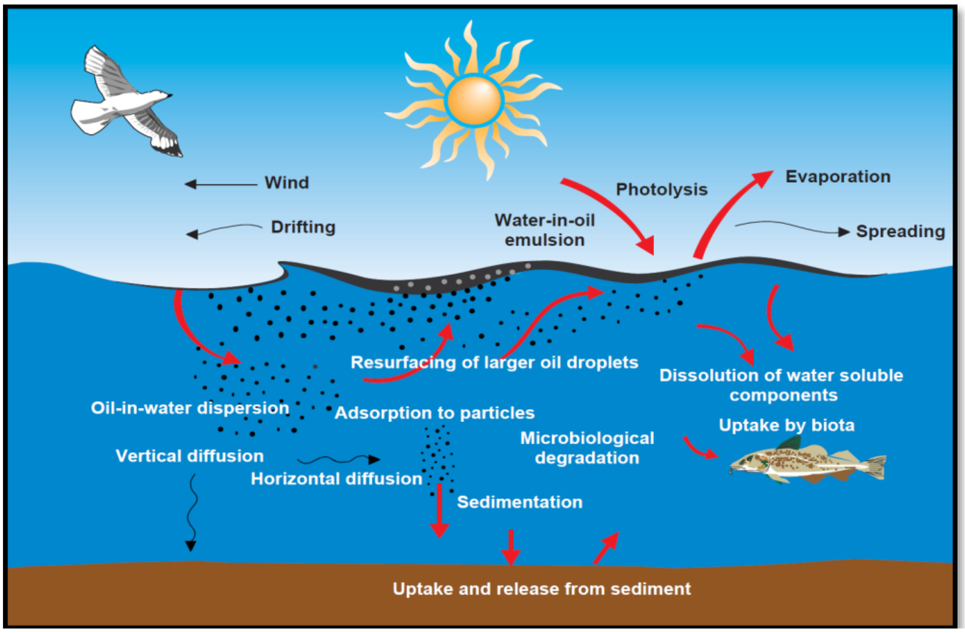
OC2020 A-050 Open

Report

Characterization of Low Sulfur Fuel Oils (LSFO) – A new generation of marine fuel oils

Weathering, dispersibility, WAF and toxicity, and ignitability / in-situ burning

Author(s)
Kristin Rist Sørheim
Per S. Daling, David Cooper, Ian Buist, Liv-Guri Faksness, Dag Altin, Thor-Arne Pettersen, Oddveig M. Bakken



SINTEF Ocean AS

2020-07-10

SINTEF Ocean AS
Address:
Postboks 4762 Torgarden
NO-7465 Trondheim
NORWAY
Switchboard: +47 46415000

Enterprise /VAT No:
NO 937 357 370 MVA

Report

Characterization of Low Sulfur Fuel Oils (LSFO) – A new generation of marine fuel oils

REPORT NO.	PROJECT NO.	VERSION	DATE
OC2020 A-050	302004929	3.1	2020-07-10

KEYWORDS:
LSFO;
Weathering;
Dispersibility;
WAF/Toxicity;
Ignitability/ISB;
Oil spill response

AUTHOR(S)
Kristin Rist Sørheim
Per S. Daling, David Cooper, Ian Bust, Liv-Guri Faksness, Dag Altin, Thor Arne Pettersen, Oddveig M. Bakken

CLIENT(S)
MPRI/DFO, ITOPF, Norwegian Coastal Administration

CLIENT'S REF.	NUMBER OF PAGES/APPENDICES:
Michal Galus, Julke Brandt, Hanne Solem Holt	112 incl. 5 Appendices

CLASSIFICATION	CLASSIFICATION THIS PAGE	ISBN
Open	Open	978-82-7174-385-7

ABSTRACT

This Multi-client project "Characterization of Low Sulfur Fuel Oils (LSFO) - A new generation of marine fuel oils" has been a 1-year project (2019-2020). The project has been funded by MPRI/DFO Canada, ITOPF and the Norwegian Coastal Administration.

In order to meet new requirements for lower sulfur oxides (SOx) emissions to the air, new generation of low-sulfur marine fuels are now replacing the traditional Intermediate fuel oil (like IFO 180 and IFO 380) with "Ultra Low Sulfur Oils" – ULSFO (S≤0.10 % m/m), for use in the Sulfur Emission Control Area (SECA) in Europe and North America from 2015, and a Global Sulfur Cap regulation was implemented from 2020 with "Very Low Sulfur Oils" (S≤0.50 % m/m). This project aims to provide responders better knowledge and preparedness for spills involving new generation of low sulfur residual marine fuel oil on the market today. The project included laboratory studies with focus on fate and behaviour, potential toxicity and with relevance to the effectiveness of different oil spill response options (use of dispersants and in-situ burning). Test methodologies was also subjected to an interlaboratory study and experiments were performed both in Norway (SINTEF) and in Canada (SL Ross) on one of the tested oils.

The companies mentioned in this report provided samples for investigation of the fuel's characteristics when spilled in seawater to help with the development of an industry response strategy for a new generation of low-sulfur fuel oils. Many of the low-sulfur fuels being developed by the industry share similar compositions, so it is important to note that the findings of this report are not unique to the fuel samples analysed. The results of this study are indicative of a new generation of marine fuel oil across the wider industry. Further laboratory analysis of low-sulfur fuel oils from other suppliers is needed to give a clearer understanding of the characteristics and behaviours of individual products.

PREPARED BY	CHECKED BY	APPROVED BY
Kristin Rist Sørheim	Ivar Singsaas	Mimmi Throne-Holst

This document has been approved according to SINTEF's approval procedure, and is digitally secured

Document History

VERSION	DATE	VERSION DESCRIPTION
1.0	2020-04-03	Draft version
2.0	2020-05-06	Final version
3.0	2020-07-08	Updated final version
3.1	2020-07-10	Updated with decimals (SECA and ECA) sulfur limits

Table of Contents

Preface and acknowledgments

This Multi-client project "Characterisation of Low Sulfur Fuel Oils (LSFO) - A new generation of marine fuel oils" has been a 1-year project (2019-2020) funded by three individual partners. SINTEF was awarded financing from:

- The government funded MPRI (Multi-partner Oil Spill Research Initiative) program in Canada (2019-2020) / DFO (Fisheries and Oceans Canada), in cooperation with a Canadian partner (SL Ross Ltd., in Ottawa),
- The ITOPF R&D Award fund in 2019,
- The Norwegian Coastal administration (NCA) as a part of their R&D strategical initiatives

The funding partners are acknowledged for financial support and constructive dialogue during the execution of the project. ITOPF has, through their extended connections worldwide assisted the project in getting two relevant samples of Very Low Sulfur Fuel Oils (VLSFO) from Chevron in Singapore and from the Shell refinery in the Netherland. The project team wants to acknowledge Chevron and Shell for their willingness to support and ship the oils for testing at SINTEF. Furthermore, due to the challenge during the project period to get a relevant residual marine fuel oil from Canada, an Ultra-Low Sulfur Fuel oil (ULSFO) from the Shell refinery was provided from the NCA. NCA had a larger batch of ULSFO in their stock. An aliquot of the ULSFO sample was further shipped from SINTEF to SL Ross in Canada for interlaboratory testing, as a part of this project. Finally, RelyOn Nutec (Trondheim, Norway) is acknowledge for use of their facilities and assistance when conducting the ignitability (*in-situ* burning) experiments.

