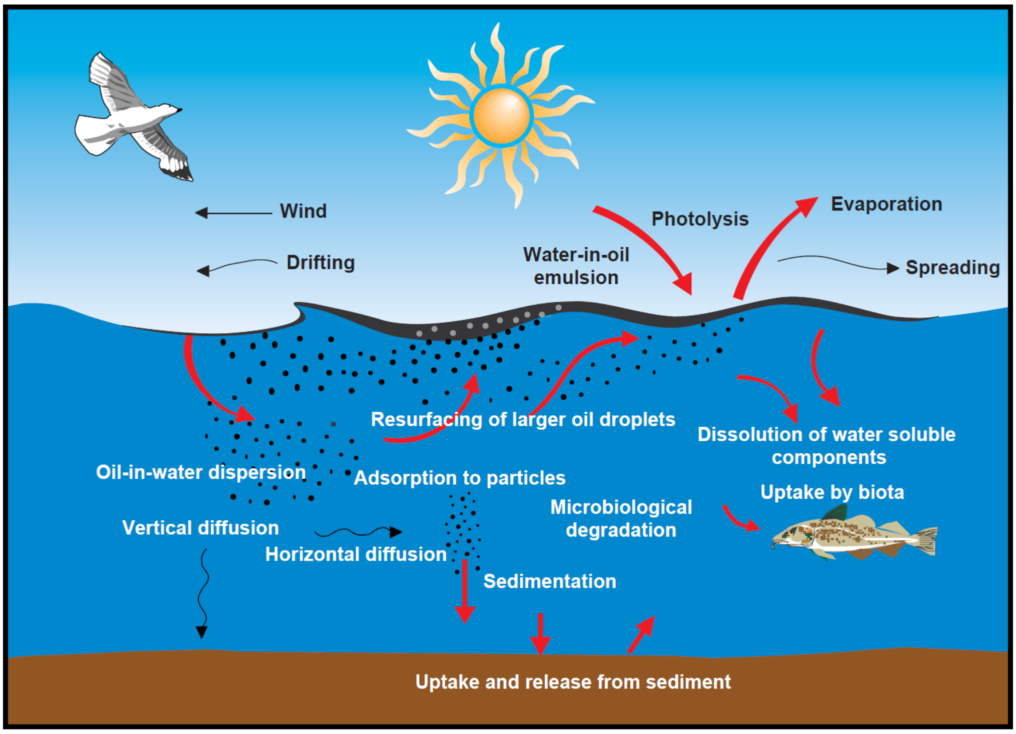
A27496- Unrestricted

Report

Bøyla crude oil – properties and behaviour at sea

In relation to oil spill response

Author
Kaja Cecilie Hellstrøm



SINTEF Materials and Chemistry
Oil Spills Research
2016-01-28

SINTEF Materialer og kjemi
SINTEF Materials and Chemistry

Address:
Postboks 4760 Sluppen
NO-7465 Trondheim
NORWAY

Telephone:+47
Telefax:+47

Enterprise /VAT No:

KEYWORDS:
Weathering of oil
Dispersibility
Emulsion properties

Report

Bøyla crude oil – properties and behaviour at sea

In relation to oil spill response

VERSION
Final

DATE
2016-01-28

AUTHOR
Kaja Cecilie Hellstrøm

CLIENT(S)
Det norske oljeselskap ASA

CLIENT'S REF.
Øivind Hille

PROJECT NO.
102010132

NUMBER OF PAGES/APPENDICES:
70 including appendices

ABSTRACT

A study of the weathering properties of the Bøyla crude oil was performed as a bench scale laboratory study. The study included testing of dispersibility in addition to determining several chemical, physical and emulsifying properties of the oil. The obtained data was used as input in the SINTEF Oil Weathering Model (OWM), which was used to predict the behaviour of the crude oil in a spill situation at sea. A window of opportunity for use of chemical dispersants in a spill response scenario with Bøyla crude oil was established. In this report, the weathering properties of Bøyla crude oil are discussed in relation to oil spill response operations, particularly mechanical recovery and chemical dispersion.

PREPARED BY
Kaja Cecilie Hellstrøm

SIGNATURE
Kaja C. Hellstrøm

CHECKED BY
Per S. Daling

SIGNATURE
Per S. Daling

APPROVED BY
Mimmi Throne-Holst

SIGNATURE
Mimmi Throne-Holst

REPORT NO.	**ISBN**	**CLASSIFICATION**	**CLASSIFICATION THIS PAGE**
A27496	9788214060560	Unrestricted	Unrestricted

Document history

VERSION	DATE	VERSION DESCRIPTION
Draft 1.0	2016-01-15	Draft version
Final version	2016-01-27	Final version reviewed and accepted by Det norske

Table of contents

1 Executive summary

When weathered on the sea surface both crude oils and condensates will undergo changes that affect oil spill countermeasures in various ways, as a function of time and weather conditions. This summary gives a brief overview of the main changes predicted for Bøyla crude oil when weathered on the sea surface.

Bøyla is a partly biodegraded crude oil with naphthenic features and a relatively large fraction of "unresolved complex mixture" (UCM). Bøyla has a density of 0.875 g/ml, and a low asphaltene and medium wax content of 0.07 and 3.2 wt. %, respectively. With the lighter paraffinic compounds ($< C_{17}$) removed through biodegradation, Bøyla has a low evaporative loss compared to the other presented Norwegian crude oils. The relative increase in heavy end components such as wax and asphaltenes, caused by evaporation, alters the chemical properties of the oil. Bøyla forms stable water-in-oil (w/o) emulsions with comparatively low viscosities initially, but the viscosity increases over time and may surpass 20 000 mPa·s. The water content of the emulsions is predicted to reach 72 and 77 volume (vol.) % water in winter and summer conditions, respectively.

The formation of stable emulsions prolongs the lifetime at sea for Bøyla, and the mass balance predictions show that oil will remain on the sea surface for at least five days in weather conditions with winds up to 10 m/s, in both summer and winter temperatures. At wind speeds of >15 m/s the oil is predicted to be naturally removed from the sea surface within the first four days.

When spilled on the sea surface, an oil will assume the ambient water temperature within a short time. The greatest fire and/or explosion hazard occurs for oils with a flash point which is close to or lower than the sea temperature. Furthermore, weathering processes will normally lead to a rapid decrease in the flash point of the oil. The flash point of Bøyla is predicted to be above the sea temperature within 15 min. after being spilled onto the sea surface, even in calm wind conditions (2 m/s), for both summer and winter temperatures. Small vessels may be engaged in oil recovery operations, and some of these may not be classified to carry liquids with a flash point below 60 °C. The flash point of Bøyla will be above 60 °C within approximately 6 hours after a spill in calm wind conditions at both summer and winter temperatures. It must be emphasised that this limit is not relevant for oil recovery vessels with A-class certifications for transportation of liquids.

In calm weather conditions (2 m/s wind), boom leakage may pose a challenge for mechanic recovery of Bøyla crude oil for the first 24 hours, as the emulsion viscosity will remain below 1000 mPa·s for this period. In stronger wind conditions, the 1000 mPa·s limit will be surpassed sooner. In the laboratory study, emulsion viscosities up to 19 000 mPa·s were produced, and the Oil Weathering Model (OWM) predicts emulsion viscosities above 20 000 mPa·s after approximately 3 days at sea in high wind conditions (10 m/s). Due to the low pour point of Bøyla, the use of weir skimmers will likely be possible for emulsion viscosities up to 30 000 mPa·s. "High visc.-skimmers" should be considered when emulsion viscosities surpass 30 000 mPa·s.

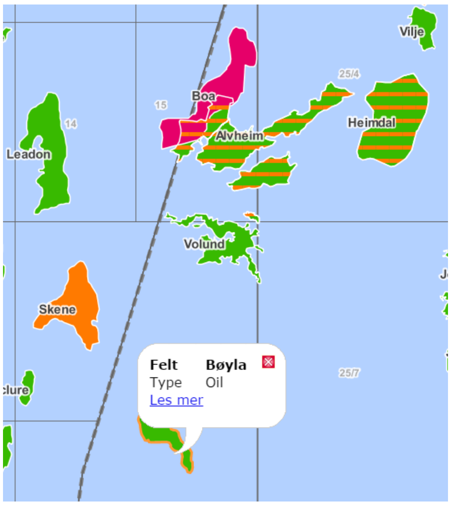
Bøyla has a potential for chemical dispersion. The window of opportunity for chemical dispersion depends on the emulsion viscosity, and while a limit for "Reduced dispersibility" was established for Bøyla based on laboratory data, an upper viscosity limit where the oil may be said to be "Not dispersible" was not reached in the laboratory study. This limit was instead estimated based on the laboratory data and experience from previous studies of other Norwegian crude oils. The lower limit where the dispersibility of Bøyla is expected to be reduced was set at 4 000 mPa·s, while the upper, estimated limit was set at 30 000 mPa·s. Once the oil is expected to have reduced chemical dispersibility, additional artificial energy and/or a higher dispersant dosage (DOR= dispersant to oil ratio) could be applied. Repeated application of dispersant may also increase the effectiveness, especially in calm sea. Additional energy can be provided using firefighting (Fi-Fi) systems, thrusters or MOB boats after dispersant application in order to enhance dispersion efficiency.

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. 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.

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 (PSA) 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. A weathering study of the Bøyla crude oil has been conducted by SINTEF Environmental Technology on request from Det norske. The obtained data have been used to predict the fate and behaviour of Bøyla crude oil if spilled at sea under different weather conditions. The study included a dispersibility study in order to obtain a window of opportunity for the use of chemical dispersants.



(http://www.detnor.no/wp-content/uploads/2014/10/B%C3%B8yla.jpg?d5b1f2, www.petroleumskartet.no)

Bøyla is the fourth oil field in production in the Alvheim area, in the northern part of the North Sea. The field was discovered in 2009 and the plan for development was approved in 2012. The Bøyla field is connected to existing infrastructure around the Alvheim FPSO through a 28 km long pipeline. Det Norske has the functions of operator and has a share hold of 65 %. Other partners are Core Energy AS and Lundin Norway AS, holding the remaining 20 % and 15 %, respectively. Production was started on 19th of January 2015 and expected maximum production is 20000 barrels of oil equivalents per day.

(http://www.detnor.no/produksjonsstart-pa-boylafeltet/)

3 Experimental results and discussion

3.1 Small scale laboratory testing results

The small-scale weathering results of Bøyla are compared with similar data of other Norwegian oils, listed in Table 3-1. These oils were selected in agreement with Det norske.

Table 3-1: Oils compared with Bøyla crude oil data in the report

Oil	SINTEF-ID	SINTEF report number	Reference
Alvheim Blend	2009-0003	A11170	Leirvik and Myrhaug, 2009
Alvheim Kneler	2007-0288	A11170	Leirvik and Myrhaug, 2009
Balder Blend	2010-0159	A16789	Sørheim and Leirvik, 2010
Statfjord A	2000-0036	F00138	Moldestad *et al.*, 2001

The Bøyla crude oil used in this study was given the SINTEF-ID 2015-0063.

3.1.1 Chemical composition and physical properties

The chemical composition of Bøyla and other crude oils are shown in Figure 3-1and Figure 3-2 as GC/FID chromatograms. Appendix D shows the result of the chemical characterization of the fresh oil on GC/MS.

Gas chromatographic flame ionization detector (GC/FID) characterization

The chemical composition of Bøyla, as characterized by gas chromatography (GC/FID), is shown in Figure 3-1. 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 (topping) in the laboratory.

In the gas chromatograms the *n*-alkenes appear as systematic narrow peaks where the components with the lowest boiling point appear to the left. These lighter components are gradually removed with higher distillation temperatures, as can be seen in Figure 3-2. The chromatogram for fresh Bøyla oil (Figure 3-1) shows a reduction in lighter alkanes compared to heavier alkanes, a sign of bacterial biodegradation in the reservoir.

More complex components, such as resins and naphthenes, are not as easily separated as *n*-alkanes and form a broad and poorly defined hump below more pronounced peaks, a hump often described as "Unresolved Complex Mixture", or UCM. Bøyla has a pronounced UCM hump with visible *n*-alkanes in the C_{16}-C_{30} area. The large UCM hump indicates that also the heavier *n*-alkanes have been biodegraded though to a lesser extent compared to the lighter *n*-alkanes, resulting in an overall reduction in *n*-alkanes.

The chromatograms of fresh oils for some other Norwegian crude oils are presented in Figure 3-2, and the variation in UCM hump size can be clearly seen. Heavier compounds such as asphaltenes (> nC_{40}) are not possible to analyse with this gas chromatographic technique. Bøyla crude oil is a characterised as a partly biodegraded naphthenic oil with medium wax and low asphaltene content.

Gas chromatography (GC/FID) is an important tool for oil characterisation and for oil spill identification as an initial step. Common screening parameters used for identification, as well as for the degree of biodegradation, are the nC_{17}/Pristane and nC_{18}/Phytane ratios. These parameters for Bøyla and other Norwegian oils are given in Table 3-2.

Table 3-2: nC_{17}/Pristane and nC_{18}/Phytane ratios for fresh Bøyla crude oil and other Norwegian oils

Oil	nC_{17}/Pristane	nC_{18}/Phytane
Bøyla	0.8	1.1
Alvheim	1.3	1.4
Kneler	1.1	2.4
Balder	1.8	2.5
Statfjord A	1.7	2.3

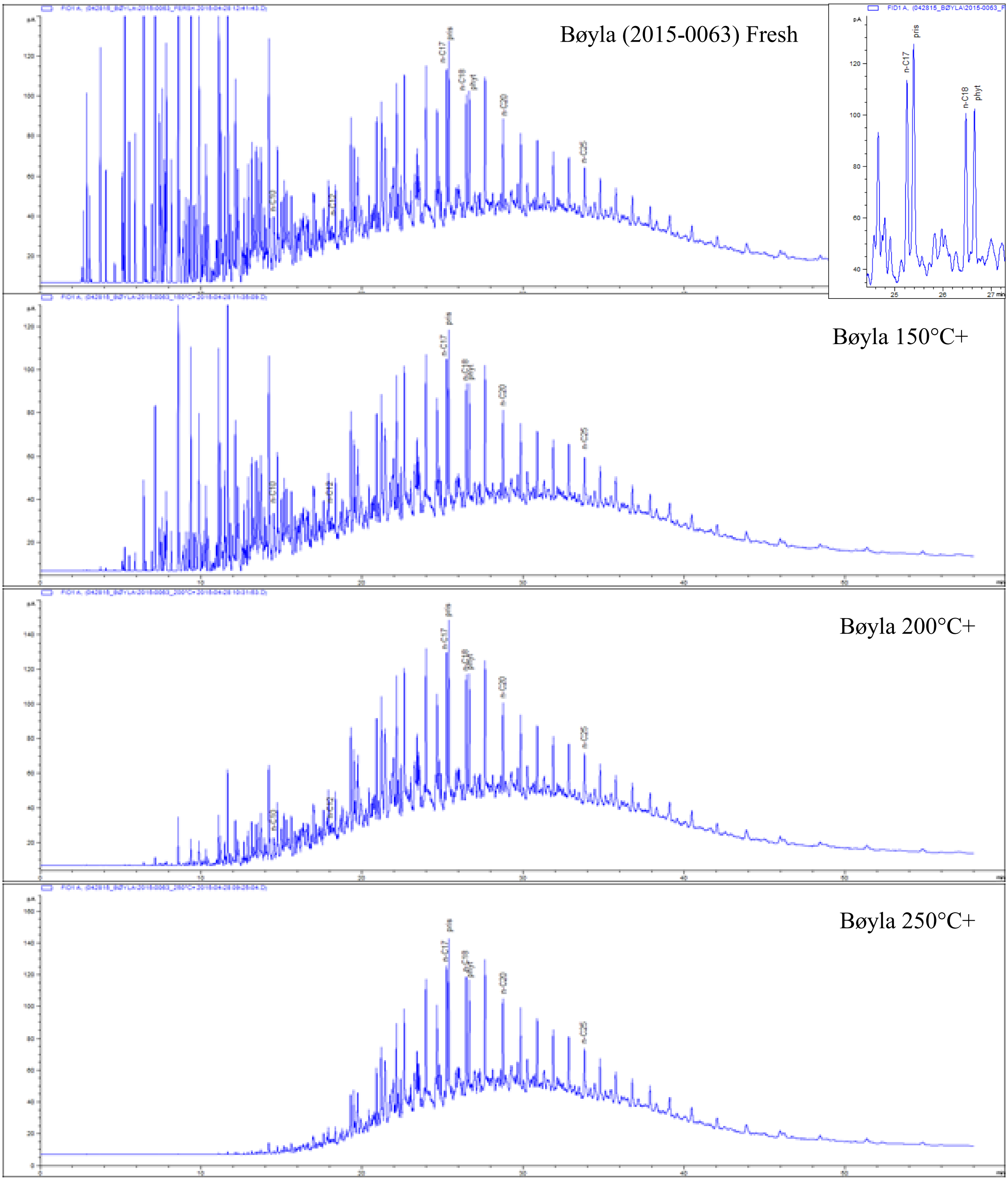


Figure 3-1: GC/FID chromatograms of fresh sample and evaporated residues of Bøyla crude oil

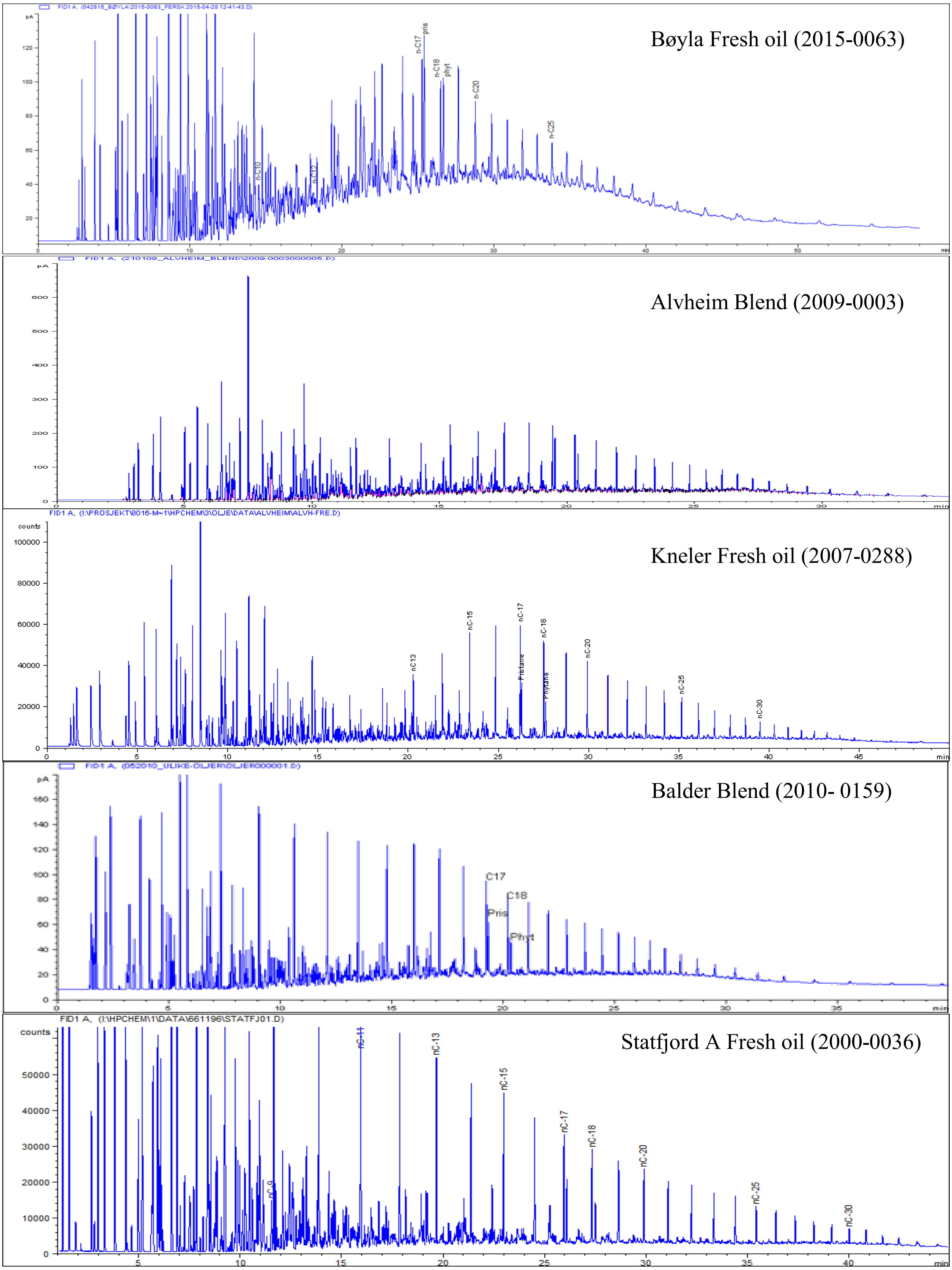


Figure 3-2: GD/FID chromatograms for fresh residues of the oils used for comparison

Asphaltene and wax content

The asphaltene and wax contents of Bøyla and other Norwegian crudes are given in Table 3-3. Bøyla has a low content of asphaltenes compared to Alvheim Blend and Statfjord A. The wax content (3.2 wt. %) is the lowest of the presented oil, followed by Balder (wax content: 3.5 wt. %).

Table 3-3: Asphaltene ("hard") and wax content for different oils and their residues

Oil	Residue	Asphaltenes "hard" (wt. %)	Wax (wt. %)
Bøyla	Fresh	0.07	3.2
	150°C+	0.08	3.5
	200°C+	0.09	3.8
	250°C+	0.10	4.4
Alvheim Blend	Fresh	0.06	5.3
	150°C+	0.07	5.9
	200°C+	0.08	6.7
	250°C+	0.09	7.8
Kneler	Fresh	0.11	4.9
	150°C+	0.14	5.8
	200°C+	0.15	6.5
	250°C+	0.18	7.6
Balder	Fresh	0.77	3.5
	150°C+	0.86	3.9
	200°C+	0.94	4.3
	250°C+	1.05	4.8
Statfjord A	Fresh	0.06	4.6
	150°C+	0.08	5.9
	200°C+	0.10	6.8
	250°C+	0.12	8.3

Physical properties of fresh and weathered residues

Physical properties of Bøyla and the other crude oils are listed in Table 3-4. Bøyla has the lowest evaporative loss of the presented oils, while Statfjord A expresses the highest evaporative loss. The densities of fresh Bøyla oil and the weathered residues are similar to those of Balder, while the flash point of the residues lies between those of Kneler and Balder. Bøyla has the lowest pour points of the oils as well as the lowest viscosities for all residues.

Table 3-4: Physical parameters in comparison with other Norwegian oils

Oil type	Residue	Evaporation (vol. %)	Residue (wt. %)	Density (g/ml)	Flash point (°C)	Pour point (°C)	Viscosity (mPa·s) 13°C (10 s^{-1})	IFT (mN/m) Init.
Bøyla	Fresh	0	100	0.875	-	-12	46	20
	150°C+	9	93	0.886	40	-6	68	21
	200°C+	18	84	0.895	81	0	153	22
	250°C+	28	74	0.904	123	12	730	25
Alvheim Blend	Fresh	0	100	0.840	-20	-3	18	-
	150°C+	13	89	0.859	34	6	93	-
	200°C+	24	79	0.870	73	15	468	-
	250°C+	33	70	0.879	107	27	1285	-
Kneler	Fresh	0	100	0.832	-21	0	51	-
	150°C+	18	85	0.856	51	6	208	-
	200°C+	28	75	0.866	88	9	1810	-
	250°C+	38	65	0.874	128	18	2100	-
Balder	Fresh	0	100	0.864	-	-	32	-
	150°C+	13	90	0.889	32	9	138	-
	200°C+	22	82	0.901	72	12	448	-
	250°C+	31	73	0.913	109	18	2191	-
Statfjord A	Fresh	0	100	0.827	-	0	43	22
	150°C+	25	79	0.867	-	12	832	21
	200°C+	36	68	0.882	-	21	1697	21
	250°C+	49	56	0.895	-	27	2894	22

-: No data available

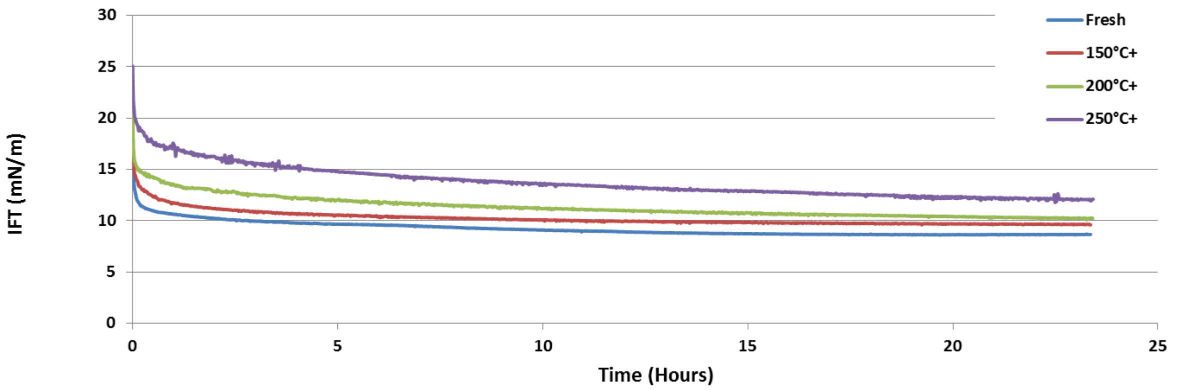


Figure 3-3: Interfacial tension decay of Bøyla crude oil and its residues with respect to time

3.1.2 Emulsifying properties of Bøyla crude oil

The emulsifying properties of Bøyla were studied by use of the rotating cylinders (Hokstad et al., 1993). Figure 3-4 shows the emulsions formed with excess of water in the rotating cylinders after 24 hours of rotation. From left to right are the 150°C+, 200°C+ and 250°C+ residues, four cylinder of each. The emulsions made from the less evaporated residues, 150°C+ and 200°C+, appear dark brown while the 250°C+ emulsions have obtained a lighter brown colour.

