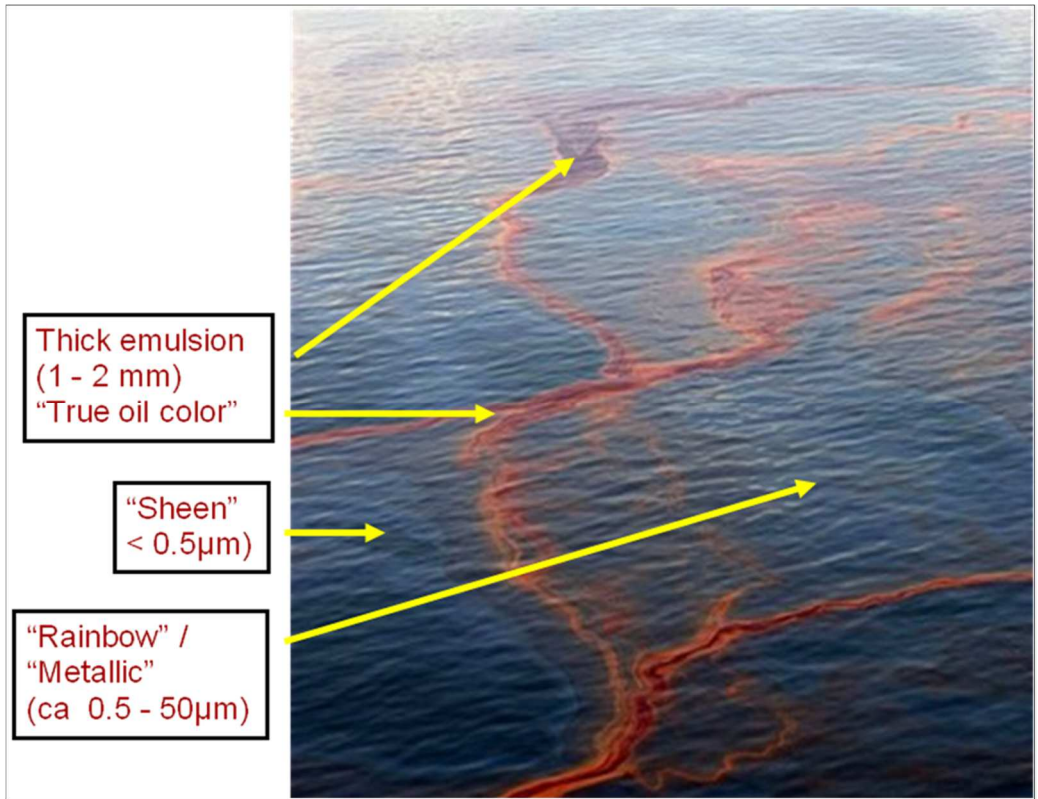
Figure A 12 Surface oil slick (initial thickness > 200 μm) from the DWH deep water release. Surface oil is emulsifying similar to an oil slick from a surface batch release.