The companies mentioned in this report provided samples for investigation of the fuel's characteristics when spilled in seawater to help with the development of an industry response strategy for a new generation of low-sulfur fuel oils. Many of the low-sulfur fuels being developed by the industry share similar compositions, so it is important to note that the findings of this report are not unique to the fuel samples analysed. The results of this study are indicative of a new generation of marine fuel oil across the wider industry. Further laboratory analysis of low-sulfur fuel oils from other suppliers is needed to give a clearer understanding of the characteristics and behaviours of individual products.

The results and data from this Multi-client project are available for all partners.

Abbreviations, Acronyms and Symbols

Abbreviations	Definitions
ASTM	American Society for Testing and Materials
BE	Burning effectiveness
BFT	Baffled Flask Test (dispersant Effectiveness test)
b.p.	boiling point
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
COA	Certificate of analysis
CROSERF	Chemical Response to Oil Spills: Ecological Research Forum
cP	centipois (= mPa.s)
DFO	Fisheries and Oceans Canada
DMA	Marine distillate gas oil (according to ISO 8217:2017)
DOR	Dispersant-to-oil ratio
ECA	Emission Control Area
EC50	Effective concentration causing 50 percent reduction of algae growth
GC-FID	Gas chromatography – Flame Ionization Detector
GO	Gas oil
HDME 50	Heavy Distillate Marine ECA 50

IBC	Intermediate bulk container
IFP	Institut Français du Pétrole. Low-energy dispersant test
IFO	Intermediate Fuel Oil (heavy fuel oil)
IMO	International Maritime Organization
K_{ow}	Octanol/water partition coefficient
ISO	International Organization for Standardization
LC50	Lethal concentration causing lethal immobilisation in 50 percent of a species
LE-WAF	Low Energy Water Accommodated Fraction
LIMS	Laboratory Information Management System
LSFO	Low Sulfur Fuel Oil
MARPOL	The International Convention for the Prevention of Pollution from Ships
m/m	mass by mass
mPa.s	millipascal second. Unit for dynamic viscosity
m/s	meter per second
MGO	Marine gas oil
MNS	Mackay, Nadeau, and Steelman. High energy dispersant test
MPRI	Multi Partner Research Initiative
Newtonian fluid	Fluid whose viscosity does not change with rate of flow
NOFO	Norwegian Clean Seas Association for Operating Companies
NCA	Norwegian Coastal Administration
Non-Newtonian fluid	A non-Newtonian fluid is a fluid that does not follow Newton's law of viscosity, i.e. constant viscosity independent of stress
OWM	Oil Weathering Model
PAH	Polyaromatic hydrocarbon
ppm	parts per million
R&D	Research and Development
S	Sulfur
s^{-1}	reciprocal second
SECA	Sulfur Emission Control Area
SI	International System of Units
SIMDIS	Gas Chromatographic Simulated Distillation
SOx	Sulfur oxide
SVOC	Semi-volatile organic compound
TBP	True Boiling Point
TPH	Total Petroleum Hydrocarbons
TU	Toxic Unit
ULSFO	Ultra-low sulfur fuel oil: ≤ 0.10 S wt. % (SECA, 2015)
UCM	Unresolved Complex Mixture
VLSFO	Very Low Sulfur Fuel oil: ≤0.50 wt. % (outside SECA from 2020)
vol.%	volume percent
WAF	Water Accommodated Fraction
WRG	Wide range gas oil
WOR	Water-to-oil ratio
wt. %	weight percent

1 Executive summary

Objective and introduction

The main objective of this Multi-client project has been to provide better documentation of the variability of the weathering properties and behaviour of new low sulfur marine fuel oils when spilled at sea, and to determine mitigation effectiveness of different oil spill response options.

New generation of "Ultra Low Sulfur Fuel Oils" (ULSFO, (S≤ 0.10 % m/m) marine fuel oils were from 2015 replacing the traditional intermediate fuel oils (like IFO 180 and IFO 380) for use in the Sulfur Emission Control Area (SECA) in Europe and North America. Outside these designated emission control areas, a new Global Sulfur Cap regulation was implemented (IMO/MARPOL convention, Annex VI) from January 2020 for "Very Low Sulfur Fuel Oils (VLSFO, S ≤0.50 % m/m).

To reduce the amount sulfur oxides (SOx) emissions to the atmosphere, the ships globally will now have to use low sulfur marine fuel oils with a sulfur ≤0.50 % in contrast to the former sulfur limit of 3.50 %. As referred by IMO, this reduction of sulfur in marine fuel oils should have major health and environmental benefits for the world, particularly for populations living close to ports and coasts. This project contributes to provide oil spill responders an increased knowledge and preparedness for spills involving these new generation of low sulfur fuel oils that are currently coming on the market.

Selection of test oils

Spilled oils undergo changes when weathering on the sea surface affects the fate and behaviour and the oil spill countermeasures in various ways. The oil weathering processes varies over time depending on both the parent composition of the spilled oil itself and the environmental conditions. In this project, three different low sulfur residual fuel oils (LSFOs) were selected and characterized for their weathering properties, dispersibility, toxicity of water-soluble fraction in addition to ignitability / *in-situ* burning (ISB):

- VLSFO from Chevron, Singapore (S≤0.50 % m/m)
- VLSFO from Shell, The Netherlands (S≤ 0.50 % m/m)
- ULSFO from Shell, The Netherlands (S≤0.10 % m/m)

The aim was to select representative marine residual fuel oils used primarily by vessels operating in European/ Norwegian and Canadian waters. However, there was a limited access to residual low sulphur fuel oils (VLSFO) in 2019. This was because the timing for the selection of oils had to be taken before the 2020 compliant Sulfur Cap. A sample of VLSFO was a blend of residual type of fuel oil supported mainly from the big Chevron joint-venture refinery in Singapore, in addition to two different marine residual fuel oils provided from the well-known European Shell refinery in Rotterdam. The oil tested in this project were evaluated as relevant LSFOs based on available Certificate of Analysis (COA).

Physico-chemical properties and weathering of oil

Bench-scale studies of chemical composition, physical properties and emulsifying properties were investigated on the three low sulfur fuel oils. The testing was performed at two seawater temperatures, representing cold climate /arctic conditions (2 °C) and typical summer conditions in the North Sea (13 °C). The test temperatures are also relevant for Canadian waters and was decided in agreement with the multi-partner clients. Experimental data was further customized in tables for use as input to numerical Oil Weathering Model (OWM), to obtain reliable and robust weathering predictions of spill scenarios. *In-situ* burning (ISB) experiments were also included on the fuel oils. As part of an inter-calibration of methodologies, selected analysis was performed both at SINTEF Ocean and in Canada /SL Ross on one of the fuel oils (ULSFO Shell 2019).

The residual fuel oils tested expressed very low evaporative loss in the range of 5-8 vol.% of the 250°C+ topped residue for VLSFO Shell 2019 and ULSFO Shell 2019. The VLSFO Chevron 2019, however, showed a negligible evaporative loss, and the tests were only conducted on the fresh oil (no evaporation). The densities of these residual fuel oils are in the range of 0.917-0.99 g/mL (15.5 °C). The pour point varied among the oils (+3 to +24 °C, fresh oils). High pour points imply solidification at sea typically with pour points 5-15 °C above the seawater temperature. ULSFO Shell 2019 expressed the highest pour point (+24 °C) among the tested oils. Moreover, the oil tested in this project are residual fuels (i.e. no distillates) based on the content of the heavy asphaltenes. The asphaltene and wax contents also showed to differ between the oils. The ULSFO Shell 2019 expresses a high wax content of 21 wt.% and a low asphaltene content (0.14 wt.%), that reflects the high pour point. VLSFO Chevron 2019 and VLSFO Shell 2019 contain similar wax contents (~5 wt.%), while the VLSFO Shell 2019 has a high asphaltene content of 4.8 wt.% compared with the other tested fuel oils.