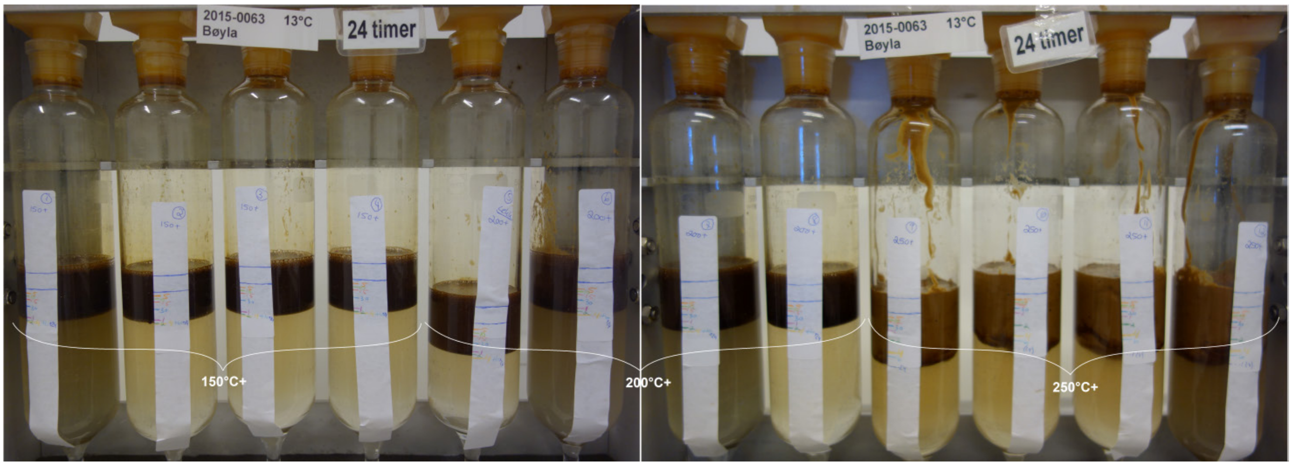


Figure 3-4: The rotating cylinders at start and after 24 hours at 13 °C

Water uptake and maximum water content

The rate of water uptake (kinetics) was studied by use of the rotating cylinders, similar to the emulsifying properties described above. The water content in the water-to-oil emulsions as a function of time at the two test temperatures, are shown in table. $T_{1/2}$ is a constant defined as the time (hours) required to incorporate half the maximum water quantity and is derived from the tabulated data for each residue.

The $T_{1/2}$ values for Bøyla reveal that less than half an hour is required for the oil to take up half the total water content for all residues. The maximum water contents of the formed emulsions from the 150°C+ and 200°C+ residues are both 67 vol. % while the 250°C+ residue form emulsions with a water content of 78 vol. %.

Table 3-5: Water uptake for the evaporated residues of Bøyla crude oil at 13 °C

Mixing time	150°C+ (Vol. % water)	200°C+ (Vol. % water)	250°C+ (Vol. % water)
Start	0	0	0
5 min	20	25	24
10 min	31	35	33
15 min	39	42	39
30 min	52	51	46
1 hour	64	61	54
2 hours	66	64	65
4 hours	67	67	72
6 hours	67	67	74
24 hours	67	67	78
$T_{1/2}$	0.20	0.17	0.33

Stability and efficiency of emulsion breaker

The stability of the emulsions from the weathered residues of Bøyla crude oil was tested by quantifying the amount of water released from the emulsion during 24 hours of settling 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.

All residues of the Bøyla oil formed stable emulsions that lost none or minimal amount of water when left at a standstill. The application of emulsion breaker (Alcopol O 60 %) had some effect at the lowest dosage of 500 ppm, particularly on the 150°C+ residue emulsion. Applying a higher dosage of 2000 ppm proved more efficient, causing the emulsions to release most of their total water content. To know the effects of emulsion breaker can be of importance in a recovery situation in order to optimize the usage of available storage facilities/tankers, as the emulsion volume decreases considerably with the treatment.

Table 3-6: Stability of emulsion and the effect of emulsion breaker at 13 °C

Residue	Emulsion breaker	Water-in-oil emulsion (vol. %) at 13 °C		
		Reference	24 hours *	Stability ratio**
150ºC+	none	67	67	0.99
200ºC+	none	67	68	1.00
250ºC+	none	78	78	1.00
150ºC+	Alc. O 60 % 500 ppm	67	17	0.10
200ºC+	Alc. O 60 % 500 ppm	67	47	0.44
250ºC+	Alc. O 60 % 500 ppm	78	70	0.63
150ºC+	Alc. O 60 % 2000 ppm	67	6	0.03
200ºC+	Alc. O 60 % 2000 ppm	67	29	0.20
250ºC+	Alc. O 60 % 2000 ppm	78	30	0.12

ppm: parts per million

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

*** Stability ratio of 0 implies a totally unstable emulsion after 24 hours settling; all the water is settled out during 24 hours settling. Stability ratio of 1 implies a totally stable emulsion*

Viscosity of emulsified residues

Table 3-7 gives the viscosities of oil residue fractions with different water content (water free, 50 vol. %, and 75 vol. % and max. water) at 13 °C. As non-Newtonian fluids, the viscosities of Bøyla fresh oil and emulsions are dependent on the shear rate; the viscosities are higher at a lower share rate (10 s^{-1}) compared to viscosities at higher shear rate (100 s^{-1}). This decrease in viscosity with increasing shear rate is likely caused by breaking up the wax lattice structure with increased mechanical force. Bøyla shows a clear increase in viscosities with increasing degree of weathering and a maximum viscosity of 17153 mPa·s (max water, 250°C+, 10 s^{-1}).

Table 3-7: Viscosity of water-free residues and emulsions of Bøyla at 13 °C

Residue	**Water content (vol. %)**	**Viscosity (mPa·s) 13 °C**	
		10 s^{-1}	**100 s^{-1}**
Fresh	0	46	44
150°C+	0	68	62
200°C+	0	153	143
250°C+	0	730	520
150°C+	50	486	343
200°C+	50	1030	665
250°C+	50	2562	1493
150°C+	75	1883	648
200°C+	75	4036	1371
250°C+	75	10644	3481
150°C+	89	1603	717
200°C+	80	3069	1297
250°C+	67	17153	4073

3.1.3 Chemical dispersibility

The dispersibility testing included:

- Screening of six different dispersants to find the best and relevant dispersant for the Bøyla oil.
- Dosage testing of the best/relevant dispersant.
- Systematic dispersant study with the best dispersant at the optimal dosage rate (DOR - Dispersant to Oil Ratio), to determine the time window for effective dispersant use on the Bøyla oil in a spill scenario.

Screening and dosage study of dispersants

A screening study was performed using the low energy test (IFP, reflecting non-breaking wave conditions) to investigate the effectiveness of different dispersants. In addition, the high energy MNS-test (reflecting breaking wave conditions) was used for testing Dasic NS and Corexit 9500. The screening study was performed at the standard test temperature of 13 °C, using a 200°C+ residue emulsified with 50 vol. % seawater. The dosage testing was performed using a similar emulsion and temperature as for the screening study. This testing involved Dispersant to Oil ratios (DOR) of 1:10, 1:25, 1:50, and 1:100.

The results of the screening are presented in Table 3-8 below and show that Corexit 9500 gave the highest dispersant effectiveness closely followed by Dasic NS. Dasic NS is the dispersant agent currently in the NOFO stock, and is considered to be the operational target agent when applying dispersant on a marine oil spill. Thus, Dasic NS was selected for use in the systematic dispersibility testing in agreement with the client. The results of the dosage testing are presented in Table 3-9 and increasing dispersibility with higher dosages for the low energy IFP-test. The results of the high energy MNS-test show similarly high dispersibility independent of the DOR.

Further dispersibility testing was performed on emulsions containing different volume per cent of water, as listed in Table 3-10 and Table 3-11 below.

Table 3-8: Screening test on Bøyla crude oil using the IFP- and MNS-tests, measured on a 50 vol. % 200°C+ emulsion with viscosity of 1030 at 13 °C

Dispersant (DOR 1:25)	Efficiency dispersant (200°C+ /50 vol. % emulsion)	
	IFP	MNS
Corexit 9500	84	100
Dasic NS	81	97
Finasol OSR 52	71	-
Gamlen OD 4000	69	-
Superdispersant	67	-

Table 3-9: Dosage rate testing on Bøyla crude oil using the IFP-and MNS-test at 13 °C and a 200°C+ 50 vol. % emulsion with viscosity of 1086

Dispersant (dosage rate)	Efficiency of dispersant on 200°C+/50 vol. % emulsion	
	IFP	MNS
Dasic NS (1:25)*	81	97
Dasic NS (1:50)	57	100
Dasic NS (1:100)	22	100
Dasic NS (1:200)	19	96

**results from screening, presented in Table 3-8 above*

Table 3-10: Efficiency of dispersant on weathered Bøyla oil/emulsions at 13 °C

Residue	Water content (vol. %)	Viscosity (mPa·s) 10 s^{-1}	Viscosity (mPa·s) 100 s^{-1}	Efficiency (%)	
				IFP	MNS
150°C+	0	68	62	83	100
200°C+	0	153	143	72	100
250°C+	0	730	520	50	100
150°C+	50	486	343	87	100
200°C+	50	1030	665	81	97
250°C+	50	2562	1493	60	100
150°C+	75	1883	648	75	67
200°C+	75	4036	1371	67	25
250°C+	75	10644	3481	3	18
150°C+	89	1603	717	77	100
200°C+	83	3069	1297	71	100
250°C+	71	17153	4073	2	17

Table 3-11: Efficiency of dispersant on weathered Bøyla oil/emulsions at 5 °C

Residue	Water content (vol. %)	Viscosity (mPa·s) 10 s^{-1}	Viscosity (mPa·s) 100 s^{-1}	Efficiency (%)	
				IFP	MNS
250°C+	50	9287	3656	-	79
200°C+	69	6565	2607	-	97
250°C+	70	19847	3291	-	41

The "window of opportunity" has been characterised based on the dispersibility limits. The dispersibility limits are estimated based on the efficiency of Dasic NS on emulsions of Bøyla crude oil, more specifically on the effectiveness of the dispersant relative to the viscosities of the Bøyla emulsions. The upper limit of dispersibility was not met with the results obtained from the testing performed at 13 °C, and a limited number of emulsions were made and tested using the MNS-test at 5 °C in attempt to obtain this upper limit.

The results are presented in Table 3-11. Unfortunately, the criteria for establishing an upper limit were not met, and the upper limit for dispersibility has been estimated based on the available data and experience from previous studies of other Norwegian crude oils.

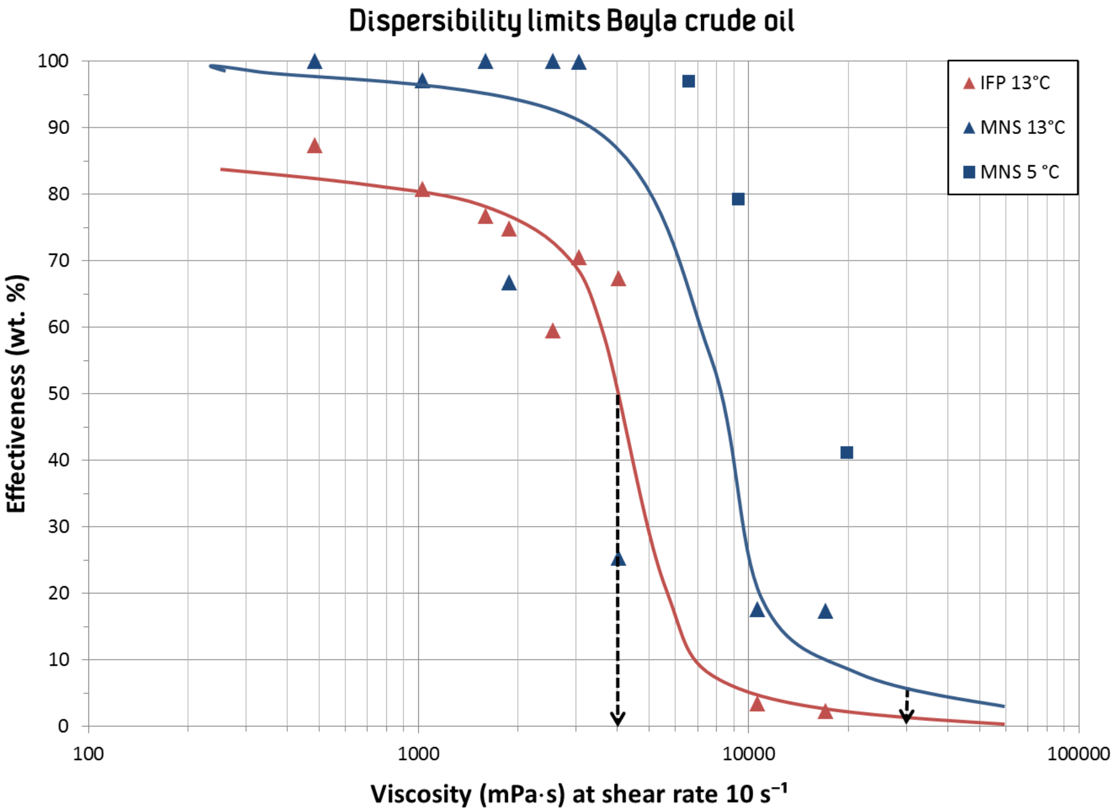


Figure 3-5: Dispersant effectiveness on emulsions and residues of Bøyla crude oil, at 5 and 13 °C

The result from the dispersibility testing is shown in Figure 3-5 along with the dispersibility limits. Observe that the upper limit is based on an extrapolation of the curve based on the laboratory results. Historically, few crude oils have been seen to be dispersible above 30 000 mPa·s, and Bøyla has been given this estimated limit. The lower dispersibility limit has been set at 4 000 mPa·s and both limits are presented in Table 3-12.

Table 3-12: Estimated viscosity limits for use of dispersant for Bøyla emulsion and the criteria for definition of time window

Dispersibility	**Criteria (wt. %)**	**Dispersibility limits based on oil viscosities (mPa·s = cP)**
Chemically dispersible	IFP efficiency > 50 %	4 000
Not chemically dispersible	MNS efficiency < 5 %	30 000*

** Estimated limit based on extrapolation of the available dispersibility data from both the low energy IFP-test and the high energy MNS-test, and experience from other similar studies of Norwegian crude oils.*

4 Predictions with SINTEF Oil Weathering Model (OWM)

4.1 Description of SINTEF OWM

A systematic stepwise laboratory procedure developed at SINTEF (Daling *et al.*, 1990) was used to isolate and map the various weathering processes that take place when oil is spilled on the sea surface. Laboratory study of the weathering properties of Bøyla crude oil was conducted at 13 °C and the analytical parameters were further used as input to the SINTEF Oil Weathering Model (OWM) (version 4.0 beta). The experimental design for the study of Alta crude oil is described in Appendix B, and the results are presented in detail in Chapter 3. The input data to the SINTEF OWM is given in Appendix C.

The SINTEF OWM relates oil properties to a chosen set of conditions (oil/emulsion film thickness, sea state and sea temperature) and predicts the change rate of the oil's properties and behaviour on the sea surface. The SINTEF OWM is schematically shown in Figure 4-1. The predictions obtained from the SINTEF OWM are useful tools in the oil spill contingency planning related to the expected behaviour of oil on the sea surface, and to evaluate the time window for operational response strategies in a spill operation. In this report, the presented predictions span a 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.

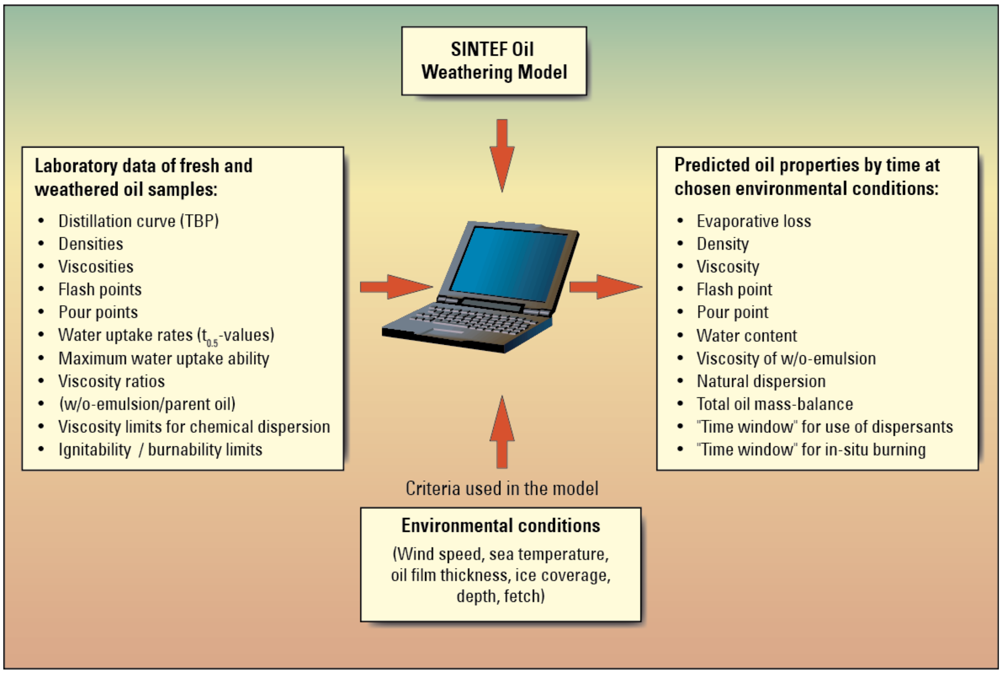


Figure 4-1: Schematic input data to the SINTEF OWM and the predicted output oil properties

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.

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.

Sea temperature

The prevailing weather conditions greatly influence the weathering rate of oil on the sea surface. Two sets of predictions are given in this report, one for average summer temperatures and one for average winter temperatures. The temperatures chosen for Bøyla as representative temperatures for the North Sea are 5 °C and 15 °C.

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

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

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

4.2 Prediction of Bøyla weathering properties

Input to the OWM

Oil type:	Crude oil
Geographical area:	North Sea
Terminal oil film thickness:	1 mm
Release rate:	1.33 metric tonnes/minute for 15 minutes; a total of 20 metric tonnes
Sea temperature:	5 °C and 15 °C
Wind speed:	2 m/s, 5 m/s, 10 m/s and 15 m/s

The data used as input to SINTEF OWM for Bøyla crude oil are given in Appendix C.

How to use the prediction charts: an example
If Bøyla 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 4-2 gives an example for the following scenario:

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

Table 4-2: Weathering properties for Bøyla obtained from the prediction charts after 12 hours of weathering

Property	Winter temperature (5 °C, 10 m/s)	Summer temperature (15 °C, 10 m/s)
Evaporation, vol. %	20	23
Water content, vol. %	69	74
Flash point, °C	96	110
Pour Point, °C	5	13
Viscosity, mPa·s*	9600	9400

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

4.3 Predictions of Bøyla crude oil weathering properties

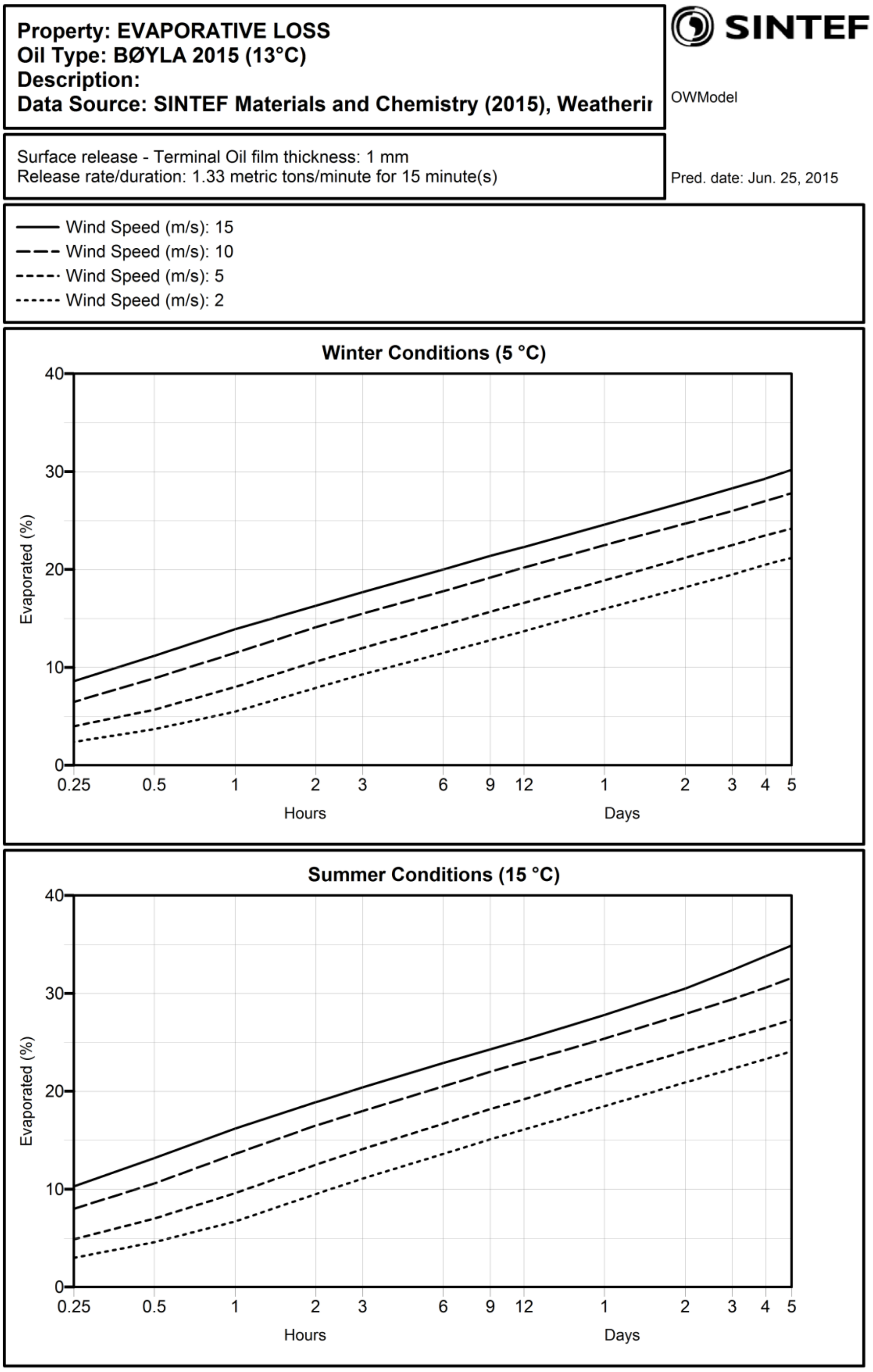


Figure 4-2: Evaporative loss of Bøyla crude oil predicted at sea temperatures of 5 °C and 15 °C