A.4.11 Shallow releases

In case of a sub-surface release of oil and gas in shallower water (<500 meter) the buoyancy of the rising water/gas/oil plume is usually sufficient to reach the surface. The gas will be released to the atmosphere, while the large volumes of water will set up a horizontal current that will create a wide and thin surface oil slick (see Figure A 13, Figure A 14 and Rye et al, 1997). This surface oil slick will in many cases be too thin to emulsify (< 200 microns) and evaporation and natural dispersion will be the predominant weathering processes.
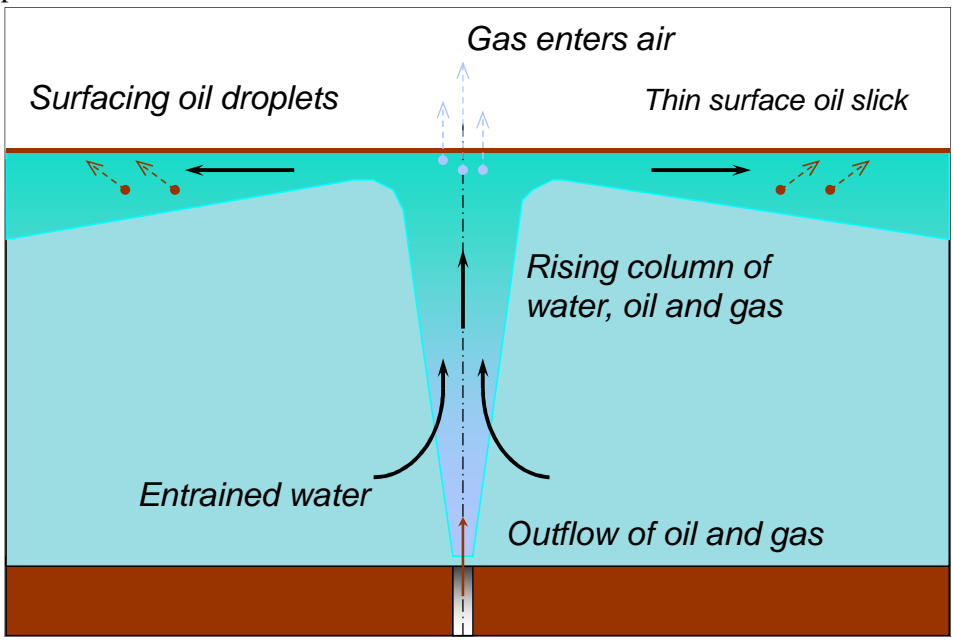
Figure A 13 Illustration of possible creation of thin surface oil slick (< 200 µm) from a shallow subsurface release (<500 m).
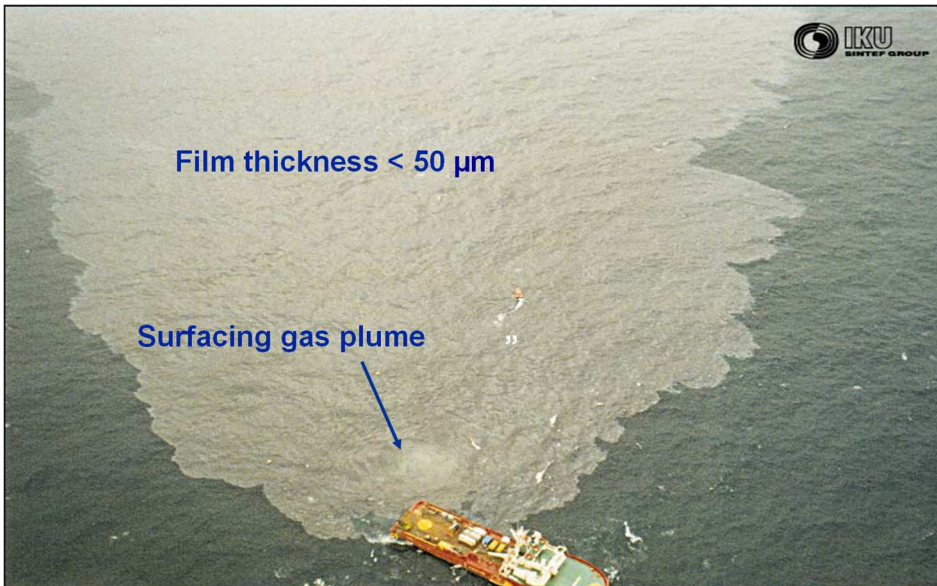
Figure A 14 Surface oil slick (< 50 µm) from experimental subsurface release at 106 m in 1996. The surface oil didn't emulsify and had a very limited life time (hours) due to the low film thickness and high rate of natural dispersion (even at < 10 m/s wind).

![SINTEF]

B   Experimental setup

B.1   Oil samples and test temperature

The Sigyn condensate was given the unique SINTEF ID 2017-113 and registered in the Laboratory Information Management System (LIMS) upon arrival to SINTEF. The condensate was received by SINTEF on Friday January 6th, 2017. Five blue barrels containing 10 L of oil each were received. The barrels were marked with the listed information:

No.: 1-5 of 5
Fluid type: Dead Cond.