The oils exhibit different hydrocarbon profiles (gas chromatography) reflecting variations in the physico-chemical properties. The VLSFO Chevron 2019 shows paraffins (*n*-alkanes) in the range of nC_{20} to nC_{30} with minor content of compounds lower than nC_{17} (b.p. 300 °C) that reflected the minor evaporative loss. The VLSFO Shell 2019 exhibits high peaks of naphthalenes relative to paraffins (the *n*-alkanes are almost absent). ULSFO Shell 2019 has a broad range of paraffins in the range of nC_9-nC_{36} that reflects the high wax content from $_{n}C_{20.}$

The oils express high viscosities at 2 and 13 °C (higher viscosities at lower temperature). A temperature-sweep from 50 to 0 °C was measured. VLSFO Shell 2019 showed similar viscosity development as a heavy bunker fuel oil (IFO 380). The viscosity at 50 °C was about 350 mPa.s for VLSFO Shell 2019. VLSFO Chevron 2019 and ULSFO Shell 2019 are both lower viscous oils (20-80 mPa.s measured at 50 °C), but their viscosities also increased significantly with decreasing temperature.

The fuel oils tested showed emulsifying properties, i.e. they can incorporate water (up to 30-60 vol%) upon weathering at sea. The oils expressed lower emulsification at 2 °C compared to 13 °C. However, the water uptake rate was slow at both temperatures. The fresh oils also expressed higher water uptake than the weathered residues at both temperatures. The emulsion formed were stable, and addition of emulsion breaker (Alcopol 60 O) was attempted to break the emulsion to release water. No effect was observed on VLSFO Chevron 2019 and ULSFO Shell 2019, and a slight effect was observed on the residue of VLSFO Shell 2019, at 13 °C. This is in accordance to previously observations of limited effectiveness of adding emulsion breaker on heavy fuel oils (e.g. IFO 180/380). However, a previously batch of ULSFO Shell 2016 showed some effect of emulsion breaker at high dosages (2000 ppm) at 2 and 13 °C.

Dispersibility and dispersant effectiveness

The very high viscous emulsions, particularly formed from VLSFO Shell 2019 at 2 °C, will highly influence on the response strategy for mechanical recovery (choice of skimmer system) in a spill operation. ULSFO Shell 2019 has solidifying properties due to the very high pour points that also may pose a challenge for mechanical recovery in oil spill response at sea. In general, the fuel oils tested had limited dispersibility efficiency by adding dispersants to the fresh oils in addition to emulsified fresh and weathered residues. Use of dispersants on VLSFO Chevron 2019 and VLSFO Shell 2019 revealed to have a potential to break up the surface slick into smaller patches at 13 °C with use of the high energy test (MNS) reflecting breaking waves conditions but showed no efficient dispersion (i.e. not forming small oil droplets). Overall, Corexit 9500A was shown to be a slightly more efficient dispersant compared with OSR-52 and Dasic NS. However, larger lumps /threads formed after treatment of dispersants re-surfaced quickly after the applied wave energy was stopped. However, ULSFO Shell 2019 was not shown to be dispersible neither at 2 °C nor 13 °C, mainly due to high pour points.

Oil weathering model predictions

The SINTEF OWM relates oil properties to a chosen set of conditions (oil/emulsion film thickness, wind speeds and sea temperature) and predicts the change rate of the oil's properties on the sea surface with time. In this report, the presented predictions span a period from 15 minutes to 5 days based on a standard release rate. The mass balances from the OWM predictions show that the fuel oils tested are very persistent on the sea surface in non-breaking waves conditions (2-5 m/s wind speeds). At higher wind speeds of 10-15 m/s, the predicted lifetime of the oils at sea was less persistent as the oils also "naturally dispersed" into the water column by increasing wave energy. It should be emphasized that "naturally dispersed" here should be considered as entrainment due to the formation of larger lumps /threads instead of smaller oil droplets. Moreover, such large lumps /threads may easily re-surface in calm conditions. Other oil weathering properties at sea were also predicted with OWM based on the input data generated from the laboratory study. In addition, comparison of predicted oil weathering properties shows both a span of variety (e.g. pour points and viscosities), but also similarities (e.g. flash point) among the tested fuel oils.

Ignitability – *in-situ* burning

The ignitability (i.e. time to ignite the oils, using a "progressive" ignition strategy) of the three LSFO residual fuel oils were tested by SINTEF in meso-scale trays at RelyOn Nutec in Trondheim. The water-free (non-emulsified) oils were all ignitable, but due to the low content of volatiles, the oils needed a prolonged time to be heated by an ignitor (gelled gasoline/diesel mixture) before the burn spread to the oil layer. Among the three oils, ULSFO Shell 2019 was the easiest oil to ignite, where the burning gel needed to burn for 3 min. before the burn was spread to the surrounding oil. For the two VLSFO oils this "heating time" was even longer (i.e.10 min. for the VLSFO Shell 2019, and 18 min. for the VLSFO Chevron 2019). 30 and 50 % w/o-emulsions of the ULSFO Shell 2019, were not possible to ignite by burning gels without adding significant amounts (1 mm and 3 mm) of diesel on the top of the emulsions. These ignitability tests indicate, therefore, that even low content of water incorporation (w/o-emulsification) makes the oils not ignitable by the present operative ignition methodologies in an ISB response operation without application of significant amount of primer (e.g. diesel) on the emulsified oil slick.

Water accommodated fractions (WAF) – chemistry and toxicity

Water accommodated fraction (WAF) of the three LSFO residual fuel oils were studied with emphasis on chemistry and acute toxicity. Low-energy WAFs solutions were prepared under controlled conditions following the guidelines established by the CROSERF forum, with an oil-to-water ratio of 1 to 40. Two pelagic species representing primary producers (the marine algae *Skeletonema pseudocostatum*) and invertebrates (the marine copepod *Calanus finmarchicus*) were tested. Additionally, the Toxic Unit (TU) of the WAFs where computed based on the chemical composition of the WAFs, where a TU > 1 for the total WAF implies that it is expected to cause more than 50% mortality in the test organisms. TUs for VLSFO Shell 2019 and ULSFO Shell 2019 were below 1 (0.51 and 0.24, respective). TU for VLSFO Chevron 2019 was 1.02, indicating that the WAF could cause mortality to more than 50% of the test organisms. The overall results from the relative and specific toxicities values for the three oils were in accordance with the relative ranking of the TU values. However, the WAF toxicity of the tested oils are low and is in the same range as other previously tested marine distillates fuels (TU<1), except from the DMA Shell diesel (2016) that had a significant higher TU value due to the its high content of semi-soluble naphthalenes and PAHs (aromatics).

Interlaboratory comparison studies

The interlaboratory comparison on ULSFO Shell 2019 conducted at SINTEF and SL Ross showed acceptable results of the physical parameters. However, the procedures and methods used may differ since both laboratories used their standard protocols for generating weathering data. Different weathering procedures explain the difference in the evaporative loss, but also due to the very low evaporation of this high pour-point oil. The discrepancy on the emulsifying properties was probably related to variations in the experimental performance and procedures between the laboratories. However, both laboratories concluded a low dispersibility on ULSFO Shell 2019 with Corexit 9500A, tested with the MNS-test at SINTEF and the BFT-test at SL Ross.