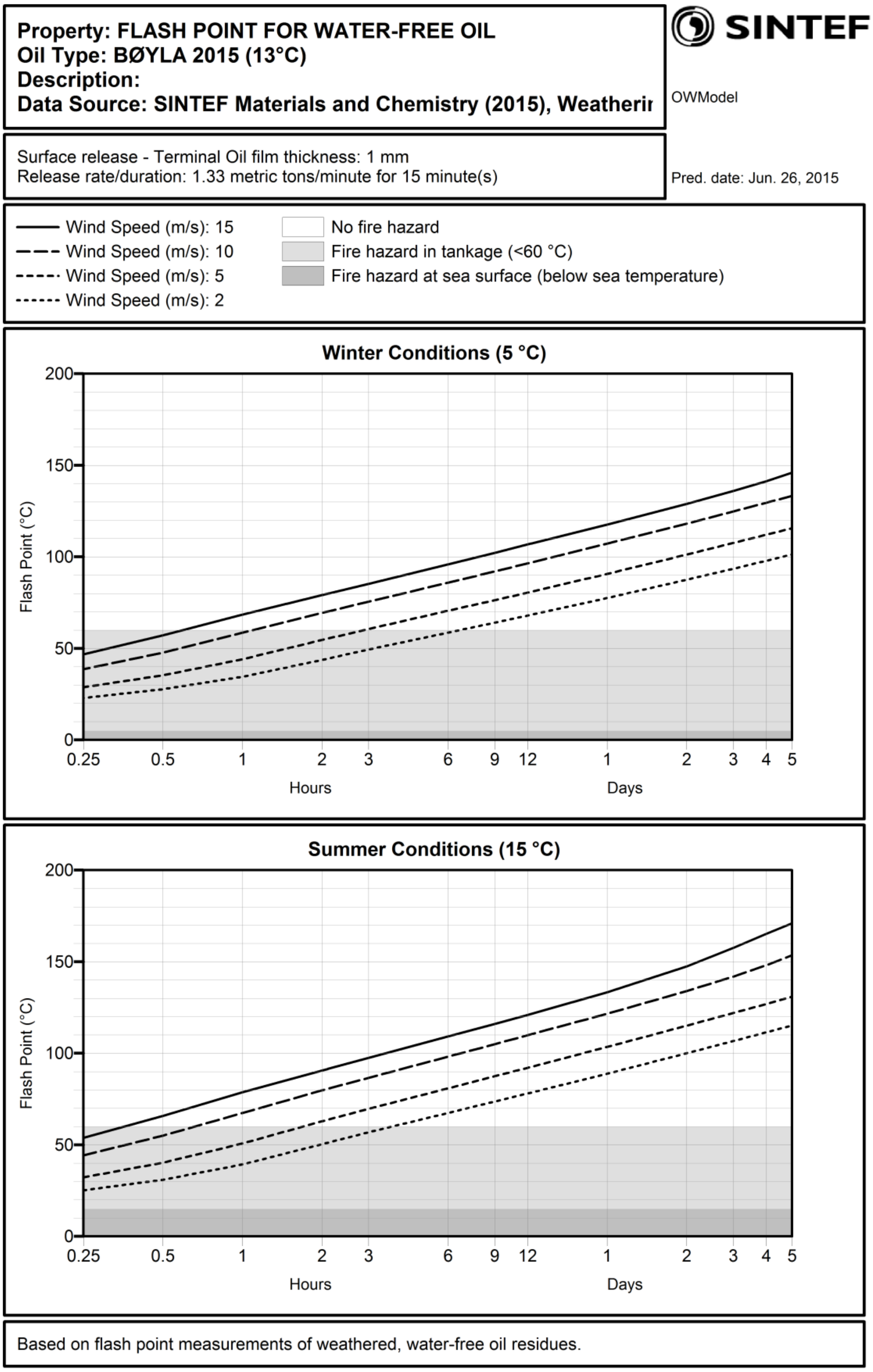


Figure 4-3: Flash point of Bøyla predicted at sea temperatures of 5 °C and 13 °C

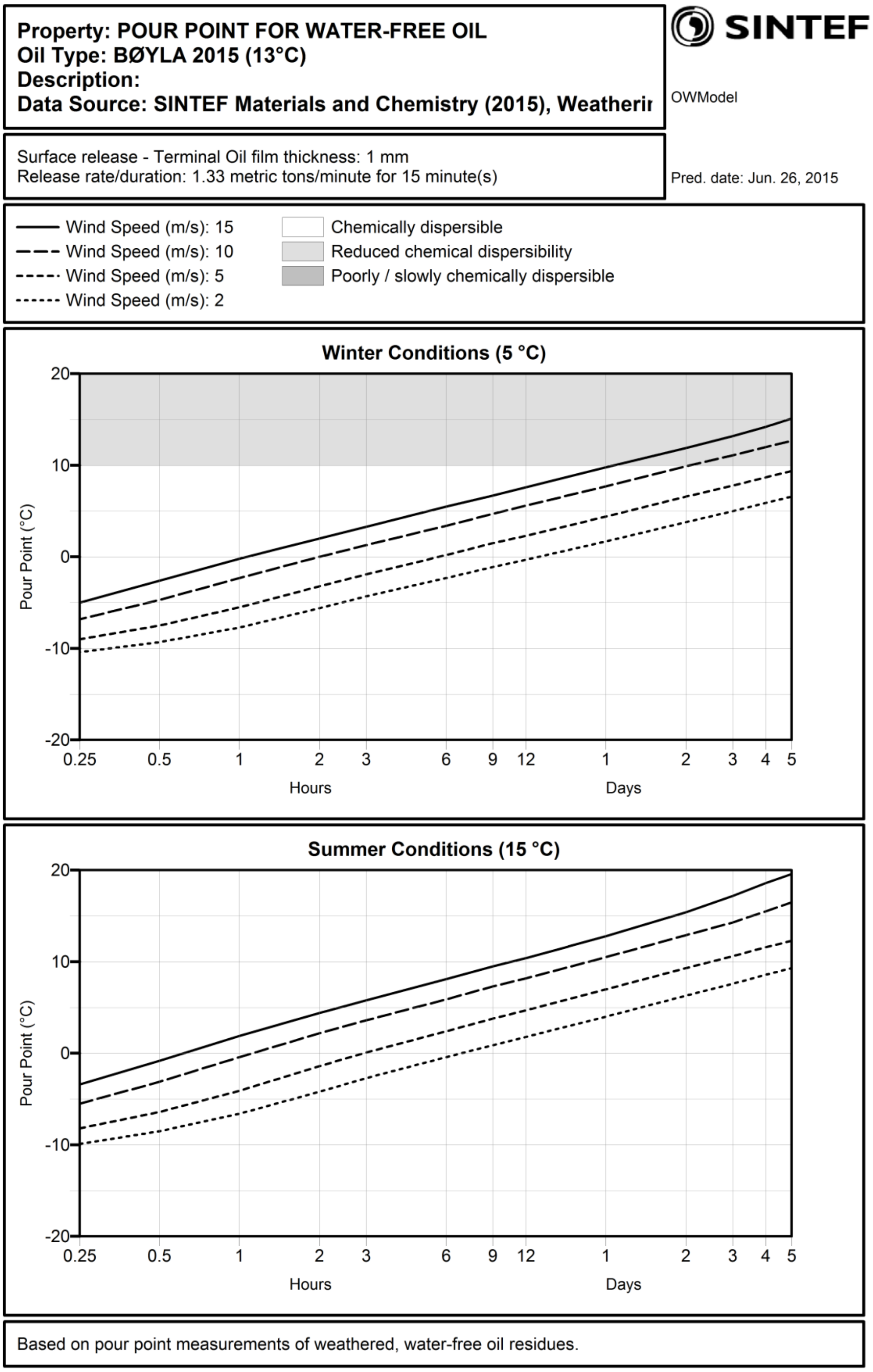
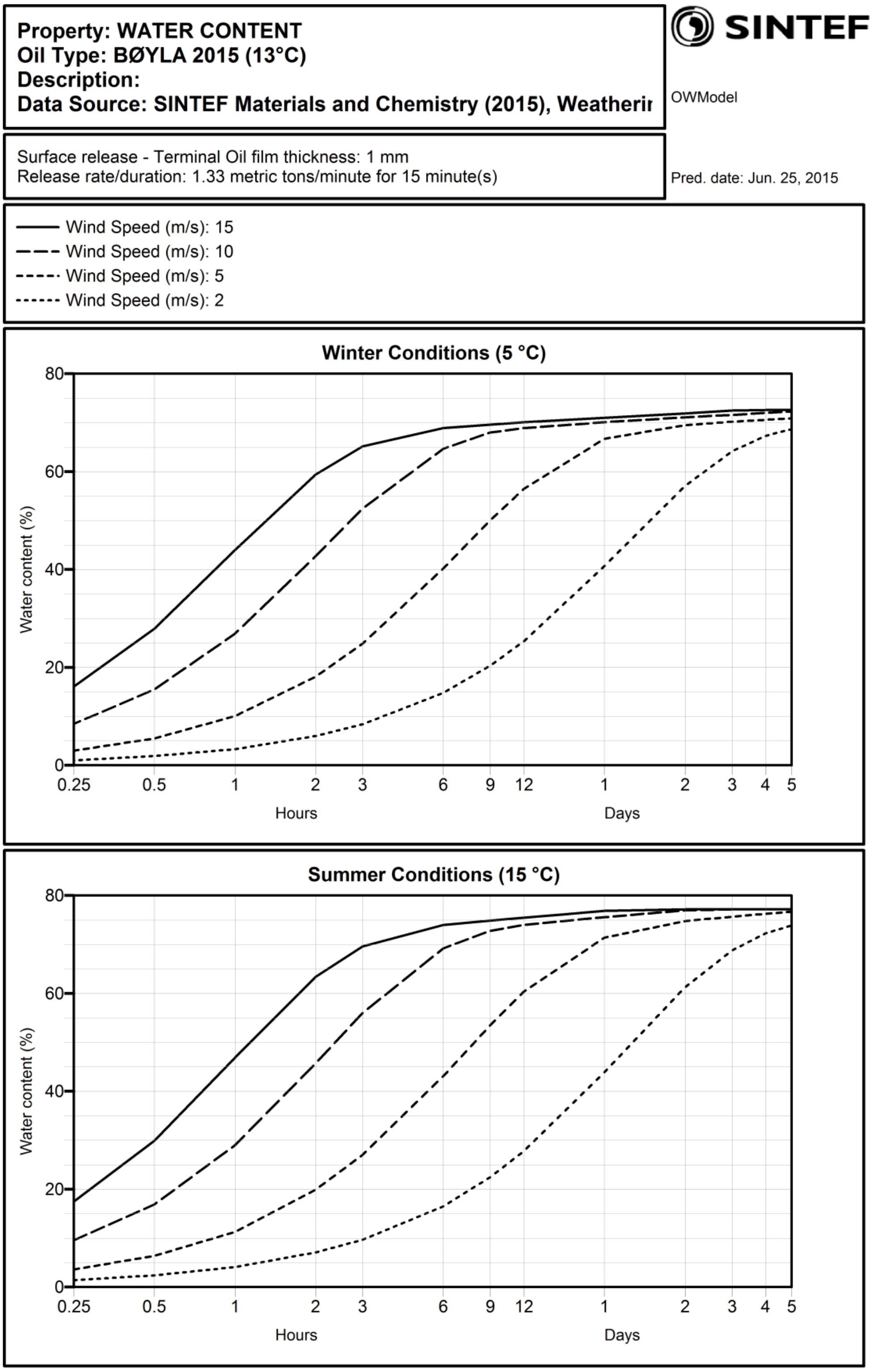


Figure 4-4: Pour point of Bøyla predicted at sea temperatures of 5 °C and 13 °C



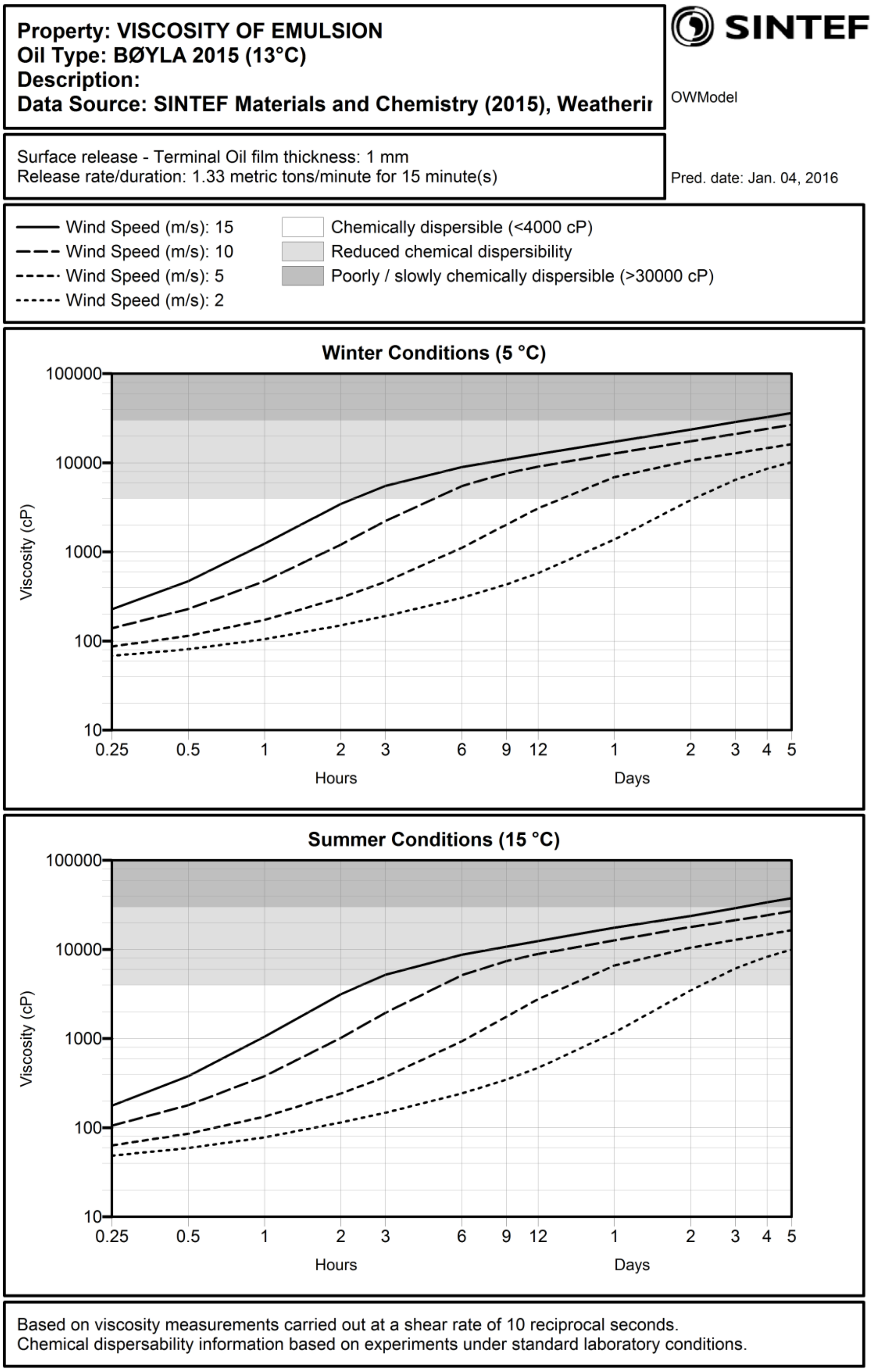
Property: WATER CONTENT
Oil Type: BØYLA 2015 (13°C)
Description:
Data Source: SINTEF Materials and Chemistry (2015), Weatherir

SINTEF
OWModel

Surface release - Terminal Oil film thickness: 1 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Jun. 25, 2015

Figure 4-5: Water content of Bøyla predicted at sea temperatures of 5 °C and 13 °C



Property: VISCOSITY OF EMULSION
Oil Type: BØYLA 2015 (13°C)
Description:
Data Source: SINTEF Materials and Chemistry (2015), Weatheri

Surface release - Terminal Oil film thickness: 1 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

SINTEF
OWModel
Pred. date: Jan. 04, 2016

—— Wind Speed (m/s): 15	☐ Chemically dispersible (<4000 cP)
— — Wind Speed (m/s): 10	▨ Reduced chemical dispersibility
- - - - Wind Speed (m/s): 5	■ Poorly / slowly chemically dispersible (>30000 cP)
------ Wind Speed (m/s): 2	

Based on viscosity measurements carried out at a shear rate of 10 reciprocal seconds.
Chemical dispersability information based on experiments under standard laboratory conditions.

Figure 4-6: Viscosities of Bøyla emulsions predicted at sea temperatures of 5 °C and 13 °C. Predictions are based on measurements performed at a shear rate of 10 s^{-1}

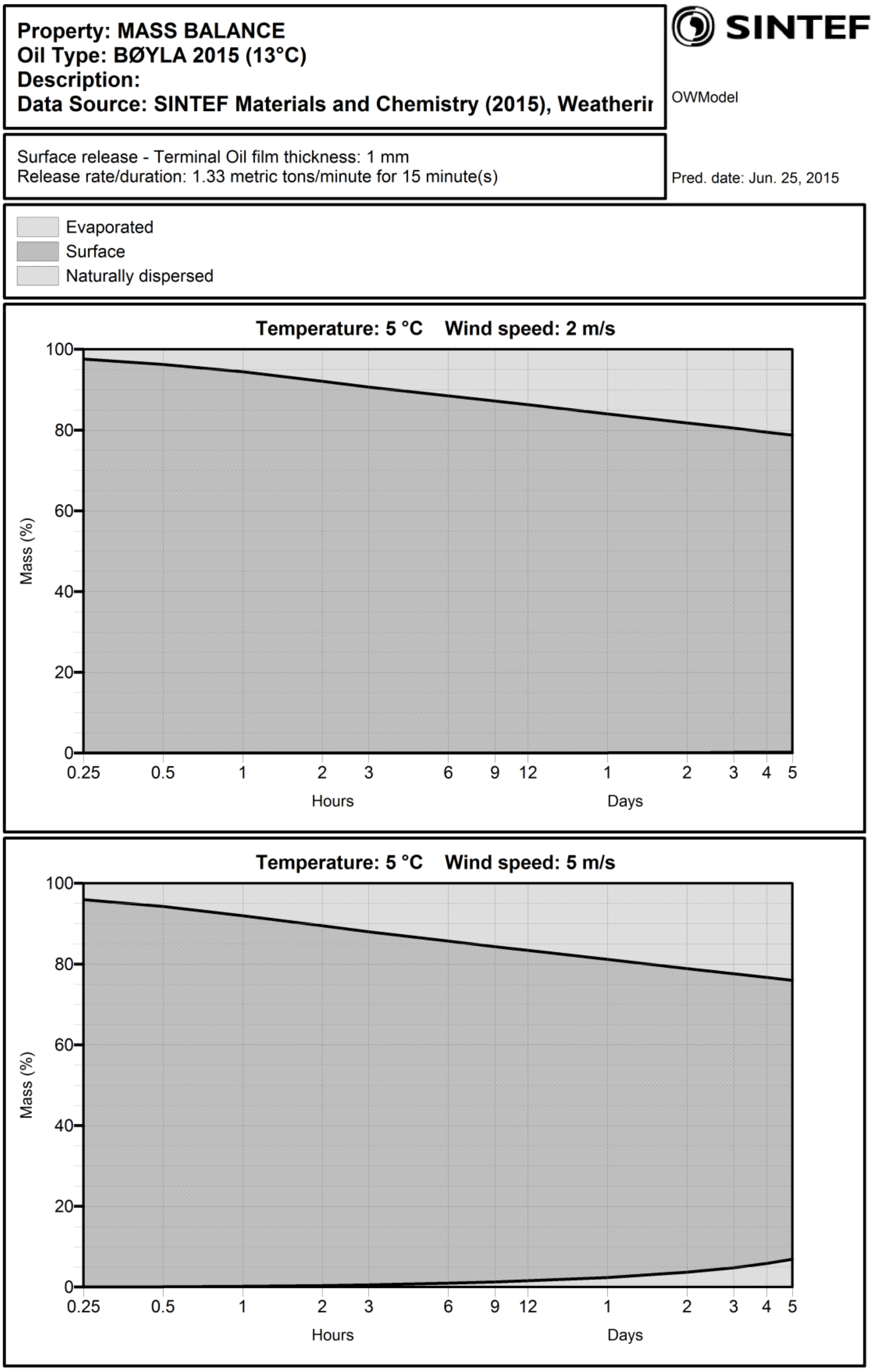
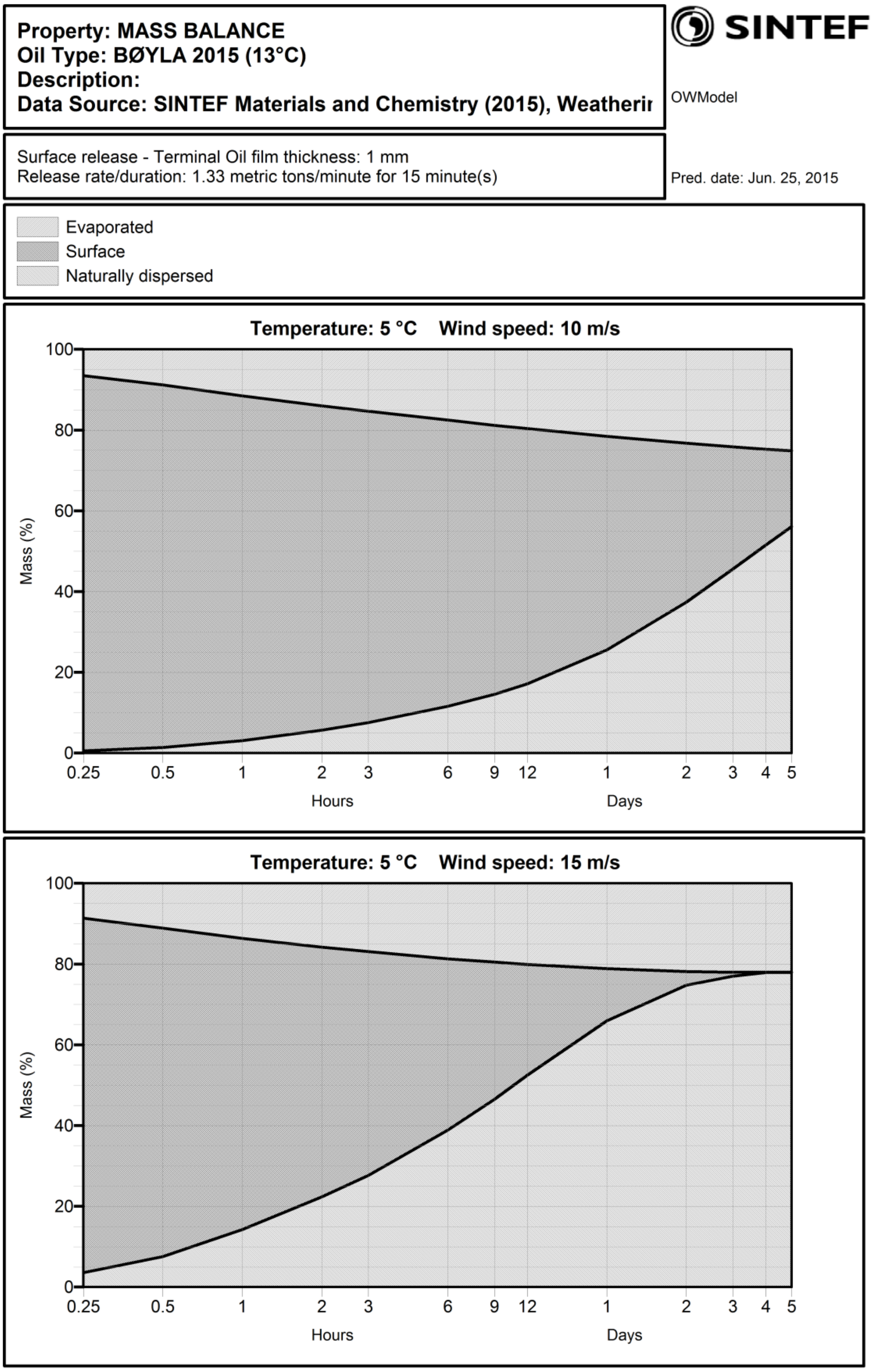