Sample ID: 1.03-1.07
Date: 3.-4.12.2016
Time: 14:00-22:45/7:45-10:45
Sample pressure: atm
Coupled with bottle No.: -

Project No.: 60461
Company: Statoil
Well: S-4
Test No.: -

Flow period: -

B.2   Small-scale laboratory testing

To isolate and map the various weathering processes at sea, the Sigyn condensate was exposed to a systematic, stepwise procedure developed at SINTEF (Daling et al., 1990). The general procedure is illustrated in Figure B 1.
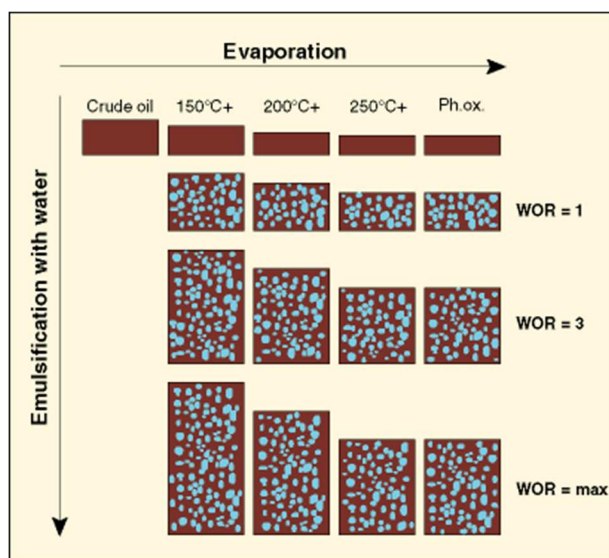
WOR: Water to Oil Ratio

WOR=1: 50 vol.% water

WOR=3: 75 vol.% water

WOR=max: the maximum water content

Figure B 1 Small-scale laboratory weathering flow chart of oil

B.2.1   Evaporation

The density of the oil was monitored during the degassing. This was performed before evaporation by standard procedure.
The evaporation procedure used is described in Stiver and Mackay (1984). Evaporation of the lighter compounds from the fresh oil was carried out as a simple one-step distillation to vapour temperatures of 150°C, 200°C and 250°C, which resulted in oil residues with an evaporation loss corresponding to

approximately 0,5-1 hour, 0,5-1 day and 0,5-1 week of weathering on the sea surface. These residues are referred to as 150°C+, 200°C+ and 250°C+, respectively.

B.2.2 Physical and chemical analysis

The viscosity, density, pour point and flash point 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
Interfacial tension (IFT)	Pendant/spinning drop method	Krüss DSA100 Drop Shape Analyser

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.2.3 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 **2**. 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.
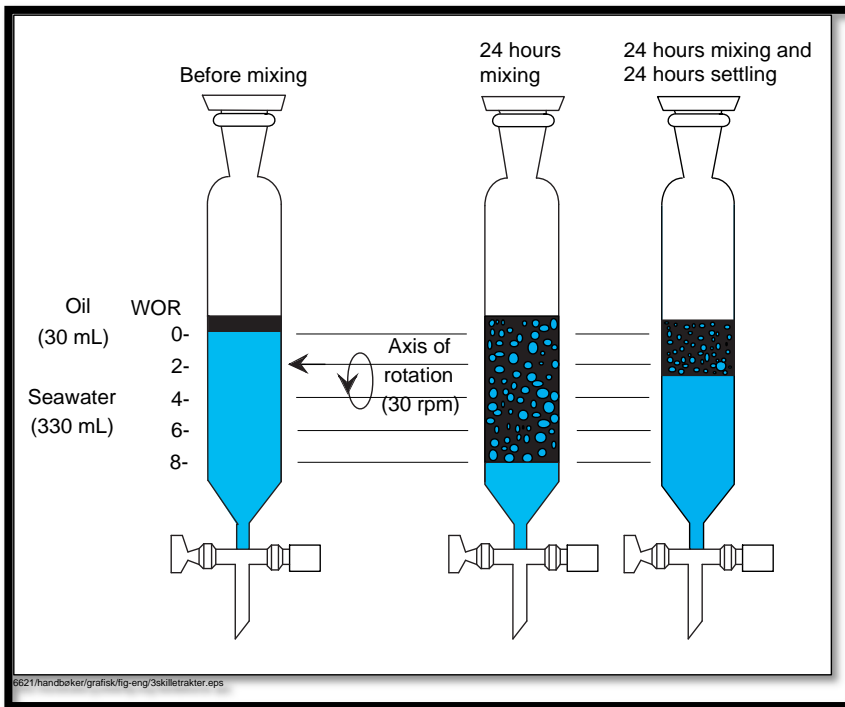
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Figure B 2 Principle of the rotating cylinder method.