The experimental setup and test procedures for the ISB experiments are also different at the two laboratories and may explain much of the span in the results of the burning efficiency. In both laboratories, the burn testing was conducted in a batch format, and with a similar starting oil layer thickness on water of 1.7 cm (SINTEF) and 2.0 cm (SL Ross) on water. However, the burn conditions at SINTEF using a tray with the oil layer on a "static" reservoir of water, is an attempt to simulate the burn of a "free" drifting oil slick, where the upper water layer beneath the burn will gradually be heated and eventually start to boil. This will generate turbulence, which will influence on the burn intensity, and promote termination of the burn. While, by having a water flow-through (circulation) under the burn containment ring as in the SL Ross test apparatus, is simulating more a burn of oil when being towed in a boom behind a ship, and where the underlayer water is continuously replaced with cold water, that delay / avoid the water to boil and thereby maintaining a much longer burning time (e.g. 17 min. vs 6 min. in the SINTEF test) and give a higher burning efficiency (BE = 93% vs. 47% at SINTEF). Because these burns are conducted in a batch format, a larger starting volume of oil within the test cell should generate better calculated efficiencies if the oil burns terminate at similar final residue slick thickness.

In general, the ULSFO Shell 2019 was a challenging oil for interlaboratory calibration studies due to its extreme high pour point, solidifying properties and stickiness that may influence on the test results. However, there has been a lot of lessons learned for both laboratories from this interlaboratory comparison study that form a good basis for further harmonisation of laboratory test methodologies and standardisation, including harmonized laboratory protocols for:

- Oil weathering (incl. evaporation, emulsification, photooxidation, etc.)
- *In-situ* burning testing (both ignitability and burning effectiveness)
- Dispersant effectiveness testing
- WAF / toxicity testing
- Implementation of experimental data into numerical models for oil weathering predictions

Further recommendations

The LSFOs tested in this project indicate a high degree of persistence on the sea surface, and the oil spill response can even be more challenging than the previous traditional intermediately fuels oils (e.g. IFO180 / 380), particularly in cold water spill situations. From an oil spill response point of view, it is therefore crucial to get a better overview and knowledge of the variability in the weathering processes, fate and behaviour and response capabilities to the new LSFOs. The ongoing change among refineries to comply with the new sulfur regulations require a need for further characterization of the increasing numbers of LSFOs coming on the marked. Further recommendations based on findings from this project are suggested as followed:

- Small-volume samples of LSFO marine fuels (both distillate and residual fuels) from a larger number of refineries should be collected for a screening testing of simple oil parameters (e.g. TBP, density viscosity, pour point, gas-chromatography, emulsifying properties) tested at relevant sea temperatures
- Based on such preliminary screening, a selection of oils should be followed up with a more extensive oil weathering characterizations and meso-scale / basin testing of relevant response techniques (dispersants, ISB, different skimmer concepts etc.), and shoreline adhesion and response techniques
- Further harmonization of test methodologies and test protocols among oil spill laboratories
- Gain a better knowledge of the differences in the chemical composition (e.g. key biomarkers and UCM; unresolved complexed mixture) between "traditional" marine fuels and the new generation of sulfur-compliant marine fuels (both distillates and residuals), by e.g. use of high-resolution analytical techniques
- A co-operation with the down-stream refinery industry would facilitate the possibility for refining marine LSFO formulations with improved oil spill response capabilities

2 Introduction

The recent changes in IMO (International Maritime Organization) regulations concerning lower limits in sulfur content in marine fuel oils have resulted in a switch to new generations of low sulfur fuel oils, developed in order to meet the new requirements for lower atmospheric sulfur (SOx) emissions. As shown in Figure 2-1, ≤0.10 % m/m ("Ultra Low Sulfur Fuel Oil" - ULSFO) came into force in 2015 for the Sulfur Emission Control Area (SECA) from 2015. Outside these designated emission control areas, a Global Sulfur Cap limit of ≤0.50% m/m S was implemented from January 2020. This 2020 compliant residual fuels (called "Very Low Sulfur Fuel Oil" - VLSFO), are therefore replacing the traditional intermediate fuel oils or heavy fuel oils (like IFO 180 and IFO 380) to reduce the sulfur content from 3.50 % m/m to 0.50 % m/m.

Furthermore, the ongoing change among refineries worldwide to comply with the new sulfur regulations means that an increasing number of marine fuel oils are now entering the marked. Therefore, facing the 2020 Global Sulfur Cap and potential other regulations (e.g. arctic areas /cold climate regions), the new generation of marine fuel oils are expected to gain importance. The variation in oil properties will be dependent on the refinery type, feedstock (e.g. switch to sweeter crude oils) and upgrading of the different conversion processes (e.g. hydro-desulfurization, catalytic cracking, visbreaking) to reduce the amount sulfur and residual material.

For oil spill responders it is crucial to gain knowledge and scientific documentation of the variability in the weathering processes and response capabilities to these new low sulfur fuel oils.

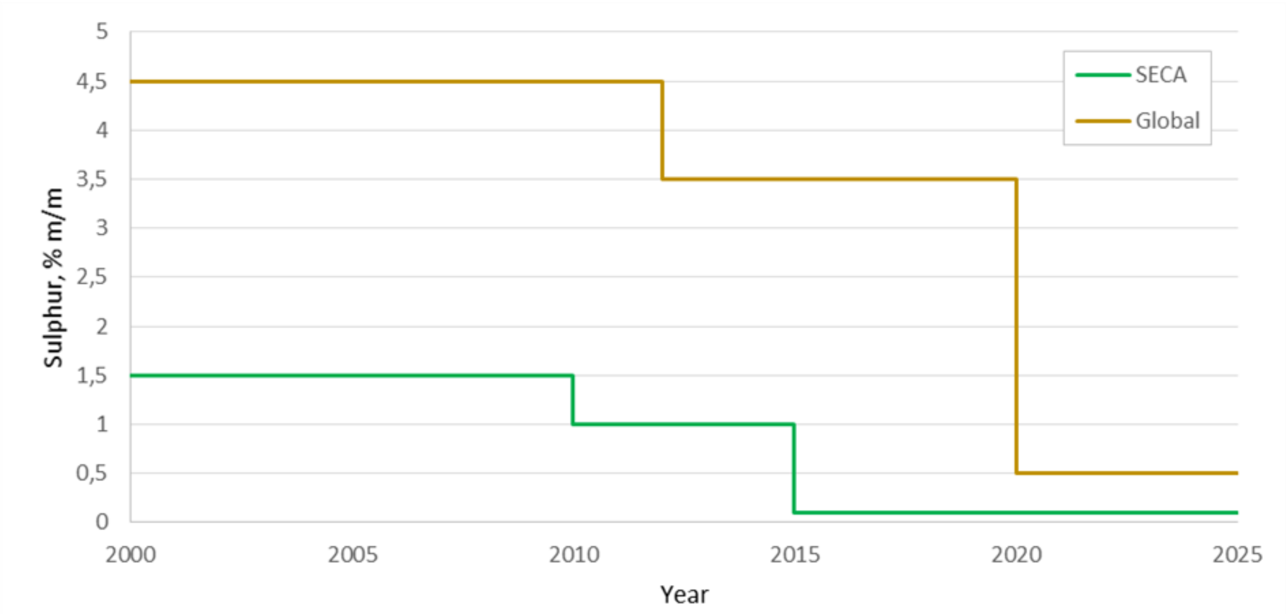


Figure 2-1 ***Previous and future changes in regulations regarding sulfur content in marine fuel oils within SECA and globally (courtesy from Hellstrøm, 2017)***

Moreover, in 2015, the Norwegian Coastal Administration (NCA) and SINTEF started to investigate weathering properties of a limited numbers of low sulfur fuel oils (S≤0.10 % m/m) with regards to relevance for oil spill response. This previous study revealed a large diversity in their physico-chemical properties among the oils (Hellstøm, 2017), and stated that the new generation of Low Sulfur Fuel Oils (LSFOs) exhibit properties both from light distillates fuels to heavier residual fuel qualities.