Figure 4-7: Predicted mass balance for Bøyla at 5°C and wind speeds of 2 and 5 m/s



Property: MASS BALANCE
Oil Type: BØYLA 2015 (13°C)
Description:
Data Source: SINTEF Materials and Chemistry (2015), Weatherir

Surface release - Terminal Oil film thickness: 1 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

SINTEF
OWModel
Pred. date: Jun. 25, 2015

Figure 4-8: Predicted mass balance for Bøyla at 5°C and wind speeds of 10 and 15 m/s

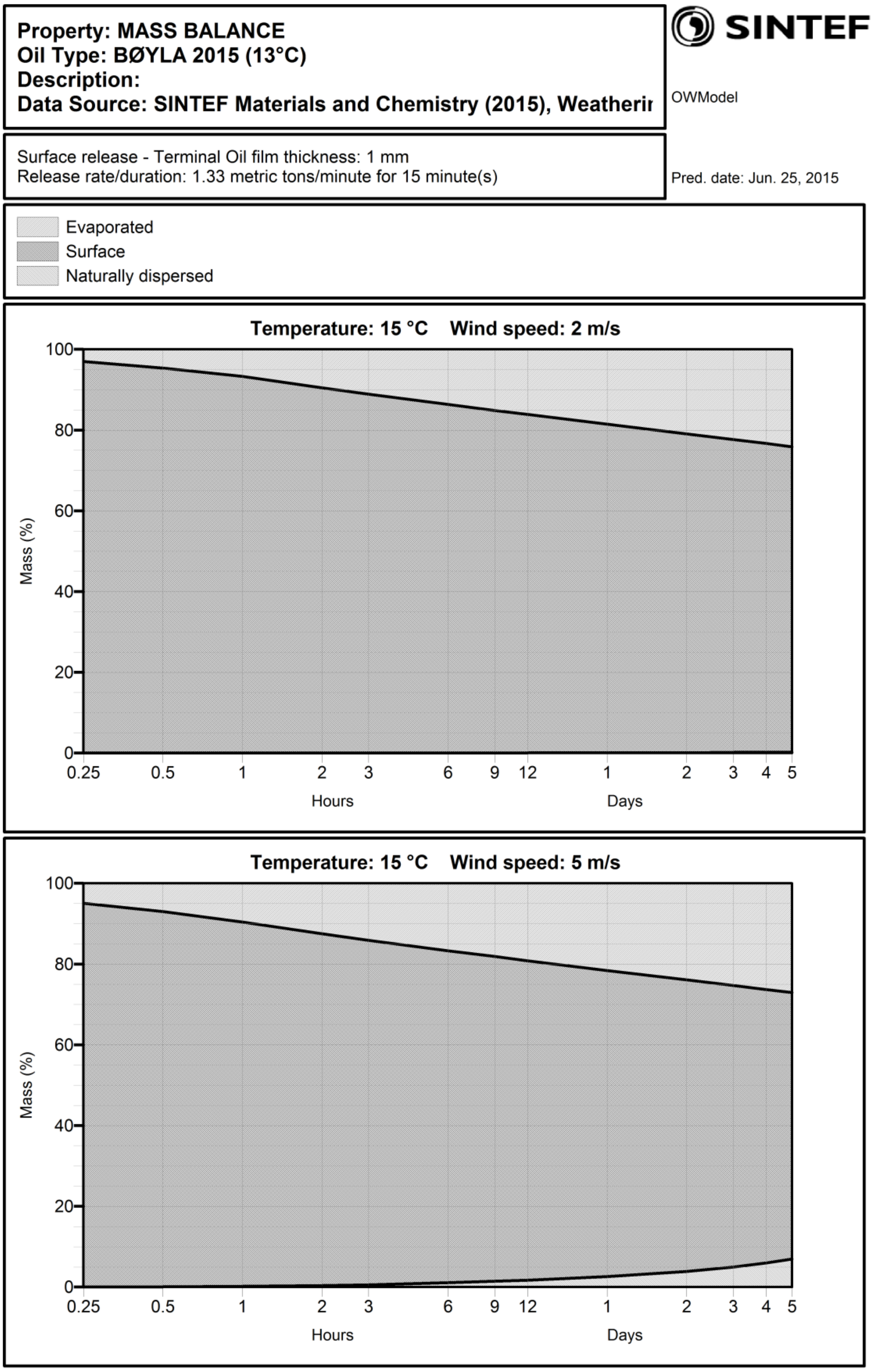
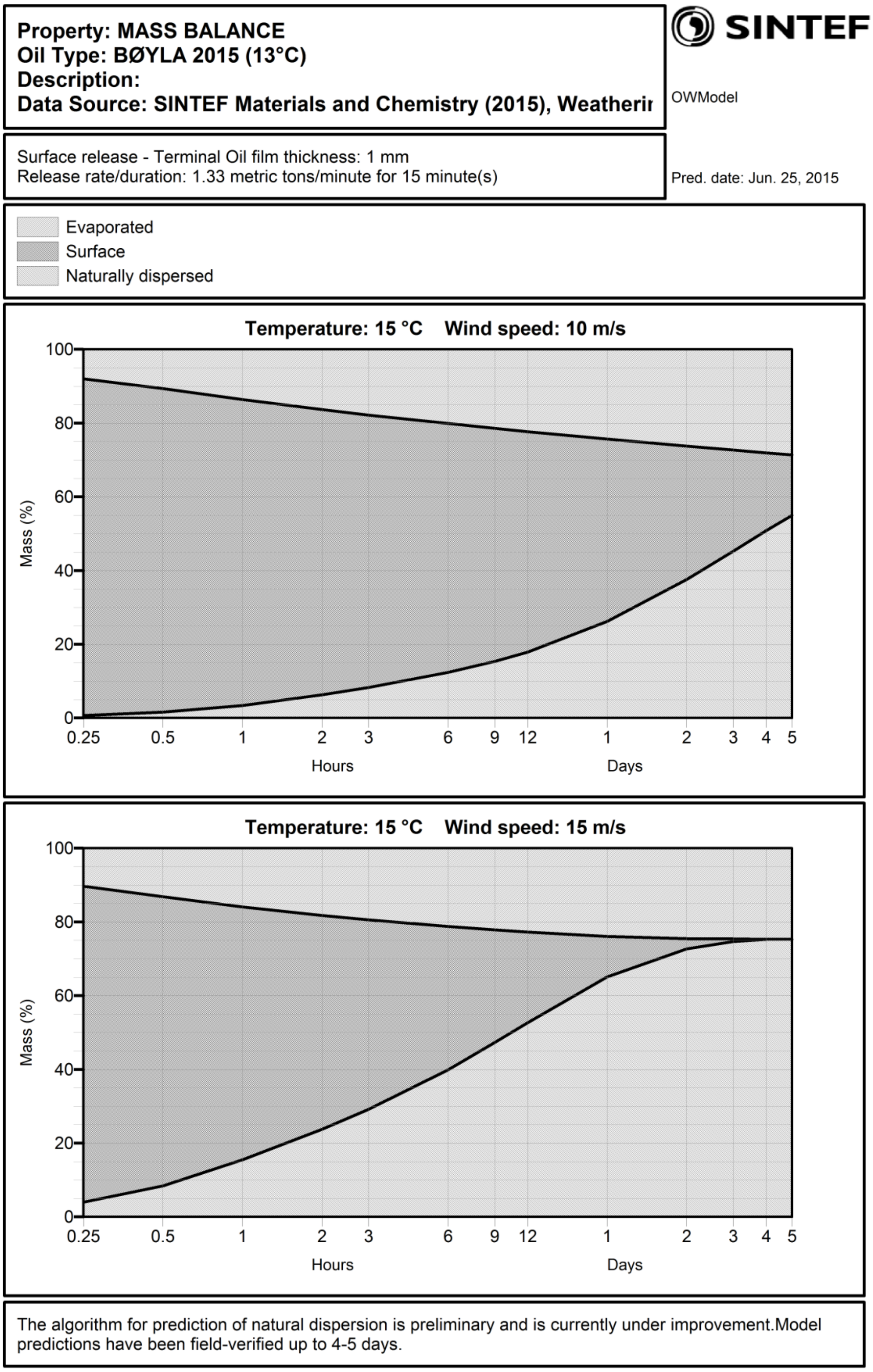


Figure 4-9: Predicted mass balance for Bøyla at 15 °C and wind speeds of 2 and 5 m/s



Property: MASS BALANCE
Oil Type: BØYLA 2015 (13°C)
Description:
Data Source: SINTEF Materials and Chemistry (2015), Weatherir

SINTEF

OWModel

Surface release - Terminal Oil film thickness: 1 mm
Release rate/duration: 1.33 metric tons/minute for 15 minute(s)

Pred. date: Jun. 25, 2015

▨	Evaporated
▨	Surface
▨	Naturally dispersed

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 4-10: Predicted mass balance for Bøyla at 15°C and wind speeds of 10 and 15 m/s

4.4 Comparison with other oils

Weathering predictions are compared to a selection of other Norwegian crude oils with varying properties. The oils chosen for comparison are Alvheim Blend, Kneler, Balder Blend and Statfjord A, as listed in Table 3-1. The presented comparisons are based on predictions limited to summer conditions (15 °C) and wind speeds of 10 m/s.

4.4.1 Evaporative loss

The evaporative loss of Bøyla and the oils used for comparison is presented in Figure 4-11 below. Bøyla has the lowest evaporative loss of the oils and is predicted to lose approximately 25 vol. % within the first 24 hours after spilled. For Statfjord, which has the highest evaporative loss of the presented oils, an evaporative loss of approximately 40 vol. % is predicted within the same period.

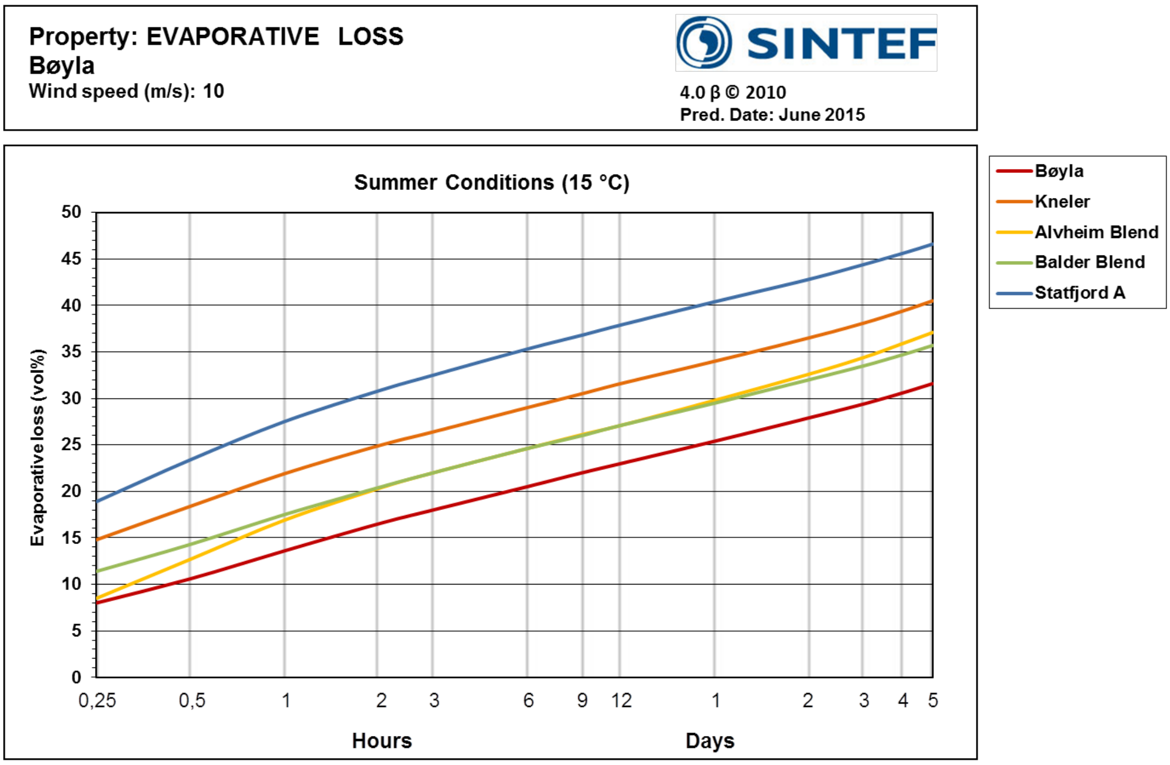


Figure 4-11: Predicted evaporative loss at 15 °C and 10 m/s for Bøyla compared to other oils

4.4.2 Flash point

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 high as long as the flash point of the oil is below the sea temperature. The fire hazard, dependent on the proportions of volatile components in oil, is usually over within a few minutes of weathering at sea due to the rapid evaporation of these components. Figure 4-12 below presents the predicted flash points for Bøyla and the other chosen oils.

For all the presented oils, the predicted flash points are higher than the ambient sea temperature after the first quarter of an hour on sea surface. Bøyla has a similar flash point to Kneler and Balder blend while Alvheim has lower flash point. Note that Statfjord is not presented due to lack of data.

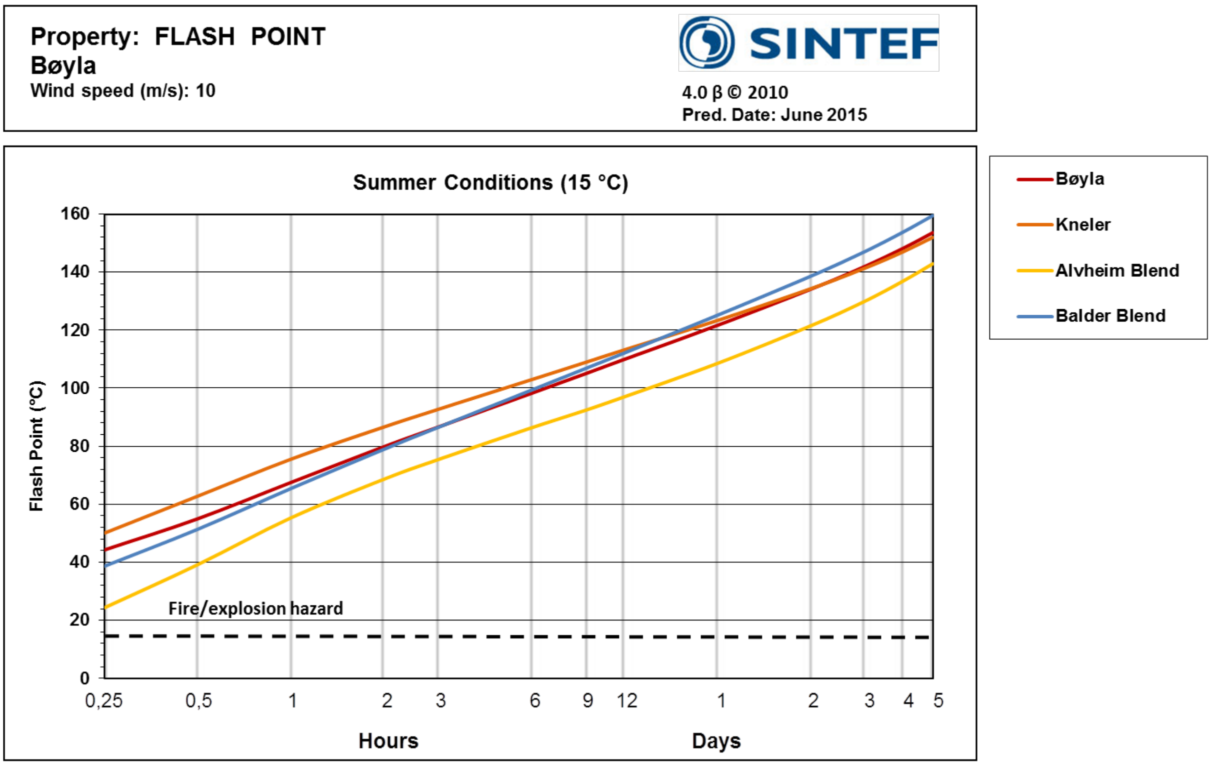


Figure 4-12: Predicted flash point at 15 °C and 10 m/s for Bøyla compared to other oils

4.4.3 Pour point

Pour point depends on the oil's wax content and the amount of lighter components that contribute to keep the waxes dissolved in the oil. In addition, high asphaltene content prevents wax precipitation and lattice formation and thus lowers the pour point. The pour point of oil may influence the dispersant effectiveness as a high pour point may cause the oil to solidify or become semi-solid which can prevent the dispersants from soaking into the oil slick.

Presented results show that Bøyla has low asphaltene content and a medium content of wax. In addition, the evaporative loss of Bøyla was lower than those of the other presented oils, and retains enough lighter components for keeping the wax dissolved and preventing solidification for the predicted time frame. Figure 4-13 below shows the predicted pour points of Bøyla and the oils chosen for comparison. Bøyla expresses the lowest pour point and is not predicted to solidify within the first five days at sea at the presented weather conditions.

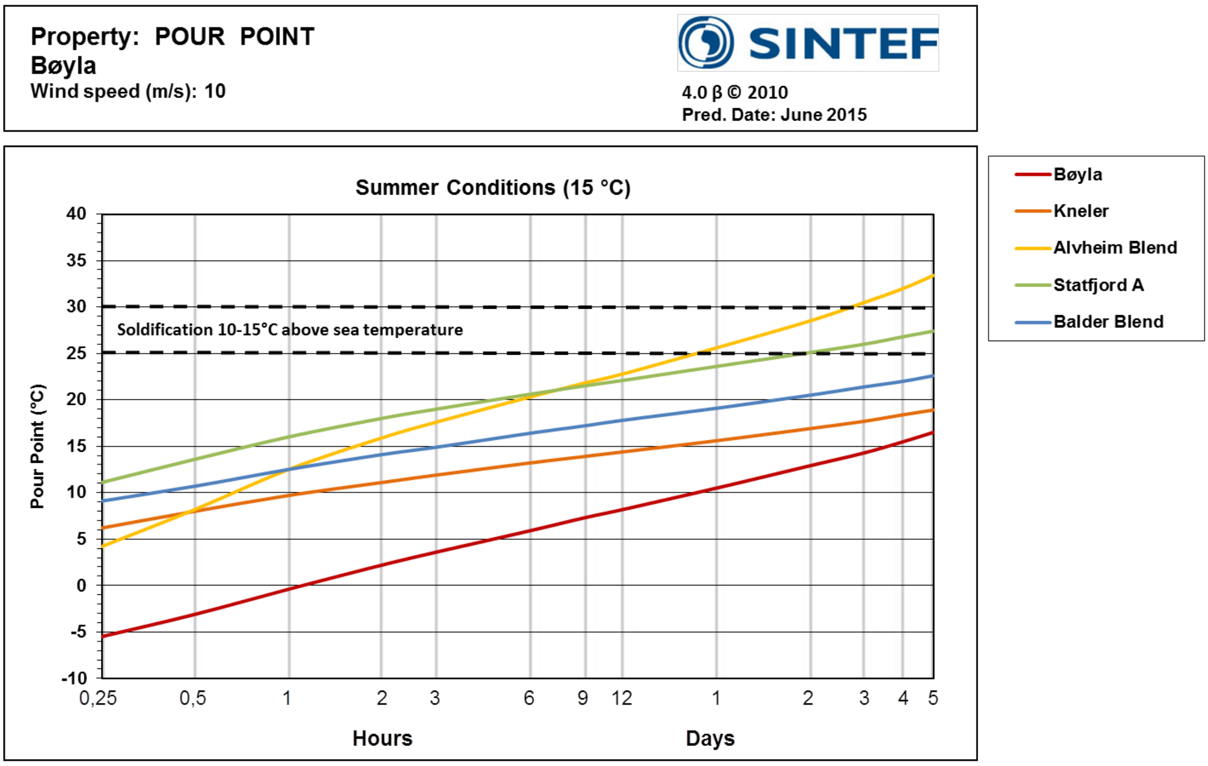


Figure 4-13: Predicted pour point at 15 °C and 10 m/s for Bøyla compared to other oils

4.4.4 Water content

Figure 4-14 below shows the water uptake and total predicted water content for Bøyla, Kneler, Alvheim blend, and Statfjord A and Balder Blend. The water uptake of Bøyla is slower than that of Kneler but more rapid than that of Alvheim blend, Statfjord A and Balder blend. The total water content stabilizes at approximately 78 vol. % for both Bøyla and Kneler, while Balder blend and Alvheim blend have lower predicted water contents.

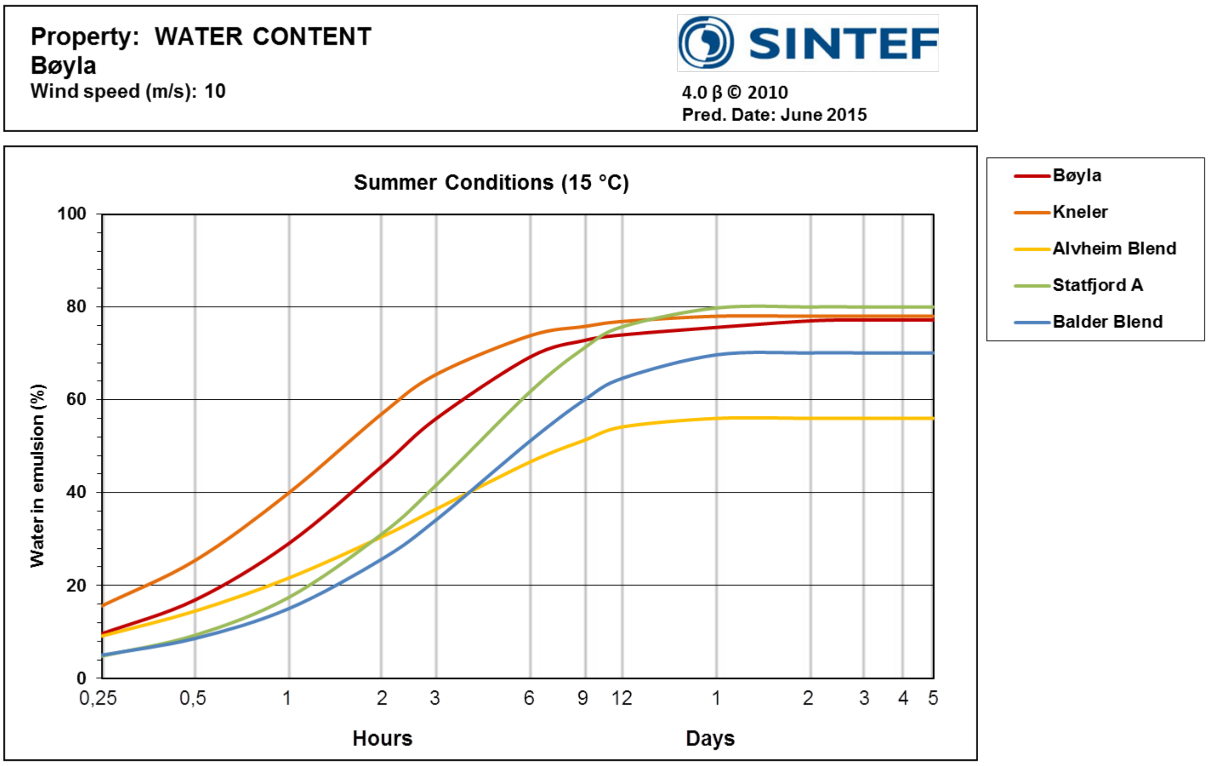


Figure 4-14: Predicted water content at 15 °C and 10 m/s for Bøyla compared to other oils

4.4.5 Emulsion viscosity

The emulsion viscosities of Bøyla and the oils used for comparison are presented in Figure 4-15 below. When spilled to the sea surface Bøyla is predicted to have a low emulsion viscosity similar to Alvheim. After 1-2 hours the emulsion viscosities rapidly increase and after three hours Bøyla is predicted to have the highest emulsion viscosities of the presented oils. A similar but less distinct development can be seen for the emulsion viscosities of Balder blend.