B.2.4 Chemical dispersibility testing

As a screening test, the oils dispersibility properties were tested using four different dispersants at a dosage of 1:25 (4 wt. %). The dispersants tested were; Corexit 9500, Dasic Slickgone NS, Finasol OSR-62 and Radiagreen. For the dispersant showing greatest dispersibility, different dosages were studied. The screening was performed using the IFP method (discussed below) on the 200°C+ residue. For the dosage testing, both the IFP and the MNS tests were used. The viscosity of all the weathered samples was determined.

There are several different tests for evaluating the effect of chemical dispersants. The energy input will differ in the different tests, and the obtained efficiency will be representative of different wave energies. At SINTEF the IFP and MNS test is used in dispersibility testing.

IFP (Institute Francais du Petrole test, Bocard et al., 1984) is a low energy test estimated to represent low wave energies (2-5 m/s wind speed). A surge beating up and down in the test vessel at a given frequency, gives energy input to the seawater column. The water column is continuously diluted, which gives a more realistic approach to field conditions, compared to other tests.

MNS (Mackay and Szeto, 1980) is estimated to correspond to a medium to high sea-state condition. The energy input in this system, applied by streaming air across the oil/water surface, produces a circular wave motion. The sample of the oily water is taken under dynamic conditions after a mixing period of 5 min.

Both IFP and MNS test apparatus is shown in **Figure B 3**.

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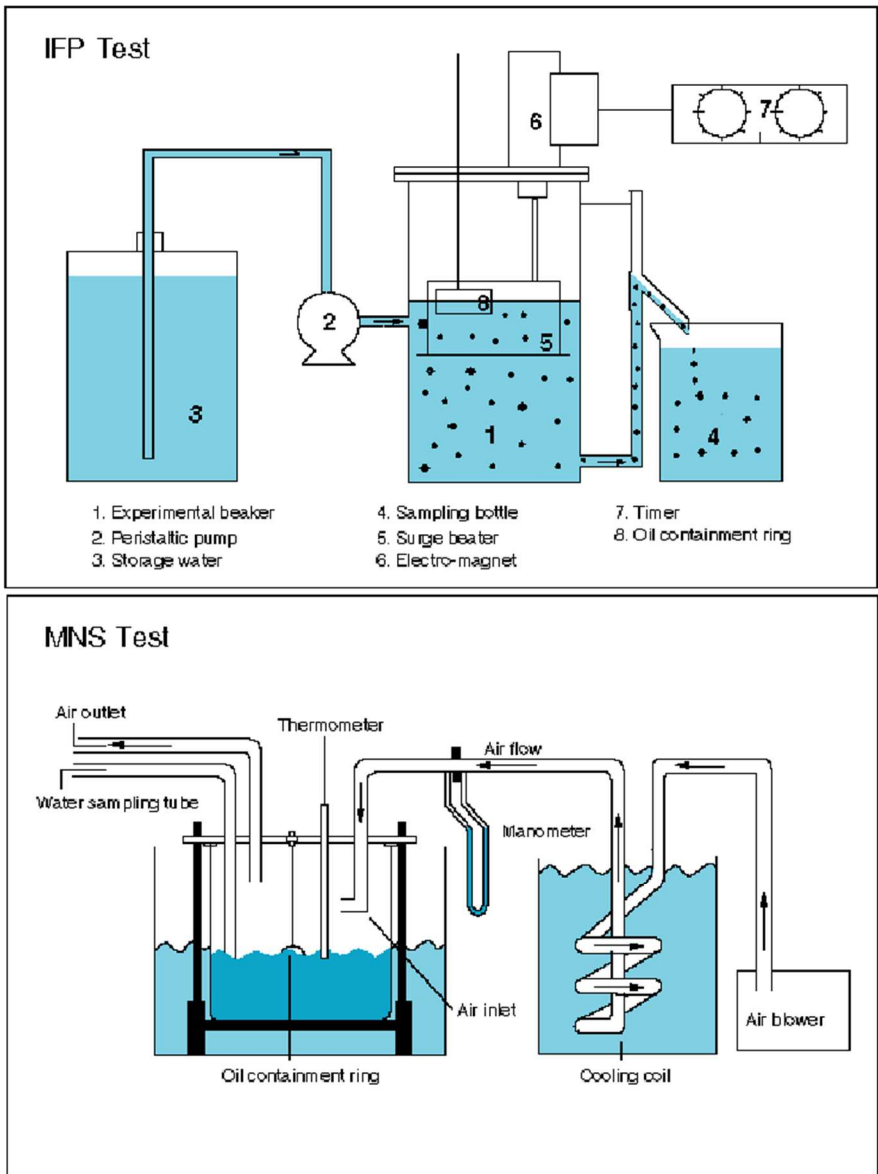
Figure B 3 IFP and MNS test apparatus.