Table 2-1 gives an overview of oil types tested within this project including reference marine fuel oils that has been used for comparison or referred to in figures and tables in this report.

Table 2-1 Overview of oil types used in this project and oils from previously studies at SINTEF

Oil name	SINTEF ID	References	Comments
VLSFO Chevron 2019	2019-3599	Current project	Project supported by DFO/MPRI, ITOPF and NCA
VLSFO Shell 2019	2019-7685	Current project	Project supported by DFO/MPRI, ITOPF and NCA
ULSFO Shell 2019	2019-11170	Current project	Project supported by DFO/MPRI, ITOPF and NCA
ULSFO Shell 2016	2016-0233	Hellstrøm, 2017 Hellstrøm et al. 2017	Project supported by NCA
HDME 50	2016-0231	Hellstrøm, 2017 Hellstrøm et al. 2017 Faksness and Altin, 2017	Project supported by NCA
DMA Shell diesel*	2016-0232	Hellstrøm, 2017 Hellstrøm et al. 2017 Faksness and Altin, 2017	Project supported by NCA
MGO**	2014-0551	Sørheim and Daling, 2015 Hellstrøm, 2017, Hellstrøm et al. 2017 Faksness and Altin, 2017	Projects supported by NCA
GO***	2014-0552	Sørheim and Daling, 2015 Hellstrøm, 2017 Hellstrøm et al. 2017 Faksness and Altin, 2017	Projects supported by NCA
WRG	2014-0553	Sørheim and Daling, 2015 Hellstrøm, 2017 Hellstrøm et al. 2017 Faksness and Altin, 2017	Projects supported by NCA
IFO 180	2013-0594	Sørheim et al. 2014	Project supported by NCA
IFO 380	2013-0609/0610	Sørheim et al. 2014	Project supported by NCA

Rotterdam diesel **MGO 500 ppm S * GO 10 ppm S*

3 Objective

The main objective was to perform laboratory studies on new marine fuel oils coming on the market with focus on fate and behaviour, potential toxicity and with relevance to the effectiveness of different oil spill response options (use of dispersants and *in-situ* burning). Test methodologies was also subjected to interlaboratory harmonisation, and experiments were performed both in Norway (SINTEF) and in Canada (SL Ross) on one of the tested oils.

The project included the following main tasks:

- Selection of test oils: A total of 3 low sulfur marine residual fuel oils were provided for testing. Two of the LSFOs came from the European Shell refinery in Rotterdam and one was delivered from the Chevron refinery in Singapore
- The LSFOs were subjected to a weathering study including analysis of relevant physico-chemical properties and testing of water-in-oil (w/o) emulsification properties, and standardised toxicity screening of the water accommodation fraction (WAF). Dispersibility and ignitability testing on different weathered samples were also included related to spill countermeasures
- Harmonisation and interlaboratory calibration of test methodologies to acquire and evaluate comparable data between the laboratories
- Evaluation of results and reporting

4 Selection of test oils

In this project, three different low sulfur residual fuel oils were selected from characterized for their weathering properties, dispersibility, toxicity of water-soluble fraction in addition to ignitability / *in-situ* burning (ISB) within this project:

- VLSFO from Chevron, Singapore (S≤0.50 % m/m). Delivered through ITOPF contacts
- VLSFO from Shell, The Netherlands (S≤0.50 % m/m). Delivered through ITOPF contacts
- ULSFO from Shell, The Netherlands (S≤0.10 % m/m). Delivered through NCA contacts

The aim was to select representative marine residual fuel oils that was used primarily by ships operating in European/ Norwegian and Canadian waters. However, there was a limited access to residual low sulphur fuel oils in 2019. This was because the timing for the selection of oils had to be taken before the 2020 compliant Sulfur Cap. A sample of VLSFO was a blend of residual type of fuel oil supported mainly from the big Chevron joint-venture refinery in Singapore, in addition to two different marine residual fuel oils from the well-known Shell refinery in Rotterdam. We were not able to get a relevant residual low sulfur fuel from a Canadian refinery or oil terminal. However, it was considered that the LSFOs tested within this project were relevant oils among the present marine residual fuel oils that are available on the marked based on accessible Certificate of Analysis (COA). Chevron has e.g. supplying 0.50% S LSFO to Asian Utilities using similar blends for more than 10 years.

Figure 4-1 shows example of visual appearance of residuals fuel oils represented by VLSFO Chevron 2019 and ULSFO Shell 2016, compared with distillates (represented by a wide range gas oil and HDME 50). The residuals in Figure 4-1 are representative for the ULSFO Shell 2019 and both the VLSFOs 2019 from this study. Distillates are translucent (light and dark colours) compared to more dense and black residual oils.

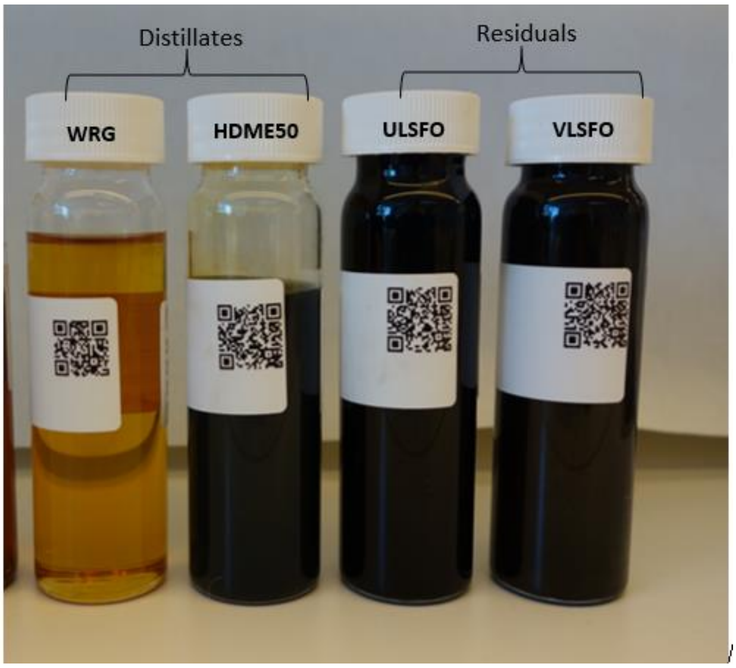


Figure 4-1 *Example of visual appearances of marine fuel distillates and residuals. The appearance of ULSFO (Shell 2016) and the VLSFO (Chevron 2019) are representative for the oils tested in this study, i.e. they are dense and black residuals marine fuel oils*

VLSFO Chevron, Singapore

A total of 60 Litres of a VLSFO from Chevron, Singapore arrived SINTEF Ocean 20 May 2019. This batch is a blend of entirely residual fuels. The shipment was registered in SINTEF lab. management system (LIMS) and given the unique SINTEF ID 2019-3955. One of the barrels from this shipment is shown in Figure 4-2, below. The marine fuel oil is a VLSFO oil based on the sulfur content ≤0.50 wt.%, refers to certificate of analysis (COA). For simplicity, the oil sample is denoted as the VLSFO Chevron 2019 throughout this report.