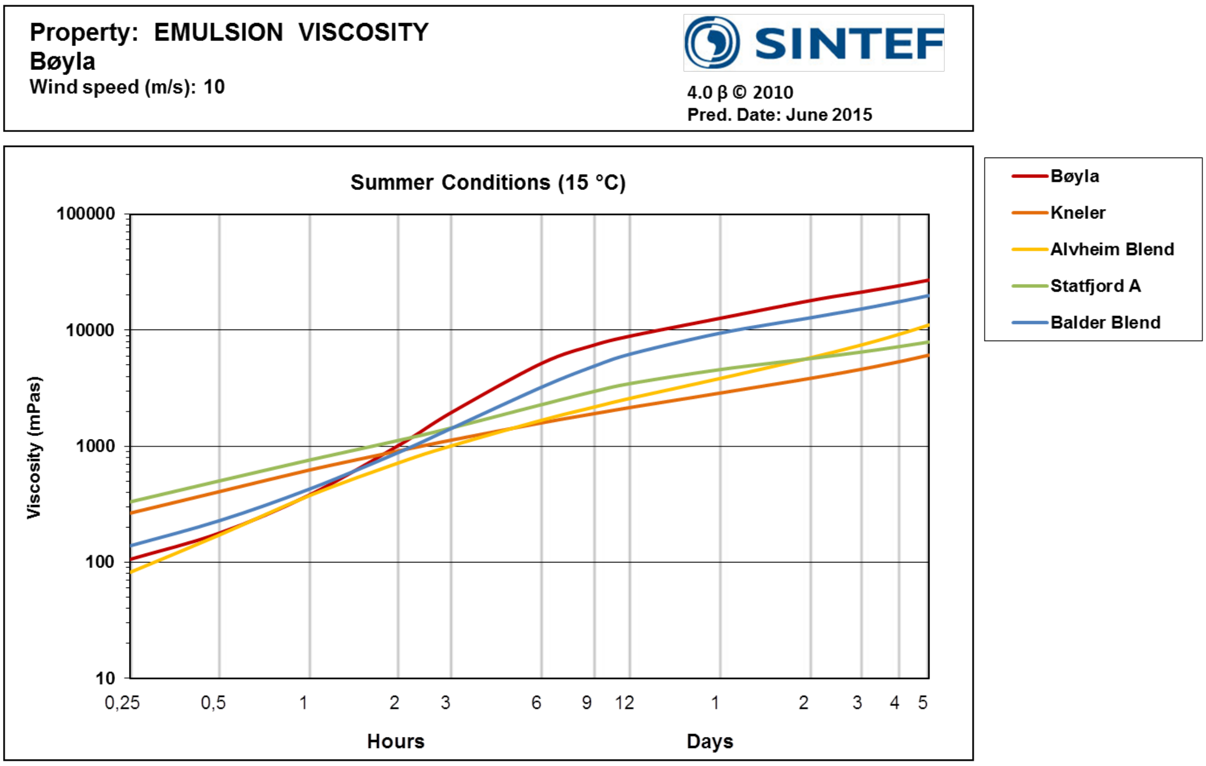


Figure 4-15: Predicted emulsion viscosity at 15 °C and 10 m/s for Bøyla compared to other oils

4.4.6 Surface oil

Due to evaporative loss and natural dispersion the oil on the sea surface will gradually be reduced. Figure 4-16 illustrates the predicted mass balance of the Bøyla surface slick compared to other oils. The lower evaporative loss of Bøyla results in a larger amount remaining on surface compared to the other oils and Bøyla is predicted to have the highest percentage of remaining surface oil of the compared crudes throughout the predicted five day period. After four days approximately 20 % of the initially spilled Bøyla oil is predicted to remain on the sea surface.

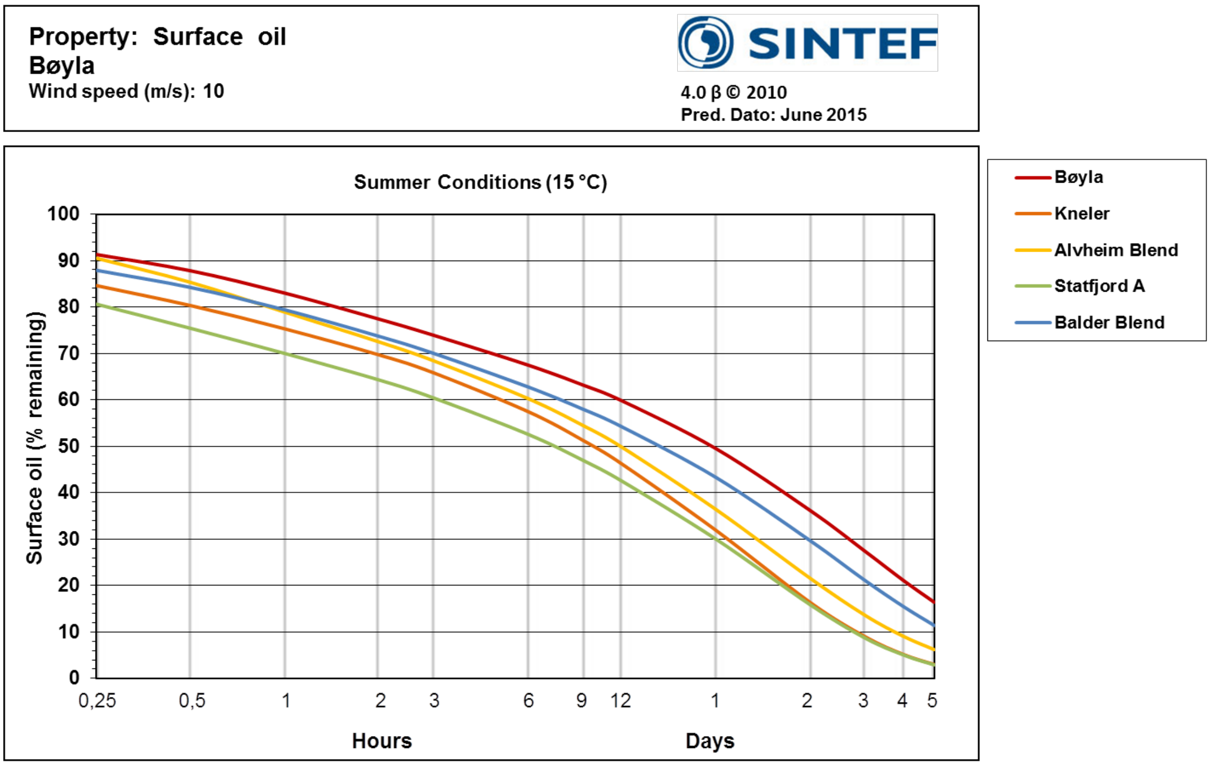


Figure 4-16: Predicted remaining surface oil at 15 °C and 10 m/s for Bøyla compared to other oils

5 Weathering properties of Bøyla crude oil related to oil spill properties

5.1 Oil properties

Fresh Bøyla crude oil has a density of 0.875 g/ml and medium wax content of 3.2 wt. %. The asphaltene content is low at 0.07 wt. % and the chromatogram of the fresh oil (Figure 3-1) shows that the oil is somewhat biodegraded. The evaporation of the remaining lighter components cause an increase in the relative content of surface active components such as wax and asphaltenes, which again contribute to stabilize the forming water-in-oil emulsions of Bøyla.

Knowledge of the alterations in physical and chemical properties caused by evaporation and other weathering processes are of importance for oil spill response.

5.2 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 Bøyla the flash point will be above the sea temperature within the first 15 minutes after a spill at 5 °C and 15 °C, as shown in Figure 5-1.

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 the emergency situation). Bøyla will surpass this limit within approximately 6 hours in low wind conditions and winter temperatures, and more rapidly in summer temperatures (approx. 4 hours).

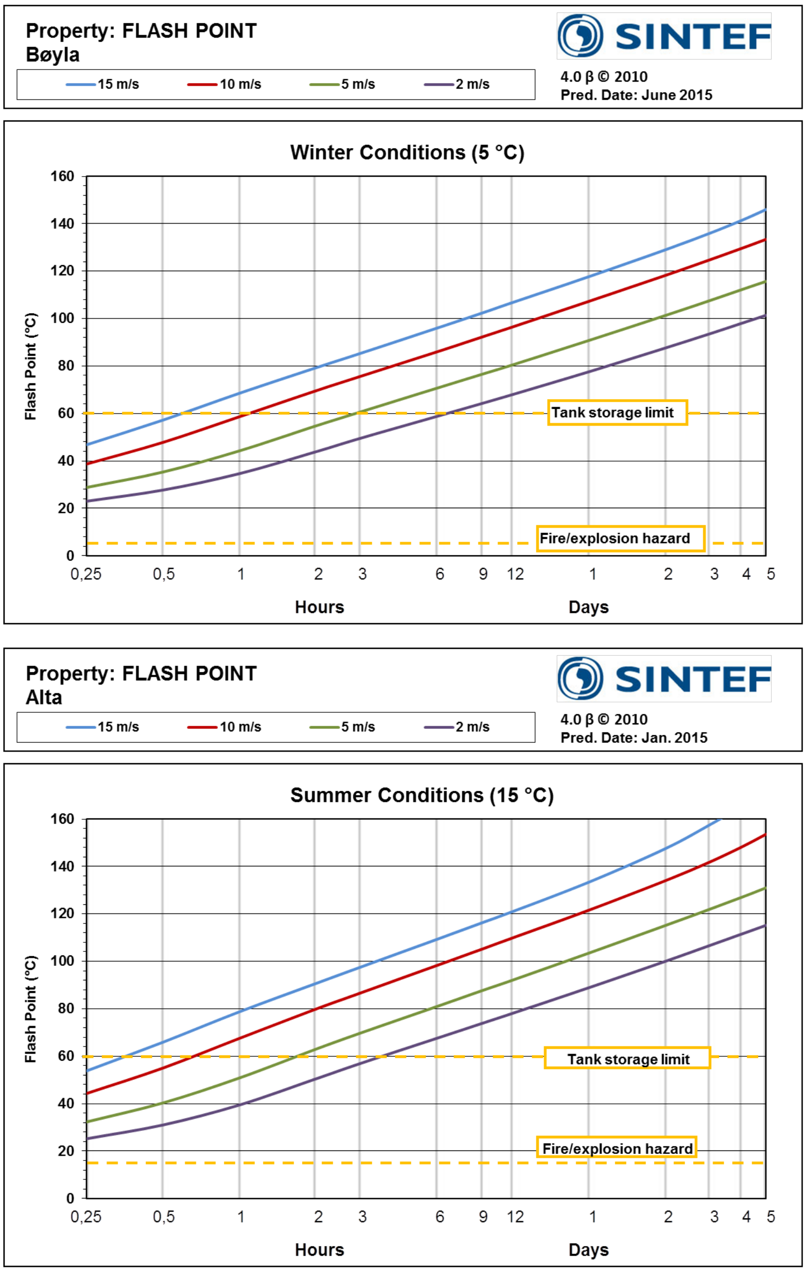


Figure 5-1: Flash point at different sea states for Bøyla crude oil in winter and summer conditions

5.3 Emulsion formation

The total amount of oil on the sea is reduced due to evaporation and natural dispersion in the early stages of weathering. However, as water is mixed into the oil and emulsions are formed, the total volume will increase. The small scale laboratory study showed that Bøyla form stable w/o-emulsions with relatively high water content, which cause a large increase in the total volume of surface oil/emulsion. Figure 5-2 shows the increase of emulsion volume relative to the volume of the remaining oil at 10 m/s wind at both 5 °C and 15 °C. As can be seen, the total volume of the emulsion may reach 210 and 230 vol. % of the originally released volume in winter and summer conditions, respectively.

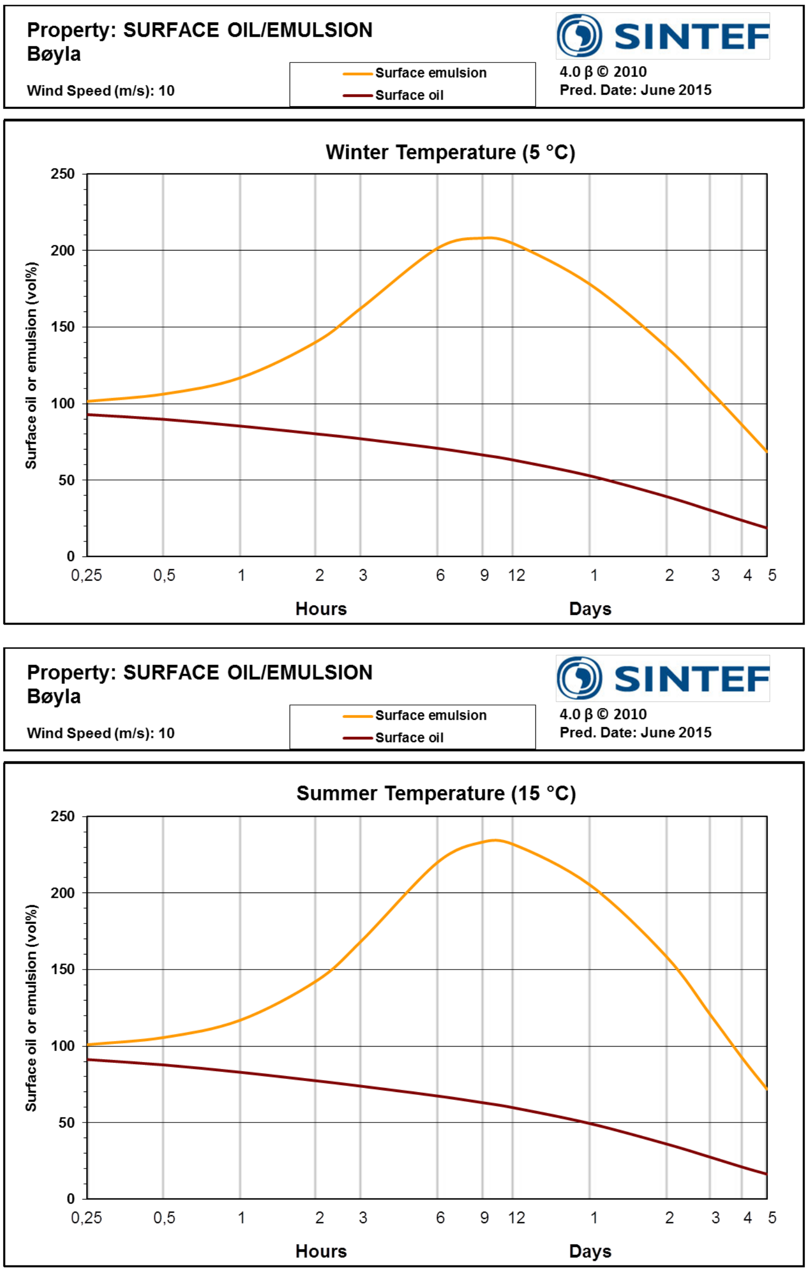


Figure 5-2: Difference in the total slick volume due to emulsification compared to non-emulsified oil. Decrease in total volume due to evaporation and natural dispersion at 10 m/s wind speed at temperatures of 5 °C and 15 °C

5.4 Addition of emulsion breaker

Emulsion breaker can be used during an oil spill operation to increase water release from an emulsion, normally after recovery prior to transfer to storage tank. The emulsion breaker is normally not added directly on the oil spill at sea surface.

Figure 5-3 illustrates the relative volumetric composition of water-in-oil emulsion and free water, for 250°+ residue of Bøyla oil both with and without the addition of emulsion breaker (Alcopol O 60 %). The two tested dosages caused a release of water from the emulsion with the higher dosage providing the highest effect. The 500 ppm dosage released approximately 20 vol. % of water while the 2000 ppm dosage released ca 40 vol. % water. The effects of emulsion breaker were also seen on emulsions of lesser weathering degrees and are presented in detail in Table 3-6 on page 8.

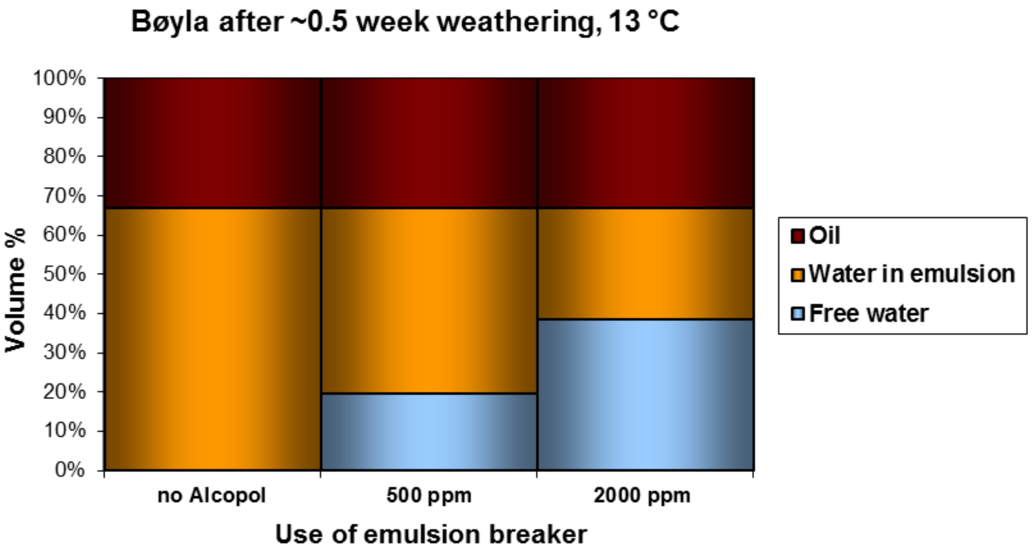


Figure 5-3: Relative volumetric composition of water-in-oil emulsion and free water for a Bøyla 200°C+ emulsion

5.5 Lifetime at sea – Natural dispersion and evaporation

The lifetime of an oil spill at sea depends on the oil's composition, the release conditions (e.g. on the surface, underwater) and environmental conditions (temperature, wind, waves). Natural dispersion and evaporation are the main weathering processes that remove an oil spill from the surface.

Figure 5-4 shows the remaining surface oil over time for different sea states and temperature conditions. Between 75-79 % of the initially spilled oil is predicted to remain on the sea surface after five days weathering in low wind conditions, for winter and summer temperatures. With higher wind conditions the removal from the sea surface will occur more rapidly and to a greater extent.

Considerably larger spills are expected to produce longer lifetimes, and individual modelling may be necessary.

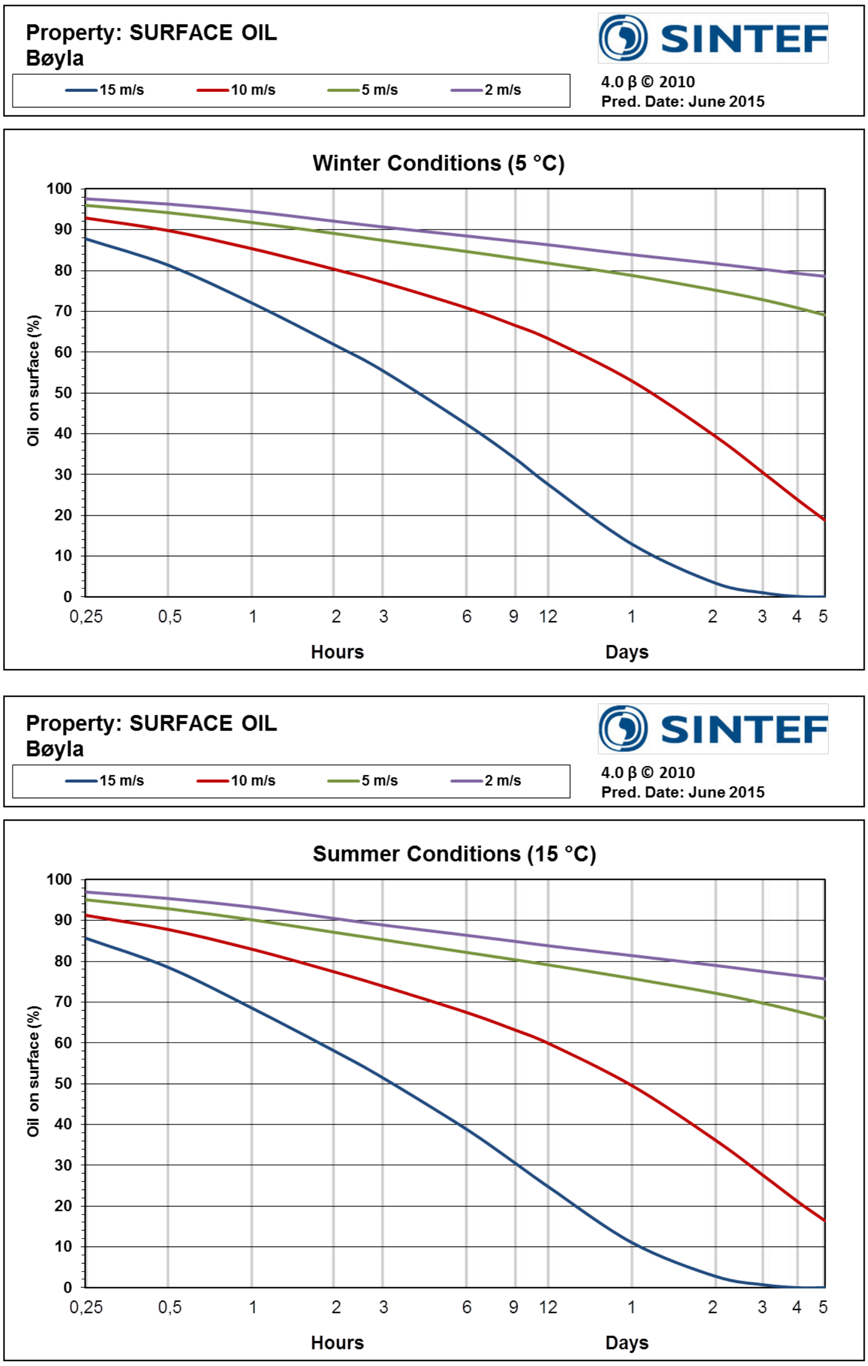


Figure 5-4: Remaining surface oil under different sea states for Bøyla at 5 °C and 15 °C

5.6 Oil spill response

5.6.1 Mechanical recovery

Experiences from Norwegian field trials have demonstrated that the effectiveness of various mechanical clean-up operations is reduced due to the high degree of leakage of the confined oil or w/o emulsion from the oil spill boom. This leakage is particularly pronounced if the viscosity of the oil or the w/o emulsion is lower than 1000 mPa·s (Nordvik et al., 1992). The lower viscosity limit for an optimal mechanical clean-up operation has therefore been set at 1000 mPa·s. It should be emphasized that boom leakage is also influenced by other factors as e.g. the operational speed of recovery vessel and weather conditions. Studies at SINTEF have shown that weir skimmers may have reduced recovery rate (m^3/t) at viscosities of 15,000-20,000 mPa·s (Leirvik et al., 2001).

The emulsion viscosities of Bøyla vary with different weather conditions. At low wind speeds (2 m/s) the 1000 mPa·s limit will be reached between 12 and 24 hours after spill, while at higher wind speeds (15 m/s) the same limit will be reached within one hour. Only small variations are observed between winter and summer conditions.

In some cases when high viscosity of the oil/emulsion is not a limiting factor, a high pour point (10-15 °C above sea temperature) could cause solidification when oil is spilled on the sea surface. The Bøyla crude oil has a low pour point and is not expected to solidify or affect the dispersibility within the first 5 days at sea in summer conditions. In winter conditions and high wind speeds (10-15 m/s), some influence on dispersibility can be expected after 24-48 hours (see Figure 4-4, page 22).

The predicted emulsion viscosity vary greatly with the various weather conditions; at the wind speeds of 15 m/s the 20 000 mPa·s limit is predicted to be reached between 24 and 48 hours after a spill, while at wind speeds of 5 and 2 m/s this limit is not predicted to be reached within the first five days after spill. Since Bøyla has a low pour point and is not predicted to solidify under the set weathering conditions, the flowability of the emulsion is believed to remain sufficient for the use of weir skimmers for mechanical recovery for emulsion viscosities up to 30 000 mPa·s. The use of "High visc.-skimmer" should be considered if the emulsion viscosities surpass 30 000 mPa·s.