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C The SINTEF Oil weathering model (OWM)

The SINTEF OWM is schematically shown in Figure C 1.
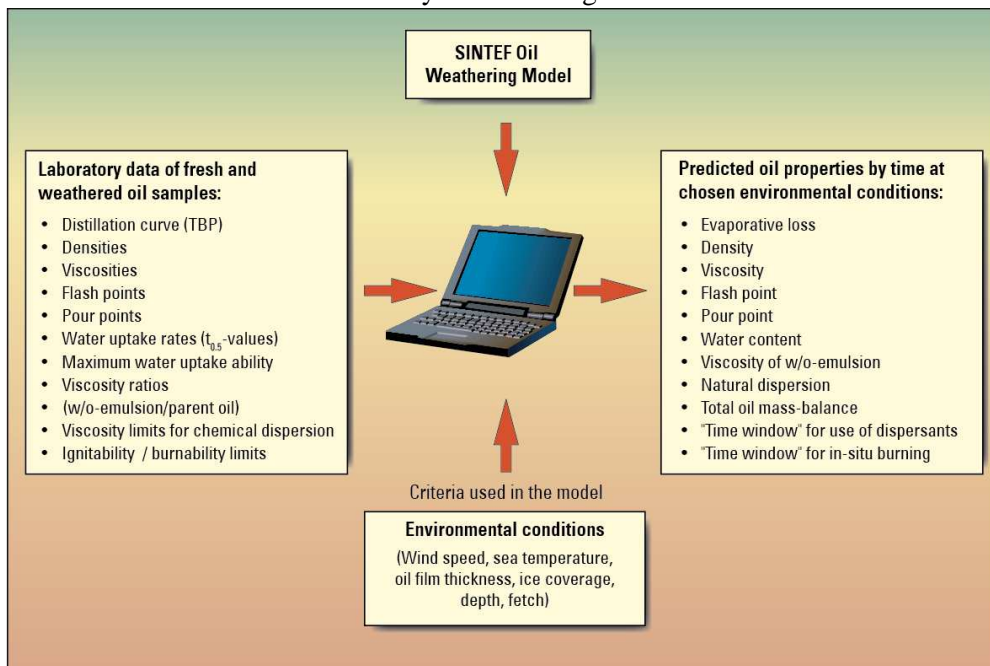
Figure C 1 Schematic input data to the SINTEF OWM and the predicted output oil properties

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 time 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.

In laboratory testing, a systematic stepwise procedure developed at SINTEF (Daling et al., 1990) is used to isolate and map the various weathering processes that take place when oil is spilled on the sea surface. The experimental design for the study of Sigyn crude oil is described in Appendix B, and the results are presented in detail in Chapter 0. The input data to the SINTEF OWM is given in Appendix 0. The experimental weathering data are processed and used as input for the SINTEF OWM.

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C.1 Input data to the SINTEF Oil Weathering Model (OWM) and OSCAR

The laboratory data used as input to the SINTEF OWM for Sigyn is given in Table C 1 to Table C *3*. The predictions were performed with 13°C laboratory data.

Table C 1 Physical and chemical properties for Sigyn condensate at 13 °C, used as input in the oil weathering model.

Properties of fresh oil	Value
Density (g/ml)	0.740
Pour point (°C)	-3
Reference temperature (°C)	13
Viscosity at ref. temp. (mPa·s = cP) *	1
Asphaltenes (wt. %)	0.01
Flash Point (°C)	-
Wax Content (wt. %)	3.14
Dispersible for visc. <*	-
Not dispersible for visc. > *	-
Maximum water uptake (%)	77***

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

** The condensate has no dispersibility limit

*** Maximum water uptake for 250°C+

\- No data available

Table C 2 Selected values to generate true boiling point (TBP) curve for Sigyn condensate. The data is based on a SIMDIST analysis conducted at Intertek in Sunbury, 2017.