VLSFO Shell 2019, The Netherlands

6 x 10 Litres (60 litres) of a VLSFO from the Shell refinery in the Netherlands (Rotterdam) arrived SINTEF Ocean 8 October 2019. The shipment was registered in SINTEF lab. management system (LIMS) and given the unique SINTEF ID 2019-7685. One of the cans is shown in Figure 4-2, below. The VLSFO has a sulfur content ≤0.50 wt.% (COA). For simplicity, the oil sample is denoted as the VLSFO Shell 2019 throughout this report.

ULSFO Shell 2019, The Netherlands

NCA supported SINTEF, on the 16 December 2019, with 1 m^3 (IBC) of an ULSFO (Sulfur ≤ 0.10 %) from the Shell refinery in the Netherlands (Rotterdam). The shipment from NCA was registered in SINTEF lab. management system (LIMS) and given the unique SINTEF ID 2019-11170. The (IBC) container was heated in a 50 °C storage room at SINTEF and achieved an oil temperature of approx. 39 °C. The oil was further homogenized by a circular pumping system, and aliquots of 2 x 60 litres were sampled from the IBC tank. About 100 litres were further shipped to Canada /SLRoss. For simplicity, the oil sample is denoted as the ULSFO Shell 2019 throughout this report. This batch of ULSFO is a similar batch that was used on the NOFO /NCA oil-on-water field trial 2018.

Figure 4-2 *Left: Oil sample (1 of 3 barrels) of VLSFO Chevron 2019*
Right: VLSFO Shell 2019 (1 of 6 cans)

5 Bench-scale weathering study

The bench-scale laboratory studies on weathering and dispersibility were conducted at 2 and 13 °C, reflecting typically seawater temperatures in the Arctic/cold climate regions, North Sea, and Canadian waters. The methodology is described in Appendix A. The weathering data were further input to the SINTEF Oil Weathering Model (OWM) to predict the weathering properties of the oil by time. The fuel oils from this project were also compared with weathering data of two other low sulfur fuel oils from a previously study (Hellstøm, 2017), in addition to IFO 180 and IFO 380 (Sørheim et al. 2014) when applicable.

- ULSFO Shell 2016, SINTEF ID: 2016-0233
- HDME 50 (Heavy Distillate Marine ECA 50) ExxonMobil, SINTEF ID: 2016-0231
- IFO 180, SINTEF ID; 2013-0594
- IFO 380, SINTEF ID: 2013-0609/0610

5.1 Evaporation

The standardized evaporation procedure is a simple one-step distillation to vapour temperatures of 150 °C, 200 °C and 250 °C (Stiver and Mackay, 1984). The results from the evaporation of the tested oil are tabulated in Table 5-2.

- The fresh VLSFO Chevron 2019 was attempted distillation to 250 °C, but due to low degree of light compounds (volatiles) only a negligible evaporative loss was observed. The bench-scale laboratory testing was therefore conducted on the fresh oil, only
- The fresh VLSFO Shell 2019 was evaporated to 250°C+. The bench-scale laboratory testing was conducted both on the fresh oil and the 250°C + residue
- The fresh ULSFO Shell 2019 was evaporated to 200 and 250°C+ residues. The bench-scale laboratory testing was conducted both on the fresh oil, 200 and 250°C + residue

5.2 True boiling point (TBP) curve

The true boiling point (TBP) or distillation curve is obtained by measuring the vapour temperature as a function of the amount of oil distilled, shows the relative distribution of volatile and heavier components in the oil. The boiling point of a chemical component depends on its vapour pressure, which is a function of its molecular weight and chemical structure. 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.

The TBP curves of VLSFO Chevron 2019, VLSFO Shell 2019 and ULSFO Shell 2019 were analysed by use of "simulated distillation of marine fuel oils" in accordance to ASTM D7169 (Intertek UK). The TBP curves (wt.%) of the tested oils are shown in Figure 5-1 in comparison with ULSFO Shell 2016 and HDME 50. For comparison, TBPs of two traditional heavy fuel oil (IFO 180 /380) are also included in the figure. As shown in Figure 5-1 the two batches of ULSFO (2016 and 2019) differs significantly. ULSFO Shell 2019 is heavier than the batch from 2016. However, ULSFO Shell 2019 and VLSFO Shell 2019 have very similar boiling point development, particularly up to 350 °C. VLSFO Chevron 2019 and the distillate HDME 50 have similar shape of the boiling point curve. The IFOs have lower TBPs than the other oils (Figure 5-1), and the VLSFO Shell 2019 has an evaporative loss closest to the IFOs.