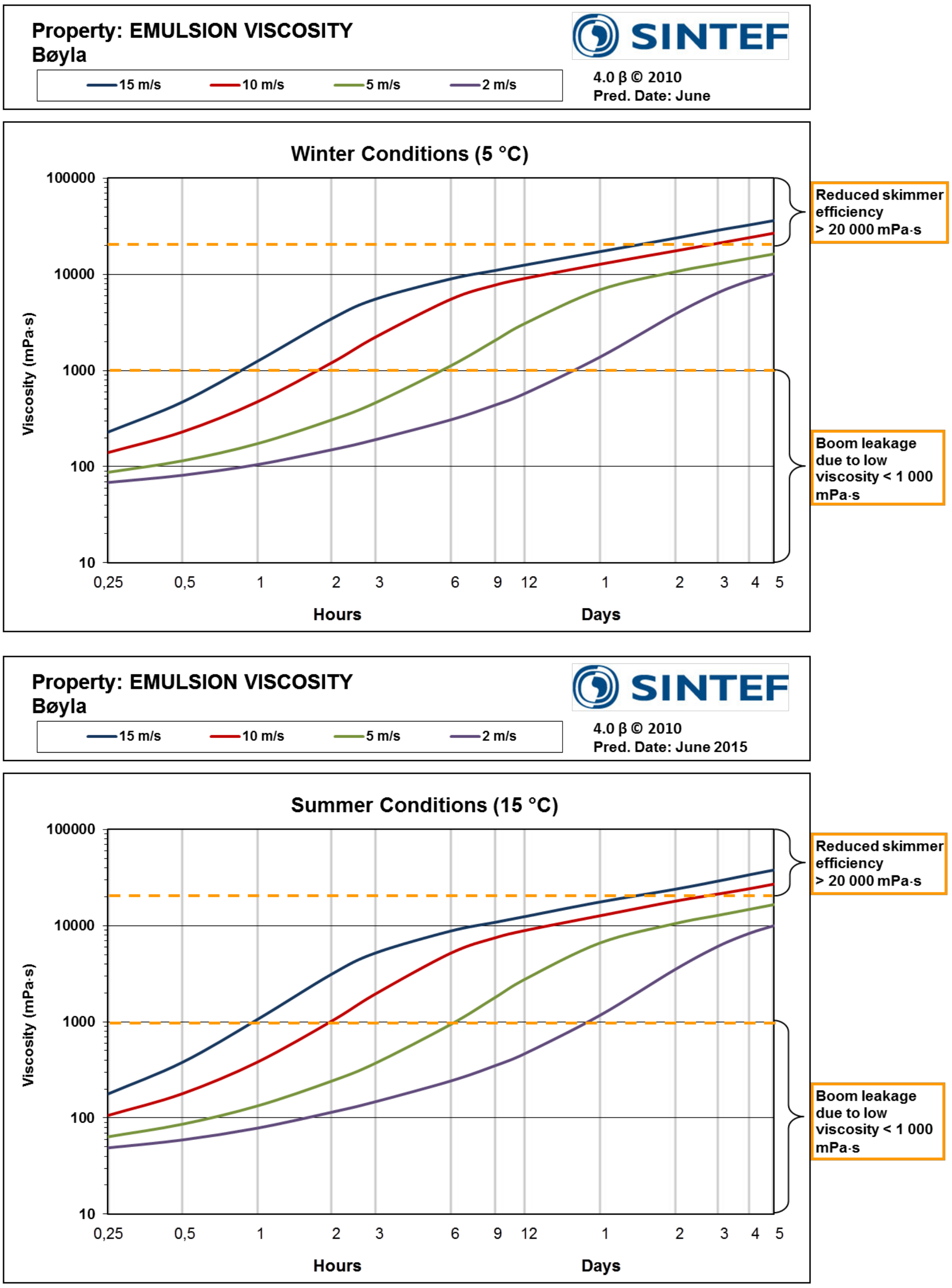


Figure 5-5: Predicted emulsion viscosity for Bøyla at 5 °C and 15 °C compared with expected viscosity limits for boom leakage and poor flow to weir skimmers.

5.6.2 Use of chemical dispersant

The window of opportunity for use of chemical dispersant (Dasic NS) is given in Figure 3-5 based on the dispersant effectiveness on different emulsion viscosities of Bøyla. The viscosity limit for when the oil is expected to be dispersible was estimated to 4000 mPa·s based on the IFP low energy test (reflecting non-breaking waves), while the limit for when the oil is not dispersible was estimated to 30 000 mPa·s based on available laboratory data and experience from previous weathering studies. For viscosities between 4000 and 30 000 mPa·s, the dispersibility of Bøyla emulsions is considered reduced. Once the oil is expected to have reduced chemical dispersibility, additional artificial energy and/or a higher dispersant dosage (DOR= dosage to oil ratio) could be applied. Repeated application of dispersant may also increase the effectiveness, especially in calm sea state. Additional energy can be provided using firefighting (Fi-Fi) systems, thrusters or MOB boats after dispersant application in order to enhance dispersion rate more efficiently.

The predicted emulsion viscosities along with the dispersibility limits are shown in Figure 5-6.

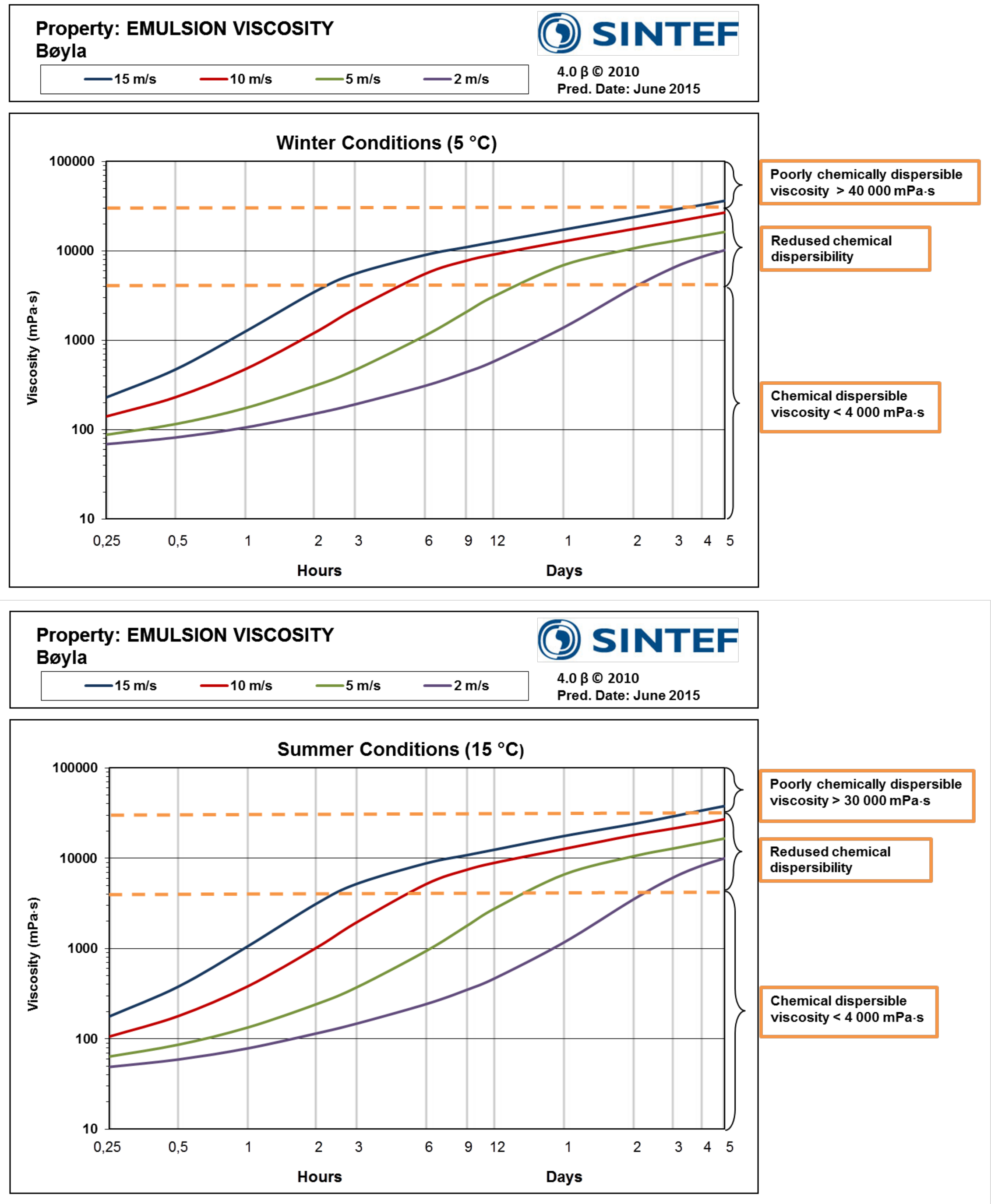


Figure 5-6: Time window for use of chemical dispersants based on predicted emulsion viscosity for Bøyla at 5 °C and 15 °C

6 Comparison of Bøyla to other Norwegian crude oils and condensates

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 sea water temperature is 10-15 °C below the pour point.

The categorization of a selection of Norwegian crude oils is presented below. Bøyla as well as the crude oils used for comparison are found in Figure 6-1.

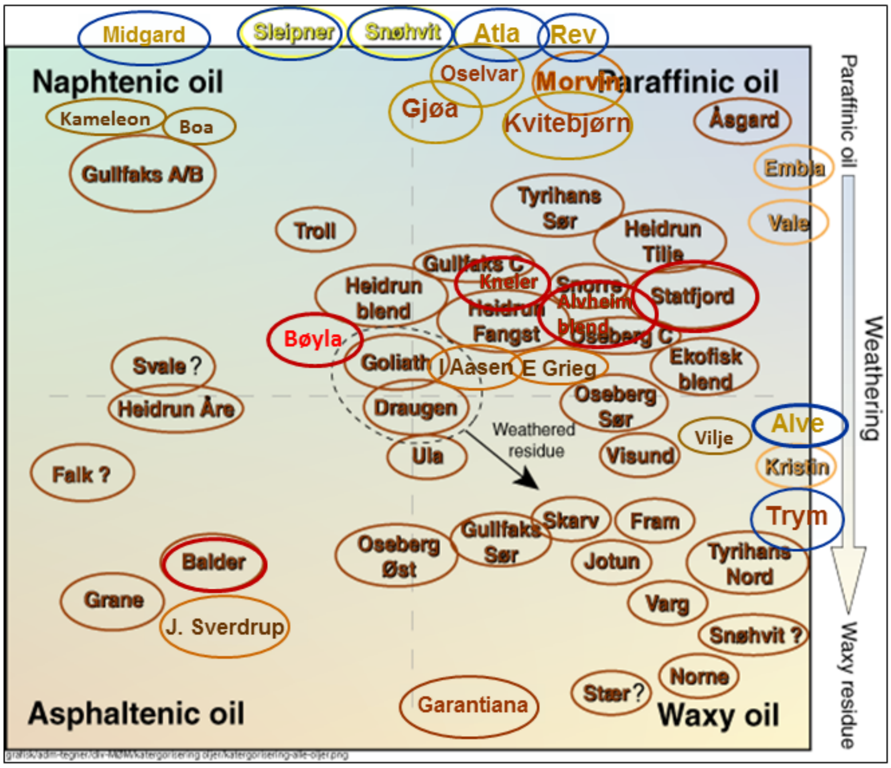


Figure 6-1: Categorization of a selection of Norwegian crude oils; blue rings = condensates, red rings = oils presented in this report for comparison, brown rings = previously studied oils

7 References

1. Bocard, C., Castaing, C. G. and Gatellier, C. 1984. "Chemical oil dispersion in trials at sea and in laboratory tests: The key role of the dilution process." Oil spill chemical dispersants: Research Experience and recommendations, ASTM STP 840. (T. E. Allen, ed.), Philadelphia, USA, pp. 125-142.
2. Brakstad, O.G., and Faksness, L.-G., (2000). Biodegradation of water-accommodated fractions and dispersed oil in the seawater column. Proceedings for the International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, Stavanger, 26-28 June 2000
3. Brakstad, O-G and A.G.G Lødeng 2005. "Microbial diversity during microbiodegradation of crude oil in seawater from the North Sea." Microbial Ecology 49:94-104
4. Commission Internationale De L'Eclairage (CIE), ISBN No. 3 900 734 22 4, 1989.
5. Daling, P. S., Brandvik, P. J., Mackay, D. and Johansen, Ø. (1990): "Characterisation of crude oils for environmental purposes." Oil & Chemical Pollution 7, 1990, pp. 199-224.
6. Hokstad, J. N., Daling, P. S., Lewis, A. and Strøm-Kristiansen, T. 1993: "Methodology for testing water-in-oil emulsions and demulsifiers. Description of laboratory procedures." Proceedings Workshop on Formation and Breaking of W/O Emulsions. MSRC, Alberta June 14-15, 24 p.
7. Johansen, Ø. 1991. "Numerical modelling of physical properties of weathered North Sea crude oils." DIWO-report no. 15. IKU-report 02.0786.00/15/91. Open.
8. Leirvik, F., and Myrhaug, J. L., 2009. "Weathering properties of the Alvheim crude oils Kneler, Boa, Kameleon, and the Alvheim Blend". SINTEF report no.: A11170, ISBM: 9788214047561
9. McAuliffe, C.D. (1987). Organism exposure to volatile/soluble hydrocarbons from crude oil spills - a field and laboratory comparison. In: Proc. 1987 Oil Spill Conference. Washington, D.C., American Petroleum Institute. pp. 555-566.
10. Mackay, D. and Zagorski, W. 1982. "Studies of W/o Emulsions". Report EE-34: Environment Canada, Ottawa, Ontario.
11. Mackay, D. and Szeto, F. 1980. "Effectiveness of oil spill dispersants - development of a laboratory method and results for selected commercial products." Institute of Environmental Studies, University of Toronto, Publ. no. EE-16.
12. McDonagh, M., Hokstad, J. N. and Nordvik, A. B. 1995. “Standard procedure for viscosity measurement of water-in-oil emulsions”. Marine Spill Response Corporation, Washington, D.C. MRSC Technical Report Series 95-030, 36 p.
13. Moldestad, M. Ø., Singsaas, I., Resby, J. L. M., Faksness, L.-G., Hokstad, J. N., 2001. "Statfjord A, B og C – Egenskaper og forvitring på sjøen, karakterisering av vannløslige komponenter relatert til beredskap". SINTEF report no.: F00138, ISBN: 8214022703
14. Nordvik, A. B., Daling, P. and Engelhardt, F. R. 1992. "Problems in the interpretation of spill response technology studies." In: Proceedings of the 15th AMOP Technical Seminar, June 10-12, Edmonton, Alberta, Canada, pp. 211-217.
15. Perry JJ (1984). Microbial metabolism of cyclic alkanes In: Atlas RM (Ed) Petroleum Microbiology Macmillan Publ Co New York pp 61-98
16. Reed M., and C. Turner, 1991: Field Tests of Satellite tracked buoys to simulate oil drift. In Proceeding of the IOSC, SanDiego, CA. US., pp. 619 – 628
17. Reed, M., Turner, C. and Odulo, A. 1994. "The role of wind and emulsification in modelling oil spill and surface drifter trajectories." Spill Science and Technology, Pergamon Press (2): .143-157.
18. Singsaas, I., Daling, P. S. and Jensen, H., 1993. "Meso-scale laboratory weathering of oils". IKU report 22.2042.00/04/93, IKU, Trondheim, Norway, 81 p.
19. Stiver, W. and Mackay. D. 1984. "Evaporation rate of spills of hydrocarbons and petroleum mixtures." Environ, Sci. Technol., vol. 18 (11), pp. 834-840.
20. Sørheim, K. R., and Leirvik, F., 2010. "Kartlegging av forvitringsegenskaper, fargekode og spredningsegenskaper for Balder Blend". SINTEF report no.: A16789; ISBN: 9788214050158

A The behaviour of crude oil on the sea surface

The Bøyla crude oil was given the SINTEF ID 2015-0063.

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.

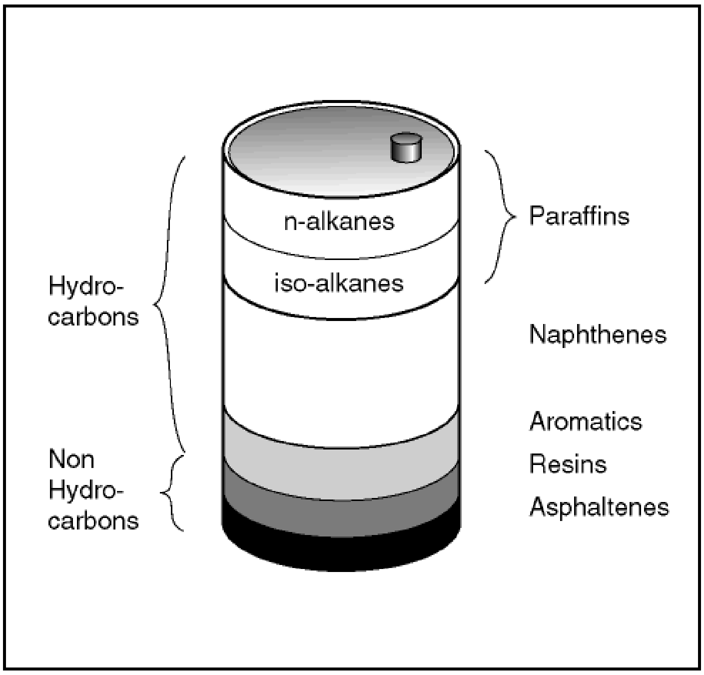


Figure A-1: The chemical composition of crude oils

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.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:

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

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

Water-in-oil (w/o) emulsions are generally more viscous than the parent crude oil; this is illustrated in Figure A-2.

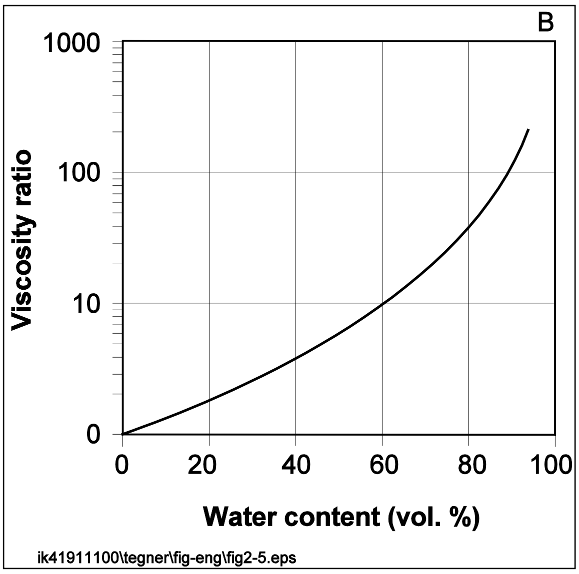


Figure A-2: Example of viscosity ratio as a function of water content

A.3.2 Pour point

The temperature at which oil ceases to flow when cooled without disturbance under standardized conditions in the laboratory is defined as the oil's pour point (ASTM-D97). The method accurately determines the temperature at which the oil become semi-solid under the specified laboratory conditions. Due to the movement at the sea surface, the oil may remain a liquid at sea at temperatures as low as *10 to 15*^{o}*C lower* than the pour point of the oil. The pour point of oil with high wax content will increase dramatically with evaporation as the lower weight molecules, which contribute to keeping the wax in solution, evaporate. The pour point for oils with high wax contents can reach 30°C, while low viscous naphthenic oils may have pour points as low as - 40°C.

In an oil spill clean-up situation, the pour point provides 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.

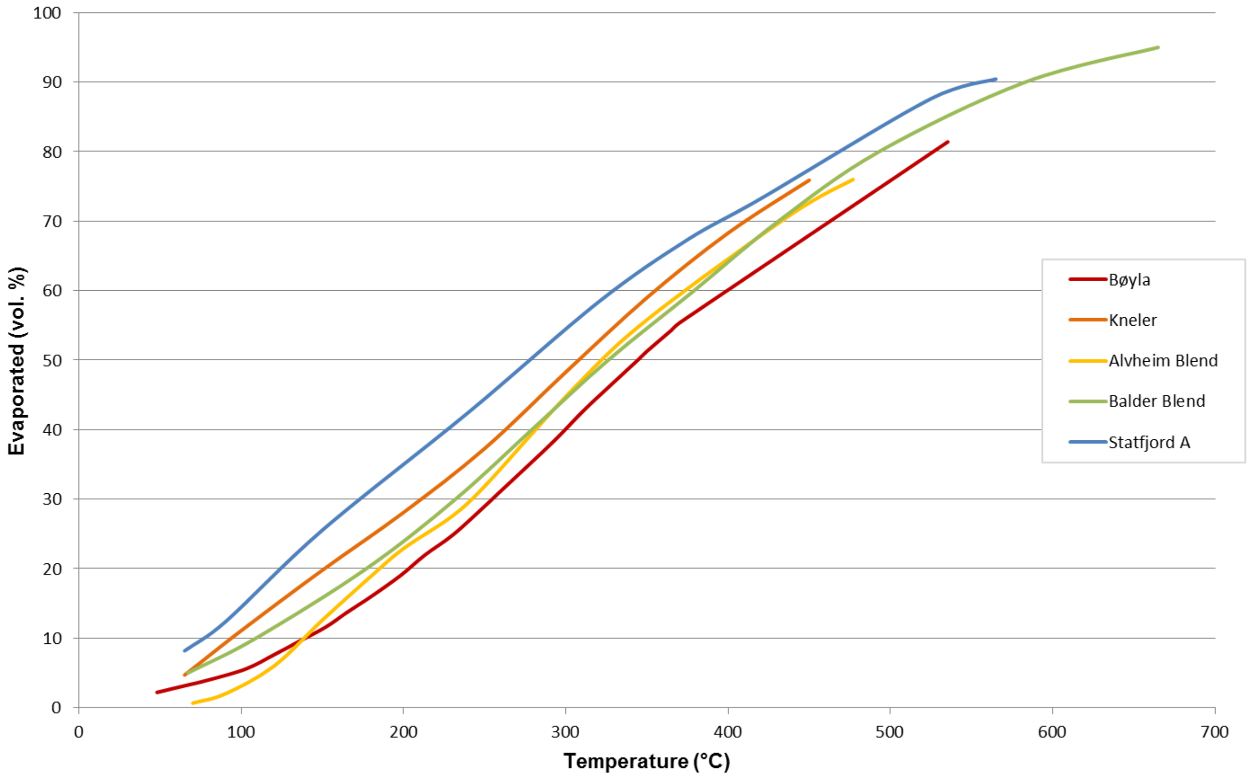


Figure A-3: Distillation curves for Bøyla crude oil in comparison with other Norwegian crude oils

A.3.4 Flash point

The flash point is the lowest temperature at which the vapour generated near the surface of the 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).

The flash point is an approximate indicator of the relative fire and explosion hazard of oil. Oils with flash point up to and slightly above the temperatures encountered during storage and/or transportation pose a fire and explosion hazard.

Rule of thumb:

Moving in an oil slick where the oil's flash point is close to or lower than the sea temperature implies a fire and/or explosion hazard.

Natural weathering processes such as evaporation and emulsion formation contribute to reducing the potential fire and/or explosion hazard by increasing the flash point of the oil.

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

A.4 The behaviour of crude oil spilled at sea

This chapter gives a general description of the main weathering processes when oil is spilled at sea.

There 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-4 illustrates the various weathering processes, and Figure A-5 shows their relative importance over time.