Temperature (°C)	Weight (%)*	Temperature (°C)	Weight (%)*
-60	1	179	68
-37	2	192	70
-22	3	201	72
-14	4	216	74
-9	5	228	76
-3	8	238	78
-1	9	252	80
15	12	264	82
28	15	276	84
39	19	293	86
50	20	304	88
57	22	320	90
60	23	331	91
71	29	334	92
77	30	357	93
148	59	369	94
151	60	384	95
157	62	401	96
164	64	418	97
173	66	439	98
		476	99

Weigh t% is used in the OWM predictions, instead of volume% due to better correspondence to the SINTEF laboratory data.

Table C 3 Lab weathering data for Sigyn condensate at 13°C, used as input in the oil weathering model

Property	Fresh	150°C+	200°C+	250°C+
Boiling Point Temp. (°C)	-	176	238	288
Vol. Topped (%)	0	61.9	73.7	82.3
Weight Residue (wt. %)	100	42.2	29.6	20.2
Density (g/ml)	0.739	0.817	0.834	0.841
Pour point (°C)	-3	18	21	27
Flash Point (°C)	-	34,5	76	111
Viscosity of water-free residue (mPa·s =cP)*	1	53	266	1120
Viscosity of 50% emulsion (mPa·s = cP)*		10	52	330
****Viscosity of 75% emulsion (mPa·s = cP)***		-	-	225
Viscosity of max water (mPa·s = cP)*		18	65	374
*****Max. water cont. (vol. %)***		20	27	77
(T1/2) Halftime for water uptake (hrs)***		0.15	0.15	0.15
******Stability ratio**		0	0	0

- No data

* Measured at shear rate 10 s⁻¹

**The emulsion formed was quite loose and did not generate 75% wio emulsions

*** Data given for emulsion testing (kinetics) due to unstable emulsions

**** Due to unstable emulsions, $T_{1/2}$ values for 150°C+ is used for all residues

***** Stability ratio of 1 implies a totally stable emulsion during 24 h settling. A stability ratio of 0 (zero) implies a totally unstable emulsion: all the water is released from the emulsion during 24 h settling.

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C.2 Chemical characterization of the fresh oil on GC/MS

The chemical characterization for Sigyn condensate derived from GC/MS is given in Table C 4.

Table C 4 Chemical composition of Sigyn condensate based on GC/MS analysis of fresh oil

Group no.	Composition	Sigyn wt%
1	C1-C4 gasses (dissolved in oil)	1.20
2	C5-saturates (n-/iso-/cyclo)	1.20
3	C6-saturates (n-/iso-/cyclo)	1.89
4	Benzene	1.61
5	C7-saturates (n-/iso-/cyclo)	7.10
6	C1-Benzene (Toluene) et. B	4.98
7	C8-saturates (n-/iso-/cyclo)	14.02
8	C2-Benzene (xylenes; using O-xylene)	7.75
9	C9-saturates (n-/iso-/cyclo)	1.64
10	C3-Benzene	4.11
11	C10-saturates (n-/iso-/cyclo)	6.00
12	C4 and C5 Benzenes	0.35
13	C11-C12 (total sat + aro)	7.95
14	Phenols (C0-C4 alkylated)	0.01
15	Naphthalenes 1 (C0-C1-alkylated)	0.45
16	C13-C14 (total sat + aro)	11.75
17	Unresolved Chromatographic Materials (UCM: C10 to C36)	0.00
37	metabolite 1	0.00
38	metabolite 2	0.00
18	Naphthalenes 2 (C2-C3-alkylated)	0.48
19	C15-C16 (total sat + aro)	7.32
20	PAH 1 (Medium soluble polyaromatic hydrocarbons (3 rings-non-alkylated;<4 rings)	0.26
21	C17-C18 (total sat + aro)	5.44
22	C19-C20 (total sat + aro)	3.70
23	C21-C25 (total sat + aro)	4.67
24	PAH 2 (Low soluble polyaromatic hydrocarbons (3 rings-alkylated; 4-5+ rings)	0.13
25	C25+ (total)	6.00

-: not analysed

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

By modelling the fate of individual 25 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.

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