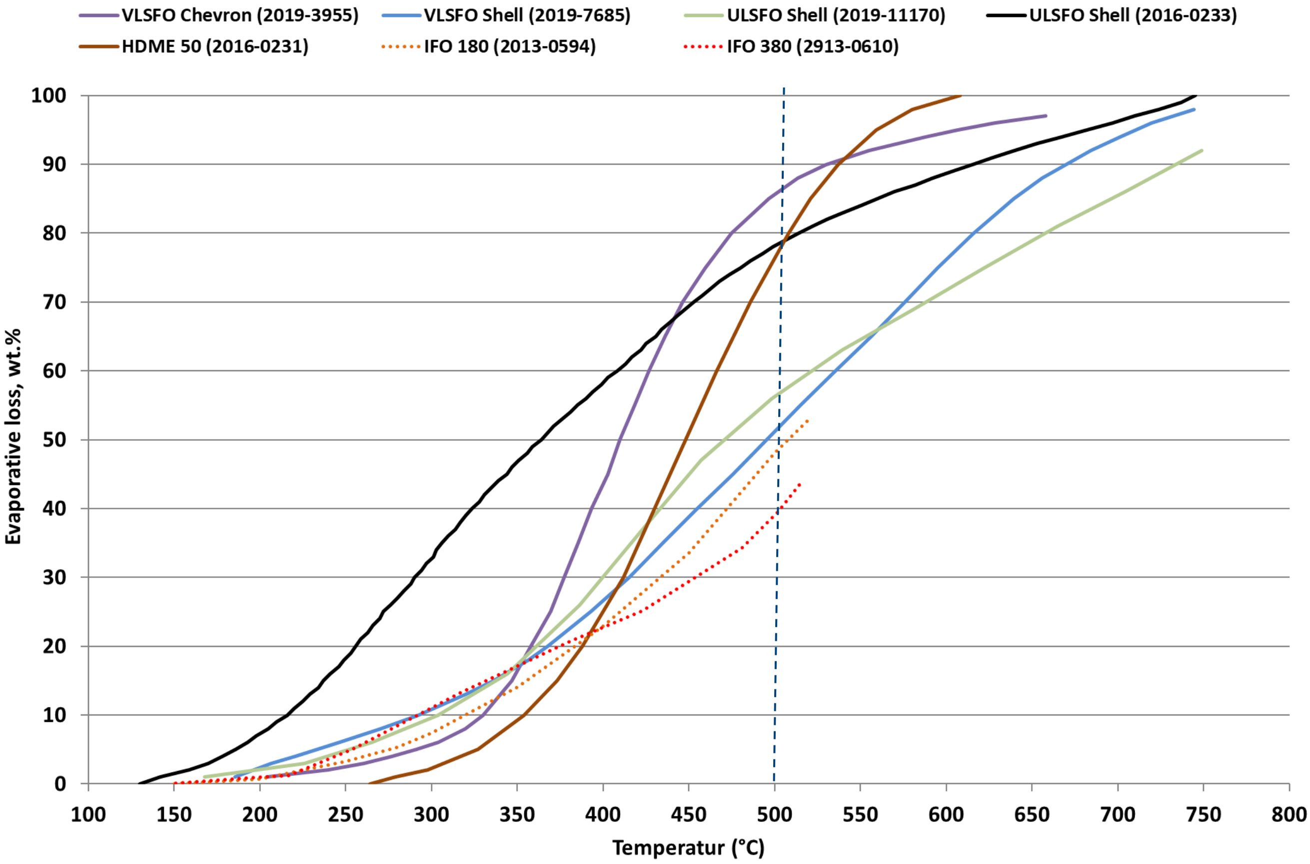


Figure 5-1 ***TBP for VLSFO Chevron 2019, VLSFO Shell 2019, ULSFO Shell 2019 in comparison with other low sulfur fuel oils (ULSFO Shell 2016, and HDME 50), and two heavy fuel oils (IFO180/380)***

5.3 Gas chromatographic analysis (GC-FID)

The gas chromatograms show the n-alkanes (paraffins) as systematic narrow peaks. The first peaks in the chromatogram represent components with the lowest boiling points. Some of the more complex components, such as resins and naphthenes, shown as a broad and poorly defined bump below the sharp peaks, are often described as “Unresolved Complex Mixture” (UCM). Heavier compounds such as asphaltenes (> nC40) are not possible to analyse with this technique.

The GC-chromatograms of the fresh oils of VLSFO Chevron 2019, VLSFO Shell 2019 and ULSFO Shell 2019 in comparison with ULSFO Shell 2016 and HDME 50 are shown in Figure 5-2. The oils exhibit different hydrocarbon profiles reflecting variations in the physico-chemical properties. The two batches (2016 and 2019) of ULSFOs show also varying chromatographic profiles. The oils, except HDME 50 contains a residual fraction of heavy compounds that has been mixed into the distillate (residual fraction not shown in the chromatograms). The HDME 50, however, is a wide range gas oil made from heavy distillation cut with minor content of heavy compounds, such as the asphaltenes. The VLSFO Chevron 2019 shows n-alkanes in the range of nC_{20} to nC_{30} with minor content of compounds lower than nC_{17} (300 °C) and reflected the negligible evaporative loss. The VLSFO Shell 2019 exhibits high peaks of naphthalenes shown as irregular compounds relative to the n-alkanes (the n-alkanes are almost absent), whilst ULSFO Shell 2016 has a broad range n-alkanes in the range of nC_9-nC_{36} that reflects a high wax content from $_nC_{20}$. However, despite the high similarities in the TBP (Figure 5-1), the chemical composition is very different. By combining TBP to the GC, the percent (%) of mass above C_{36} (boiling point, b.p.>500° C) was estimated. The vertical lines in Figure 5-2 at $_nC_{36}$ illustrate the mass % of residual components with b.p.>500 °C that is discriminated (none-chromatographable compounds) in the GC-analysis. VLSFO Shell 2019 and ULSFO Shell 2019 show mass of components above 500 °C which are almost in the same level as the traditional IFO 180/380 (52-60 % mass).

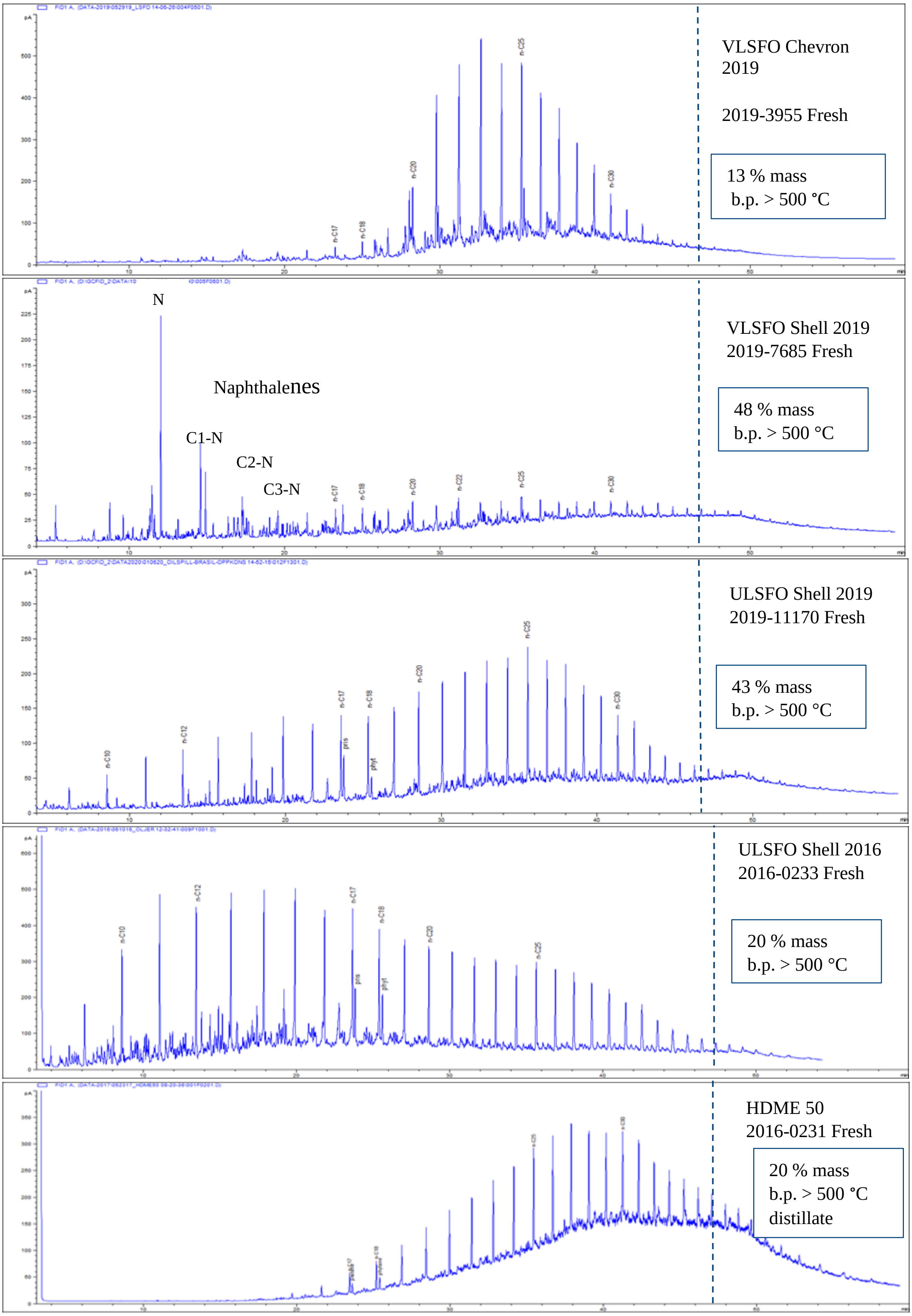


Figure 5-2 *GC-FID chromatograms of fresh samples of VLSFO Chevron 2019, VLSFO Shell 2019, ULSFO Shell 2019 in comparison with ULSFO Shell 2016 and HDME 50*

5.4 Physico-chemical properties

Generally, both wax and asphaltenes contribute to stabilize water-in-oil emulsion. Asphaltenes have a surface-active property that stabilize the water-oil interface, thereby forming a layer that stabilizes the water droplets, whilst the wax contributes to stabilize the asphaltenes near the water-oil interface.