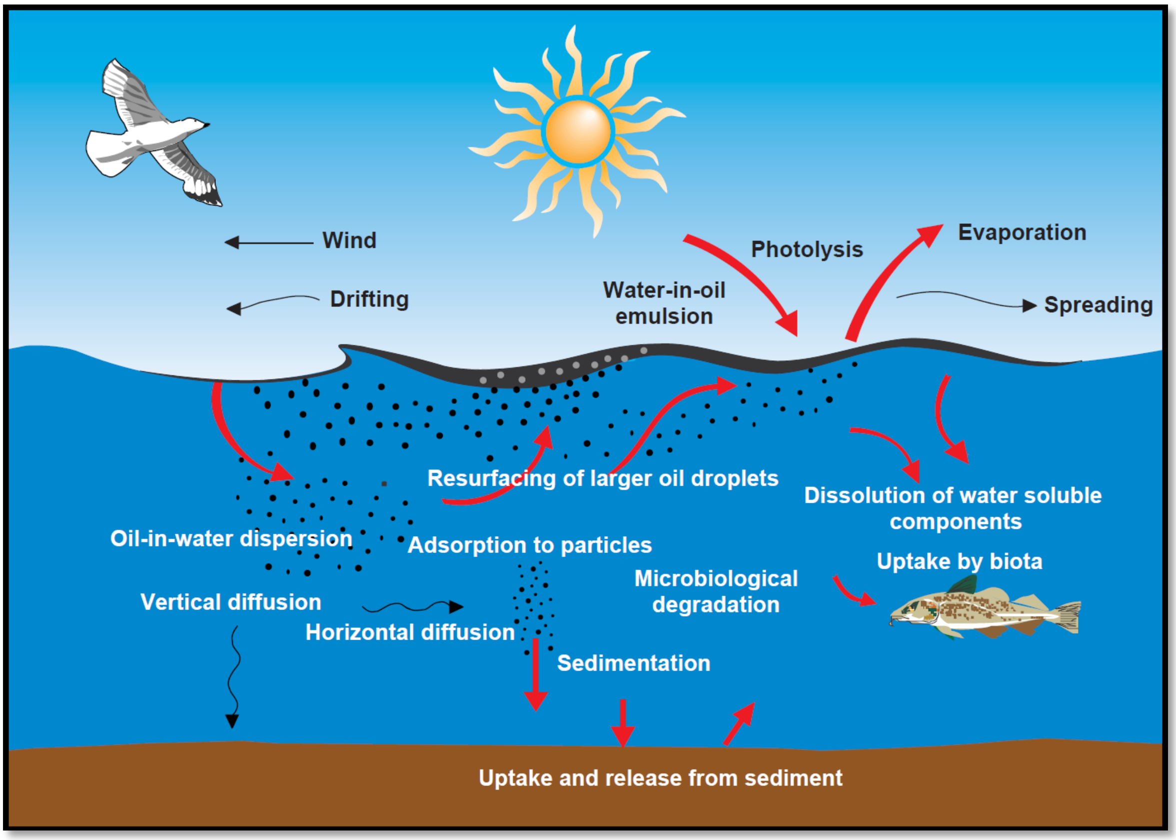


Figure A-4: Illustrating the weathering processes that take place when oil is spilled on the sea surface

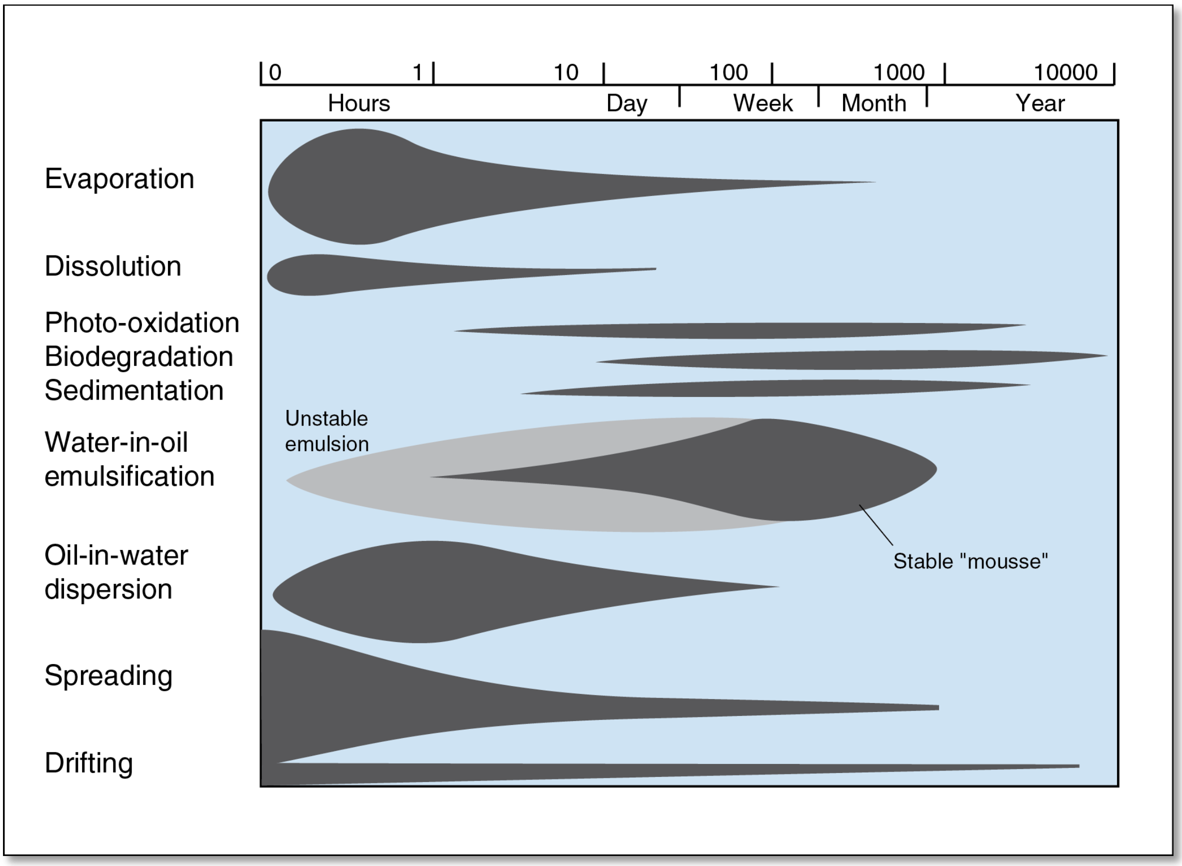


Figure A-5: Weathering processes' relative importance over time. Note: logarithmic scale

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 10-15°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-6. 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).

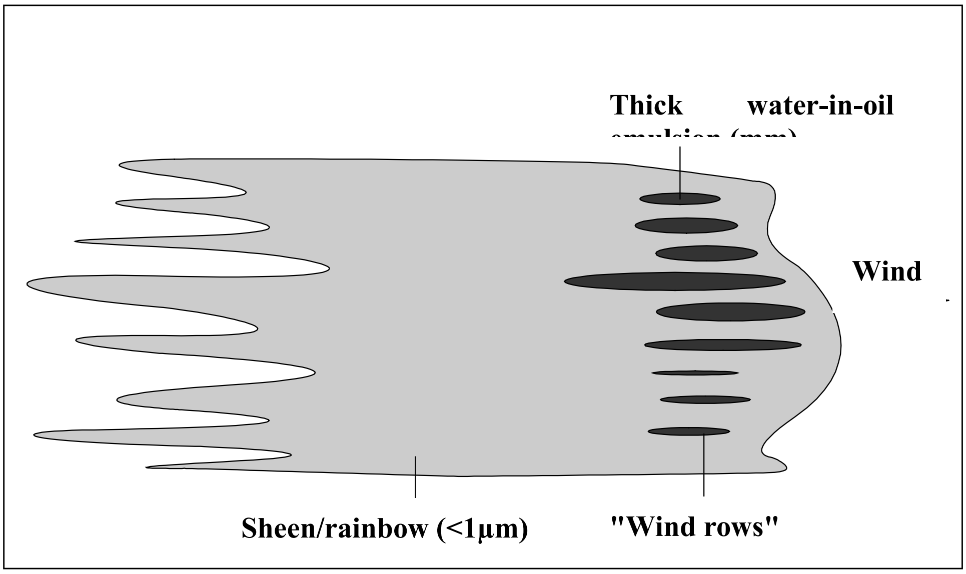


Figure A-6: The spreading of oil spilled on the sea surface and the distribution within the oil slick

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-7. 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.

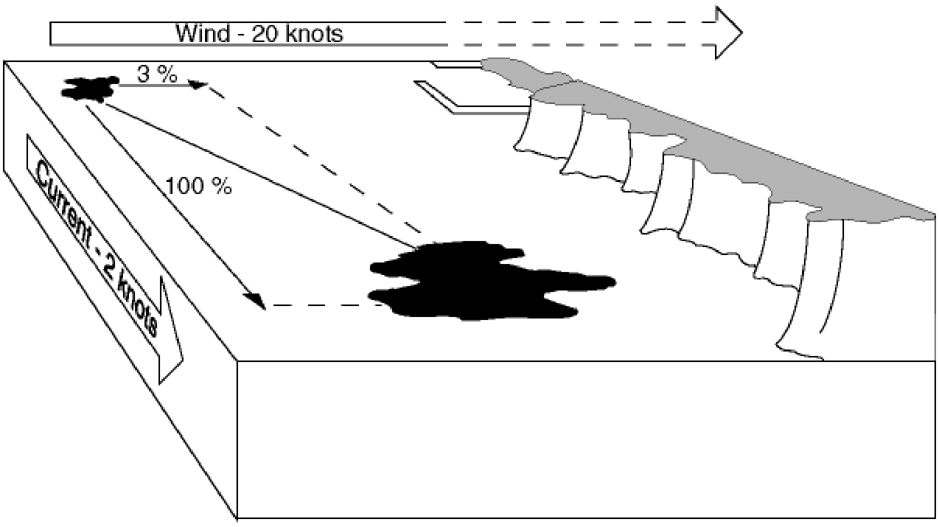


Figure A-7: An illustration showing how wind and current can influence the drifting of an oil slick

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-8 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.

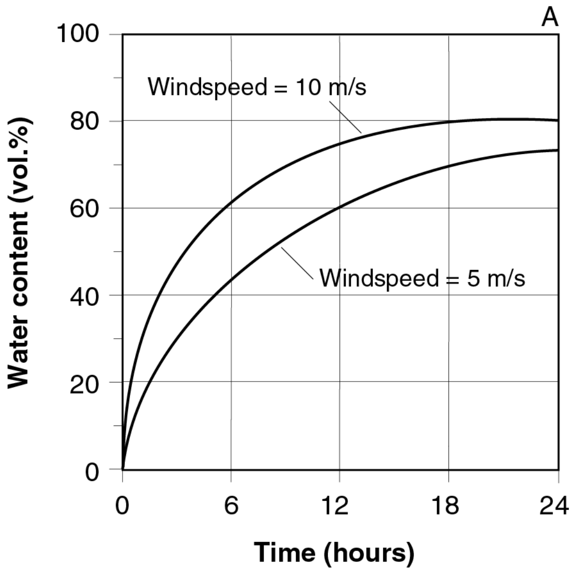


Figure A-8: Example of how weather conditions influence the w/o emulsion formation for typical oils

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.

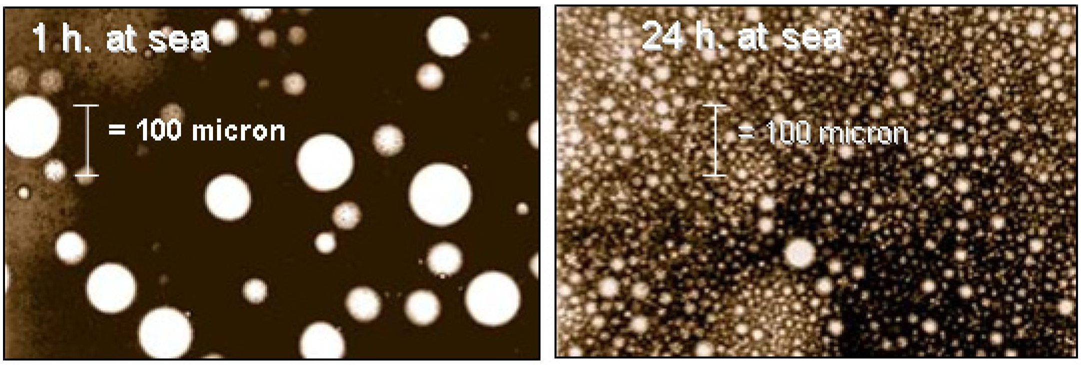


Figure A-9: Microscope pictures of w/o emulsion after (A) 1 h. and (B) 24 h. in a rotating cylinder

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

Resins and asphaltenes have both hydrophobic and hydrophilic properties and will concentrate at the interface between the water and oil, thereby forming a layer that stabilizes the water droplets. The hydrophobic properties can lead to the concentration of wax along the water droplets, which further stabilizes the interfacial "skin" layer. The interfacial layer between the oil and water forms a physical barrier that hinders the coalescence of the water droplets and will stabilize the w/o emulsion. The stabilization of the water droplets by asphaltenes and wax is shown in Figure A-10.

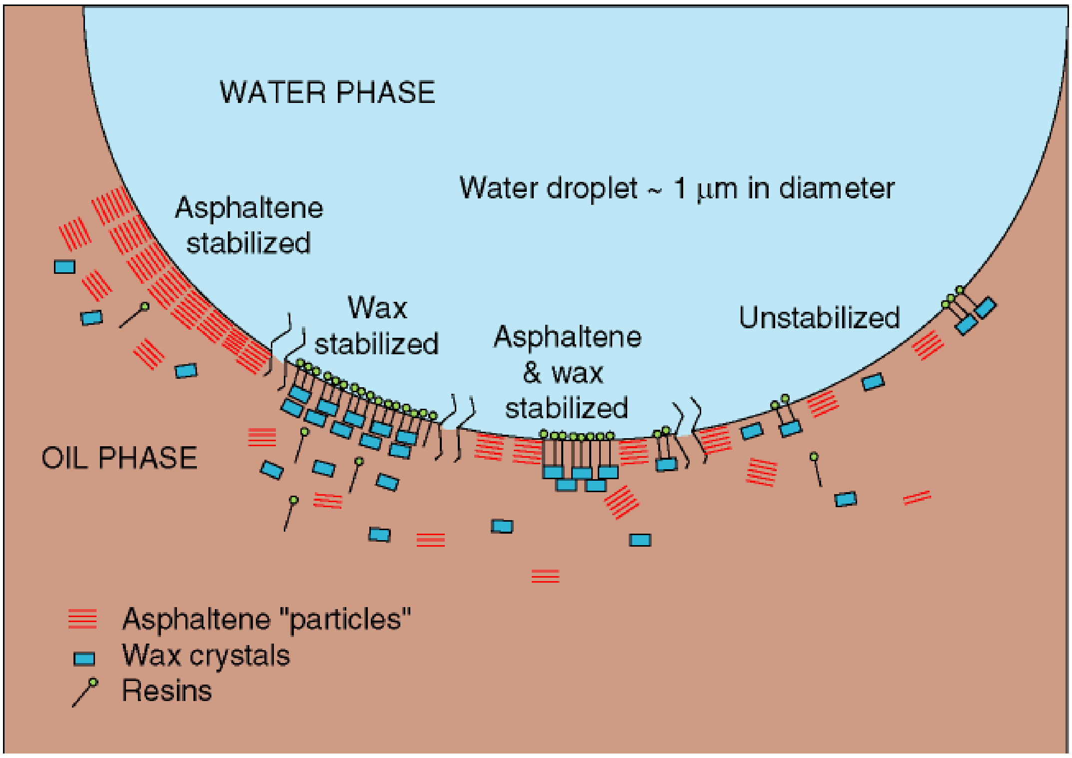


Figure A-10: Interfacial layer stabilized by wax and asphaltenes in w/o emulsion

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

Crude oil- and sea water interfacial tension (IFT) plays a key role in the process of oil droplet formation. The need to 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 we have the 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.

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 Lødeng, 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-11. This was observed both during the DeepSpill experiments in 2000 (***Figure A-12***) and the DWH oil spill in 2010 (***Figure A-13***). This emulsification will be dependent on oil properties and environmental conditions, such as temperature and sea state.

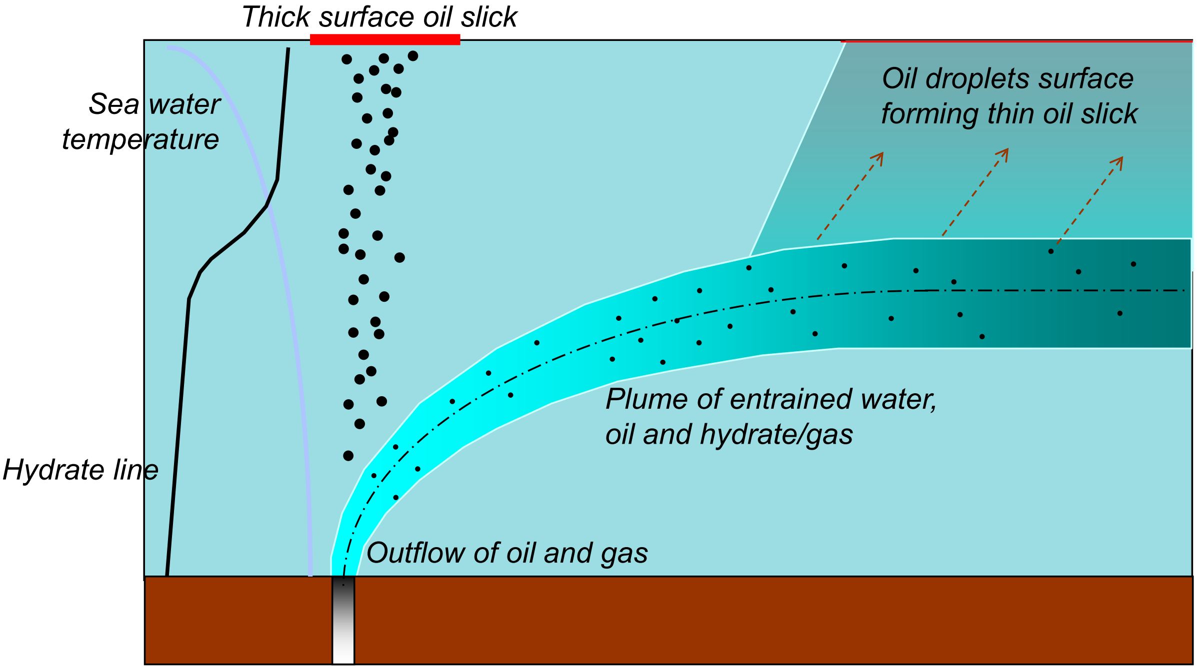


Figure A-11: Illustration of possible creation of thick surface oil slick (> 200 µm) from deep water release of oil

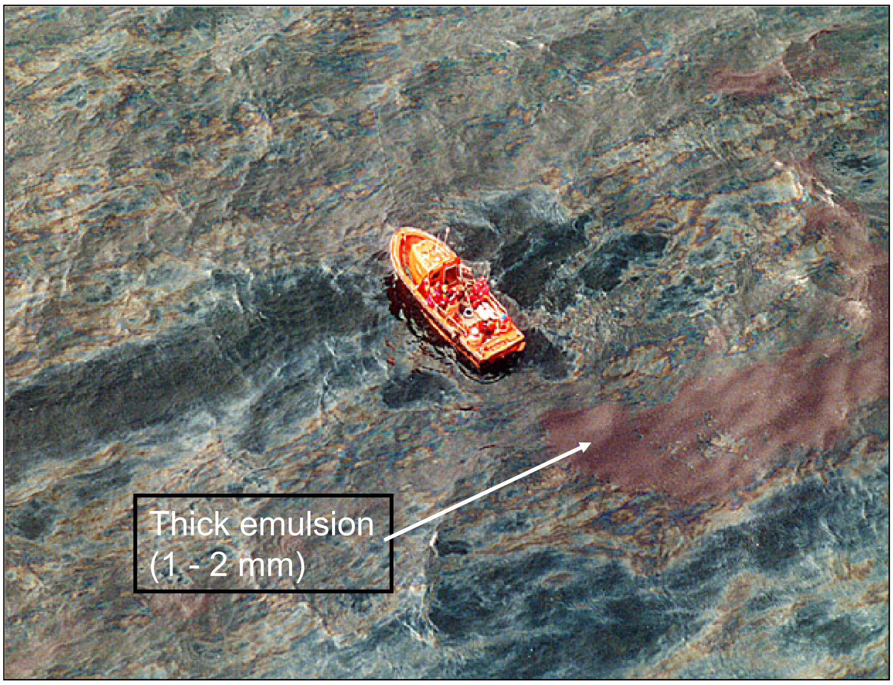


Figure A-12: Surface oil slick (initial thickness > 200 µm) from the experimental deep water release DeepSpill in 2000. Surface oil is emulsifying similar to an oil slick from a surface batch release (from Leirvik et al., 2011)

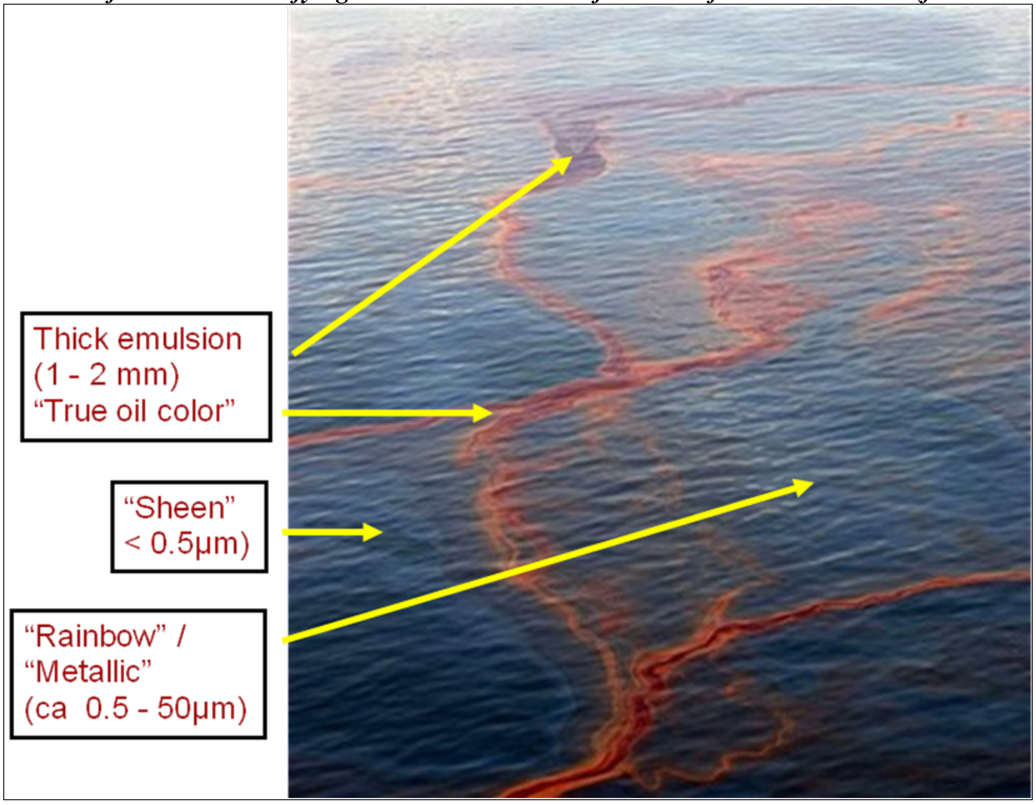


Figure A-13: Surface oil slick (initial thickness > 200 µm) from the DWH deep water release. Surface oil is emulsifying similar to an oil slick from a surface batch release

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-14***, ***Figure A-15*** 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.

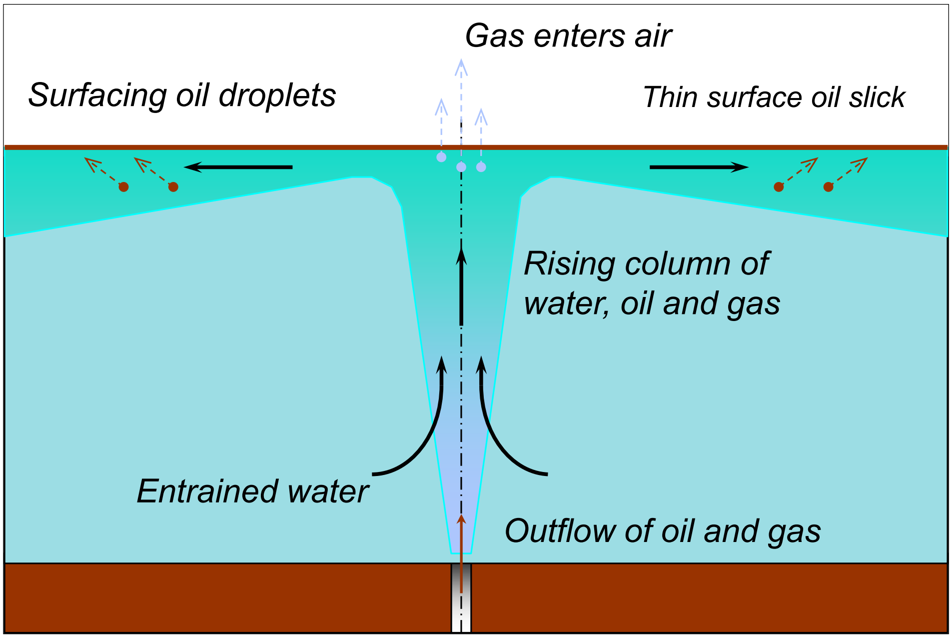


Figure A-14 Illustration of possible creation of thin surface oil slick (< 200 µm) from a shallow subsurface release (<500 m)

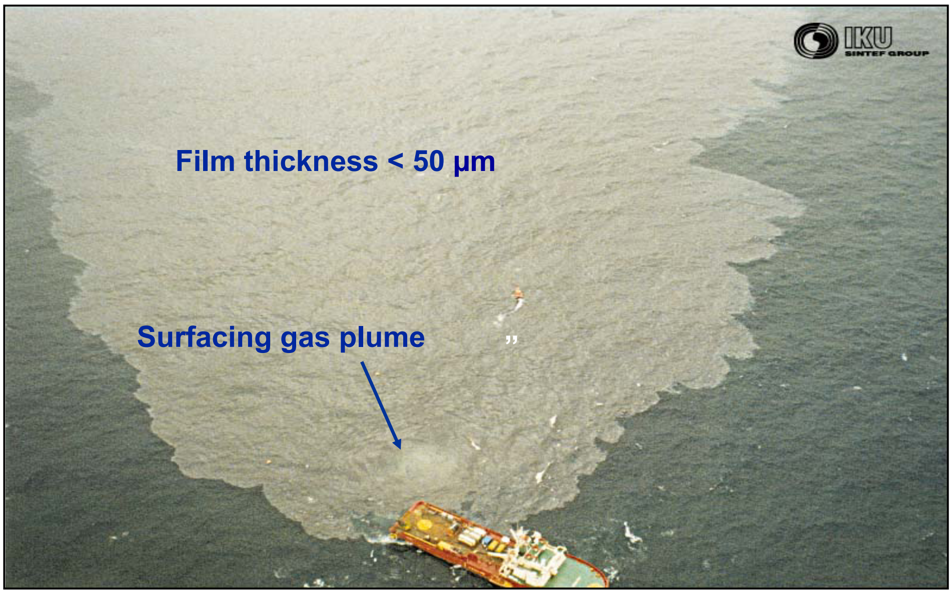


Figure A-15: Surface oil slick (< 50 µm) from experimental subsurface release at 106 m in 1996. The surface oil didn't emulsify and had a very limited life time (hours) due to the low film thickness and high rate of natural dispersion (even at < 10 m/s wind)

B Experimental setup

B.1 Oil samples and test temperature

SINTEF received two green Jerry cans (20 L) with Bøyla crude oil on the 2nd February, 2015. The cans were marked as described below, and are shown in Figure B-1.

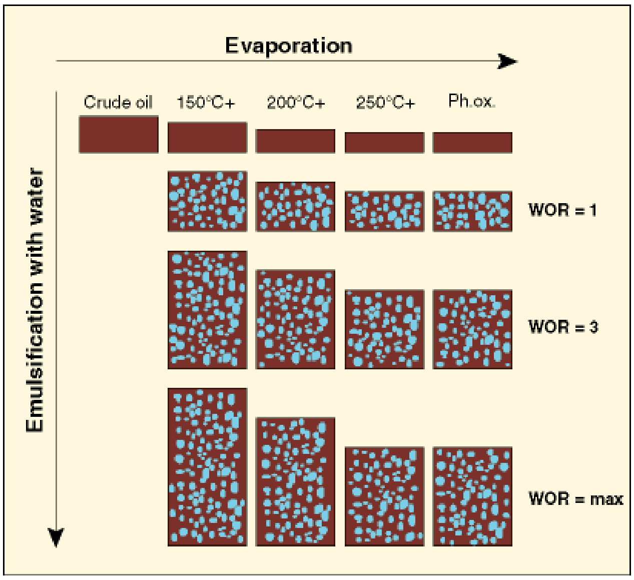
From: Alvheim FPSO
ID: SI-015-2015
Sample type: Flowline Bøyla Crude 20 L
System: 16
Contact information: Pal.Oien@detnor.no /Kristin.alne@detnor.no
Sample point: Sample Station: 16AP101 Kneler A flow line
Sampled date/time: 20.01.2015 9:30-10:30
Sampled by: Morten Jensen
Process conditions: Line Pressure: 22 bar; Line temperature: 37 deg C
Phone no.: +47 51 90 71 59

Figure B-1: Shows Jerrycans containing Bøyla crue oil as received

The Bøyla crude oil was given the unique SINTEF ID **2015-0063**.

B.2 Small-scale laboratory testing

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



WOR: Water to Oil Ratio

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

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

B.2.1 Evaporation

The 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)	-	Spinning drop video tensiometer SVT 20 N, Dataphysics

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)

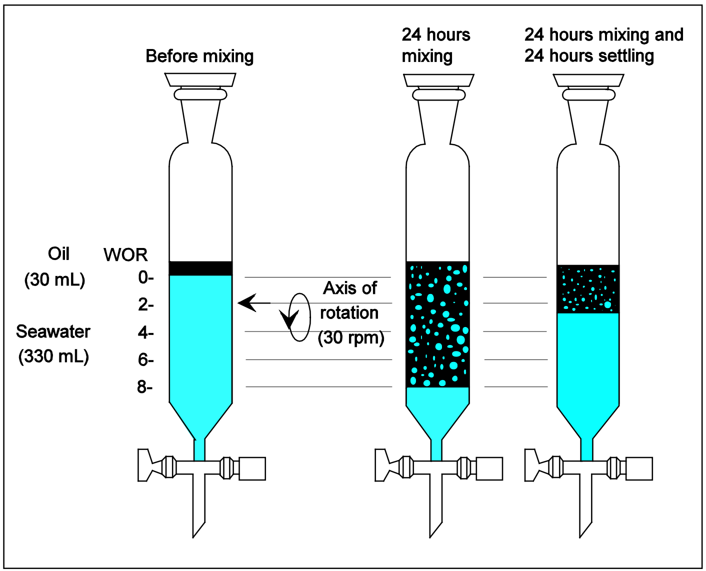
B.2.3 Emulsification properties

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



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

Figure B-3: Principle of the rotating cylinder method

B.2.4 Chemical dispersibility testing

As a screening test, the oils dispersibility properties were tested using five different dispersants at a dosage of 1:25 (4 wt. %). The dispersants tested were; Dasic Slickgone NS, Corexit 9500, Gamlen OD 4000, Finasol OSR-62 and SuperDispersant 25. 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-4.

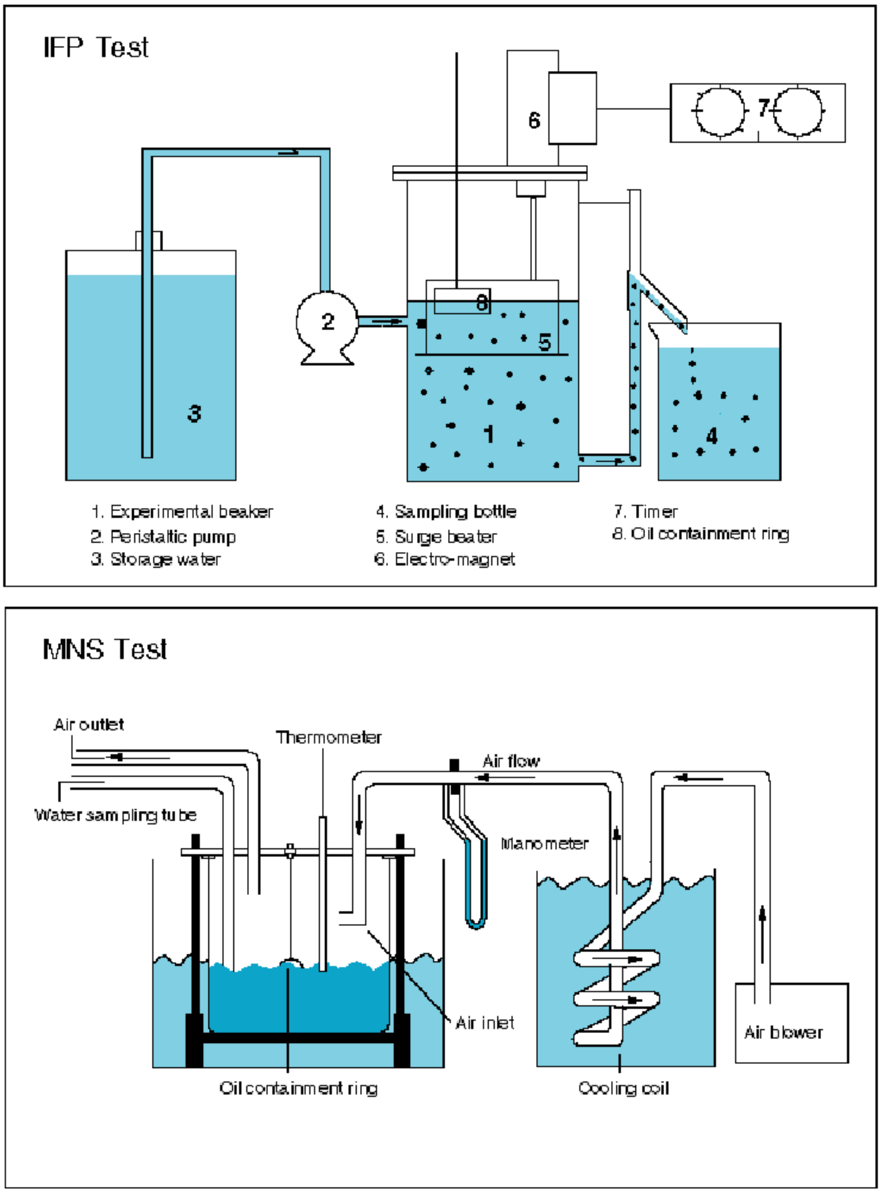


Figure B-4: IFP and MNS test apparatus.

B.3 Meso-scale laboratory testing

In an oil spill situation at sea, the weathering processes will occur simultaneously and affect each other. In the small-scale laboratory testing, these processes are studied individually. By using the meso-scale flume the weathering and effect of dispersants can be studied under more realistic conditions, having the weathering processes to occur at the same time, giving a better image of the behaviour of the oil at sea.

B.3.1 Description of the flume basin

A meso-scale flume basin (Singsaas *et al.*, 1993), located at SINTEF's Sealab, is routinely used to simultaneously study the weathering processes under controlled conditions. The meso-scale flume basin was rebuilt in 2006, having state of the art instrumentation. A schematic drawing of the flume is given in Figure B-5.

Approximately 5 m^3 seawater circulates in the 10 metres long flume. The flume basin is located in a temperature controlled room (0°C-20°C). Two fans are placed in a covered wind tunnel, controlling the wind speed. The fans are calibrated to simulate an evaporation rate corresponding to a wind speed of 5-10 m/s on the sea surface.

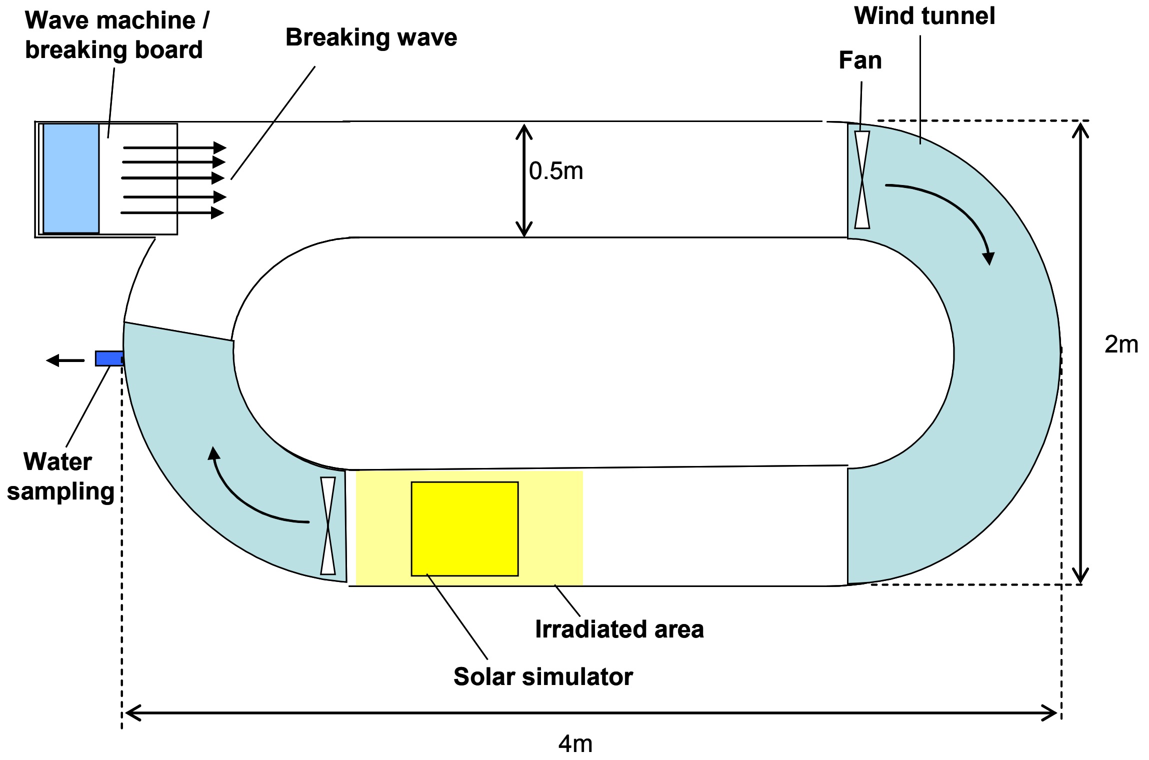


Figure B-5: Schematic drawing of the meso-scale flume

B.3.2 Oil weathering in the flume basin

In a meso-scale flume study, a standard volume sample (9 L) of the relevant oil is carefully released on the seawater surface under calm conditions. The wave machine and fans are then started and the experiment begins. A reference water sample is collected before the beginning of the experiment. Both surface oil/emulsion and water column are sampled frequently the first 6 hours, then after 12 hours and subsequently every day.

After three days (72 hour) dispersant is applied to the surface emulsion. Water samples are then collected more frequently. The addition of dispersant may be repeated once or twice, in which case water samples are also collected.

Analysis of surface oil/emulsion

Samples of the surface oil/emulsion are taken using an aluminum tray and transferred to a 0.5 L separating funnel. The free water is removed after settling for 10 minutes in the climate room. The oil phase is further handled for an analysis of its physical properties.

The physical properties determined for all surface oil samples during the experiments are:

- Viscosity
- Water content
- Density
- Evaporative loss
- Emulsion stability (for a limited amount of samples)

Analysis of water samples

Water samples are analysed for oil concentration in the water column (droplets and dissolved components). The samples are taken at a depth of 50 cm through a tap in the basin wall into a Pyrex glass bottle (1 L). The sampled water is acidified with some droplets of 10% HCl (pH < 2). The sampling position is shown in Figure B-5. Samples are then extracted by liquid-liquid extraction with dichloromethane (DCM) and quantified by Ultra Violet (UV) spectrophotometer.

Solar simulation in the meso-scale flume

Sunlight is simulated with a solar simulator from Gmbh Steuernagel. The solar lamp (4 KW) emits a wavelength spectrum calibrated to fit natural sunlight at high noon and in the absence of clouds. Figure B-6 shows the measured spectrum from the solar simulator compared to one of the most widely used standard spectra for solar irradiance (CIE publication 85, 1989).

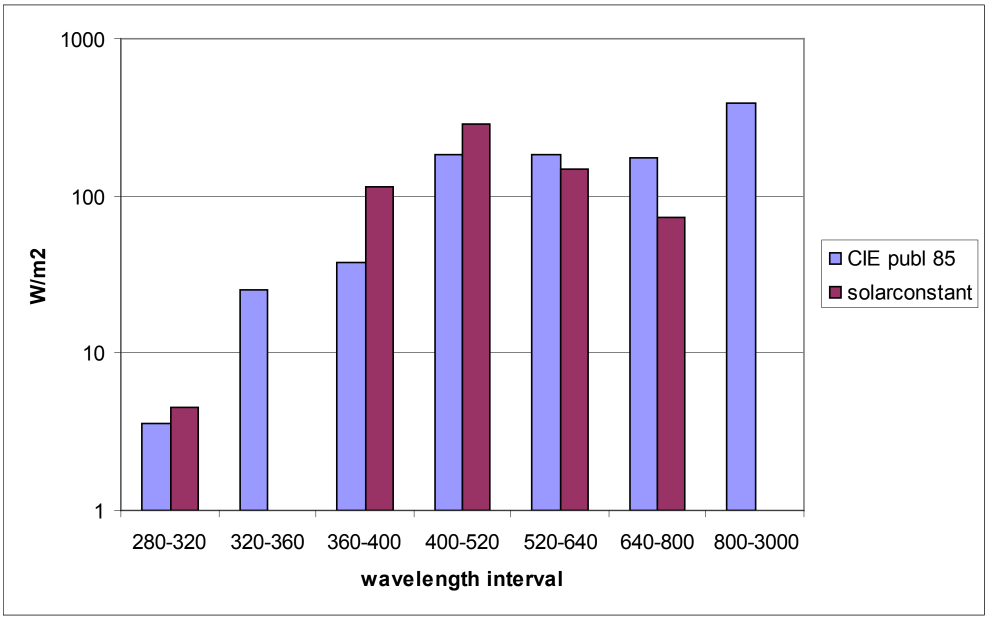


Figure B-6: Measured wavelength compared to standard spectrum suggested in CIE publication 85

The exact exposure of solar irradiance on the oil in the meso-scale flume is somewhat difficult to calculate. Since the oil is moving, it will only be within the irradiated area periodically. The exposure will be highly dependent on the distribution of the oil in the flume and the thickness of the emulsion on the water surface. An estimated irradiation pr. day using the solar simulator is compared with the average irradiation pr. day for selected Norwegian cities in Figure B-7.

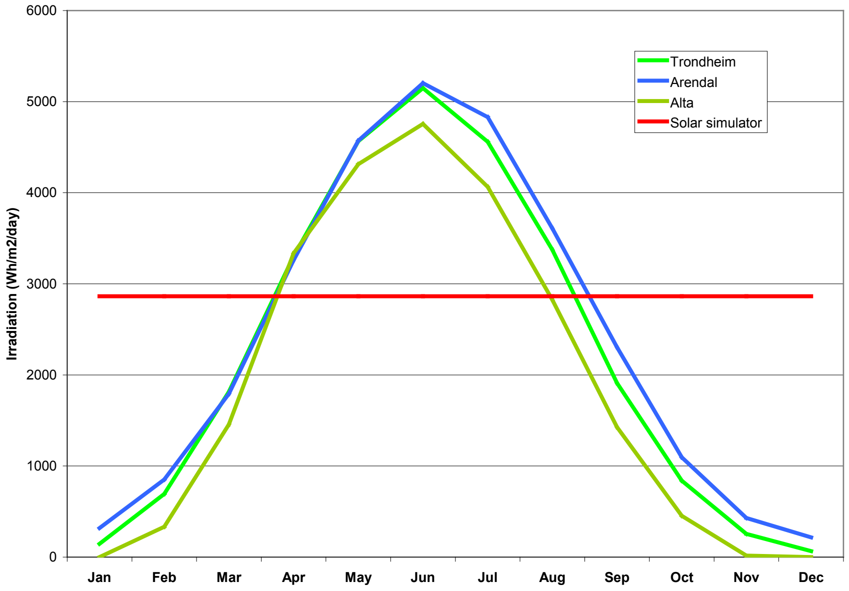


Figure B-7: Daily Irradiation for some Norwegian cities throughout the year compared with the estimated daily irradiation in the meso-scale flume

The simulated irradiance seems to be the approximate average of the daily irradiance throughout the year. It should be noted, however, that the simulations are not taking clouds into consideration. The real irradiation will be lower than that predicted in Figure B-7.

C Input data to SINTEF Oil Weathering Model (OWM)

The laboratory data used as input to the SINTEF OWM for Bøyla is given to Table C-3.

Table C-1: Physical and chemical properties for Bøyla crude oil at 13 °C, used as input in the oil weathering model

Properties of fresh oil	Value
Density (g/ml)	0.875
Pour point (°C)	-12
Reference temperature (°C)	13
Viscosity at ref. temp. (mPa·s = cP) *	46
Asphaltenes (wt. %)	0.07
Flash Point (°C)	-
Wax Content (wt. %)	3.23
Dispersible for visc. <**	4000
Not dispersible for visc. > **	30000

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

*** Estimated*

- *No data available*

Table C-2: True boiling point (TBP) curve for Bøyla crude oil, based on crude assay results provided by Det norske adjusted to the obtained laboratory results.

Temperature (°C)	Volume (%)
48	2.2
64	3.1
80	4.0
103	5.6
120	7.6
136	9.6
152	11.6
165	13.7
180	16.0
198	19.0
213	22.0
231	24.9
250	29.0
260	31.2
277	34.9
294	38.7
311	42.8
326	46.1
344	49.9
350	51.3
365	54.3
370	55.4
535	81.4

Table C-3: Lab weathering data for Bøyla crude oil at 13 °C, used as input in the oil weathering model

Property	Fresh	150°C+	200°C+	250°C+
Boiling Point Temp. (°C)	-	206.5	263.5	315.5
Vol. Topped (%)	0	8.5	17.6	28.4
Weight Residue (wt. %)	100	92.6	84.3	74.0
Density (g/ml)	0.875	0.886	0.895	0.904
Pour point (°C)	-12	-6	0	12
Flash Point (°C)	-	40	80.5	122.5
Viscosity of water-free residue (mPa·s =cP)	46	68	153	730
Viscosity of 50% emulsion (mPa·s = cP)		486	1030	2562
Viscosity of 75% emulsion (mPa·s = cP)		1883	4036	10644
Viscosity of max water (mPa·s = cP)		1603	3069	17153
Max. water cont. (vol. %)		67	67	78
(T1/2) Halftime for water uptake (hrs)		0.2	0.17	0.33
Stability ratio		0.99	1	1

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

\- *No data*

D Chemical characterisation of the fresh oil on GC/MS

Table D-1: Chemical composition of Bøyla crude oil based on GC/MS analysis of fresh oil

Group no.	Composition	Bøyla, wt.%
1	C1-C4 gasses (dissolved in oil)	0.80
2	C5-saturates (n-/iso-/cyclo)	1.00
3	C6-saturates (n-/iso-/cyclo)	1.30
4	Benzene	0.10
5	C7-saturates (n-/iso-/cyclo)	2.10
6	C1-Benzene (Toluene) et. B	0.54
7	C8-saturates (n-/iso-/cyclo)	4.15
8	C2-Benzene (xylenes; using O-xylene)	1.11
9	C9-saturates (n-/iso-/cyclo)	2.07
10	C3-Benzene	0.83
11	C10-saturates (n-/iso-/cyclo)	2.00
12	C4 and C5 Benzenes	0.02
13	C11-C12 (total sat + aro)	3.98
14	Phenols (C0-C4 alkylated)	0.00
15	Naphthalenes 1 (C0-C1-alkylated)	0.24
16	C13-C14 (total sat + aro)	7.56
17	Unresolved Chromatographic Materials (UCM: C10 to C36)	N.A.
37	metabolite 1	N.A.
38	metabolite 2	N.A.
18	Naphthalenes 2 (C2-C3-alkylated)	0.42
19	C15-C16 (total sat + aro)	5.78
20	PAH 1 (Medium soluble polyaromatic hydrocarbons (3 rings-non-alkylated;<4 rings)	0.24
21	C17-C18 (total sat + aro)	6.76
22	C19-C20 (total sat + aro)	6.50
23	C21-C25 (total sat + aro)	8.69
24	PAH 2 (Low soluble polyaromatic hydrocarbons (3 rings-alkylated; 4-5+ rings)	0.31
25	C25+ (total)	43.50

N.A. – 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.

The SINTEF OSCAR model is a 3-dimensional Oil Spill Contingency And Response model system that calculates and records the distribution (as mass and concentrations) of contaminants on the water surface, on shore, in the water column and in sediments. The model allows multiple release sites, each with a specified beginning and end to the release. This allows time-variable releases at a given location, as well as throughout the study area. The model computes surface spreading, slick transport, entrainment into the water column, evaporation, emulsification and shore interactions to determine oil drift and fate at the surface. In the water column, horizontal and vertical transport by currents, dissolution, adsorption, settling and degradation are simulated. By modelling the fate of individual 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.

SINTEF

Technology for a better society

www.sintef.no