The contents of asphaltene and wax for the for VLSFO Chevron 2019, VLSFO Shell 2019 and ULSFO Shell 2019 in comparison with ULSFO Shell 2016, HDME 50, IFO 180, and IFO 380 are given in Table 5-1. The results show a high variation of asphaltenes and wax content among the oils. VLSFO Shell 2019 has the highest content of asphaltenes 4.8 wt.%) of the oils tested in this project, but the IFOs (180 and 380) exhibit the highest contents (5.7 and 6.6 wt.%, respective). The distillate HDME 50 has expected very low content of asphaltenes (0.06 wt.%) in contrary to the residual oils. The two batches of ULSFOs (2016 and 2019) have low and similar content of asphaltenes (0.14-0.15 wt.%) compared to the VLSFOs but exhibit high wax content of 13-21 wt.%.

Table 5-1 Asphaltene ("hard") and wax content

Oil type	Residue	Asph. * (wt. %)	Wax (wt. %)
VLSFO Chevron 2019	Fresh	0.44	4.5
VLSFO Shell 2019	Fresh	4.8	4.9
	250°C+	5.2	5.3
ULSFO Shell 2019	Fresh	0.14	20.7
	200°C+	0.15	21.1
	250°C+	0.15	21.6
ULSFO Shell 2016	Fresh	0.15	13.1
	250°C+	0.18	15.5
HDME 50	Fresh	0.06	9.5
IFO 180	Fresh	5.7	4.4
	200°C+	5.7	4.4
	250°C+	5.9	4.5
IFO 380	Fresh	6.6	5.8
	200°C+	6.9	6.0
	250°C+	7.2	6.3

n-heptane (nC_7) precipitation

Table 5-2 **s**hows an overview of the physical parameters of the VLSFO Chevron 2019, VLSFO Shell 2019, and ULSFO Shell 2019 in comparison with two other low sulfur fuel oils (ULSFO Shell 2016 and HDME 50), and two intermediate heavy fuel oils (IFO 180 and IFO 380). The evaporative loss was shown to be low for the VLSFO Shell 2019 and ULSFO Shell 2019 (7.9 and 5.1 vol.%, 250°C+ residue), reflecting the relatively high-density fuel oils (0.92-0.99 g/mL). No evaporative loss was observed for the VLSFO Chevron 2019 due to the lack of light compounds < C_{10}. The oils express high pour points, particularly the two batches of ULSFO (+30 °C for 250°C+ residues), and solidification at low temperatures are a likely scenario. The IFO 380 has the lowest pour point (-6 °C) for the fresh oil in comparison with the other oils. The two ULFSOs have the lowest flash points (75-85 °C) that reflect a higher content of light compounds, whilst the distillate HDME 50 has the highest flash point (186 °C) due to the lack of components in the range of <C_{15}.

The viscosities of the fresh oil and residues behave as *non-Newtonian* fluids with decreasing viscosity with increasing shear rate, (s^{-1}). due to the wax lattice structure that breaks up with increasing shear rate. The oils have therefore higher viscosities at a lower shear rate (e.g. 10 s^{-1}) compared to the viscosities measured at higher shear rates (e.g. 100 s^{-1}). The oils tested in this project exhibit high viscosities (mPa.s) at 2 and 13 °C. VLSFO Shell 2019 has high viscosities that is most comparable with the IFO 380 at 13 °C, whilst the distillate HDME 50 has relatively low viscosities compared with the residual fuel oils. ULSFO Shell 2019 has a considerable higher viscosity than the batch from 2016 due to higher density and wax content. It should be emphasized that it is difficult to get good and reliable viscosity measurements of high-viscous/high wax oils particularly at low temperatures where oil/residue solidifies. Pre-handling and the temperature history of the oil will highly influence on the results. A shear rate of 100 s^{-1} was chosen as input to OWM predictions and harmonized with the viscosities from the temperature-sweep analysis, as described below.

Table 5-2 ***Physico-chemical properties of VLSFO Chevron 2019, VLSFO Shell 2019 and ULSFO Shell 2019 in comparison with other low sulfur fuels (ULSFO Shell 2016, HDME50), and IFO180/IFO 380***

Oil types	Residue	Evap. (vol. %)	Res. (wt. %)	Density (g/mL)	Flash point (°C)	Pour point (°C)	Visc. (mPa.s) 2°C $10s^{-1}$	Visc. (mPa.s) 2°C $100s^{-1}$	Visc. (mPa.s) 13°C $10s^{-1}$	Visc. (mPa.s) 13°C $100s^{-1}$
VLSFO Chevron 2019	Fresh	0	100	0.989	109[a]	9	71 236	28 399	5550	3948
VLSFO Shell 2019	Fresh	0	100	0.990	100[a]	3	132 46	77 638	19 450	16 507
	250°C+	7.9	93	0.996	NA	12	878 540	136 400	106 130	68 041
ULSFO Shell 2019	Fresh	0	100	0.917	85[b]	24	111 800	21 017	33 564	5986
	200°C+	2.7	98	0.920	87[c]	27	205 220	15 567	53 251	9903
	250°C+	5.1	96	0.922	89[c]	30	350 250	18 125	91496	14 826
ULSFO Shell 2016	Fresh	0	100	0.872	75	24	13 106	-	4300	-
	250°C+	14.6	86	0.878	112	30	77 782	-	33 169	-
HDME50	Fresh	0	100	0.903	186	12	11 002	-	1005	-
IFO 180	Fresh	0	100	0.973	-	6	-	-	7426	5118
	200°C+	1.2	99	0.975	-	6	-	-	7683	6368
	250°C+	3.6	97	0.978	-	9	-	-	11 355	9455
IFO 380	Fresh	0	100	0.990	-	-6	-	-	27 294	21 909
	200°C+	3.7	97	0.995	-	9	-	-	55 092	43 970
	250°C+	9.4	92	1.00	-	15	-	-	253 590	96 084

a: Certificate of Analysis (COA) b: Data from SL Ross; c: Estimated data
NA: Not analysed, -: No data

Temperature-sweep (viscosity) with a temperature range from 50-0 °C was measured (Figure 5-3). This method using oscillated force does not disturb the wax lattice as with the standardized methodology with increasing shear rates, hence the viscosity development can be followed over a wide temperature range. The temperature-sweep is therefore considered as a more robust method when comparing viscosities of high viscous oils where the pour points are considerably higher than the test temperature.

The temperature-sweeps for VLSFO Chevron 2019, VLSFO Shell 2019 and ULSFO Shell 2019 are shown in comparison with ULSFO 2016, HDME50, IFO 380 and a low-viscous diesel oil (Figure 5-3). The viscosities of the VLSFOs, ULFSOs, HDME50 increase significantly with decreasing temperature at 2-13 °C reflecting the chosen seawater temperatures for testing. The VLSFO Shell 2019 has high viscosity of 350 mPa.s at 50 °C, and is more comparable with the IFO 380, whilst the other fuel oils in Figure 5-3 have considerably lower viscosities at 50 °C (20-80 mPa.s). The DMA diesel oil has very low viscosities at the whole temperature range.

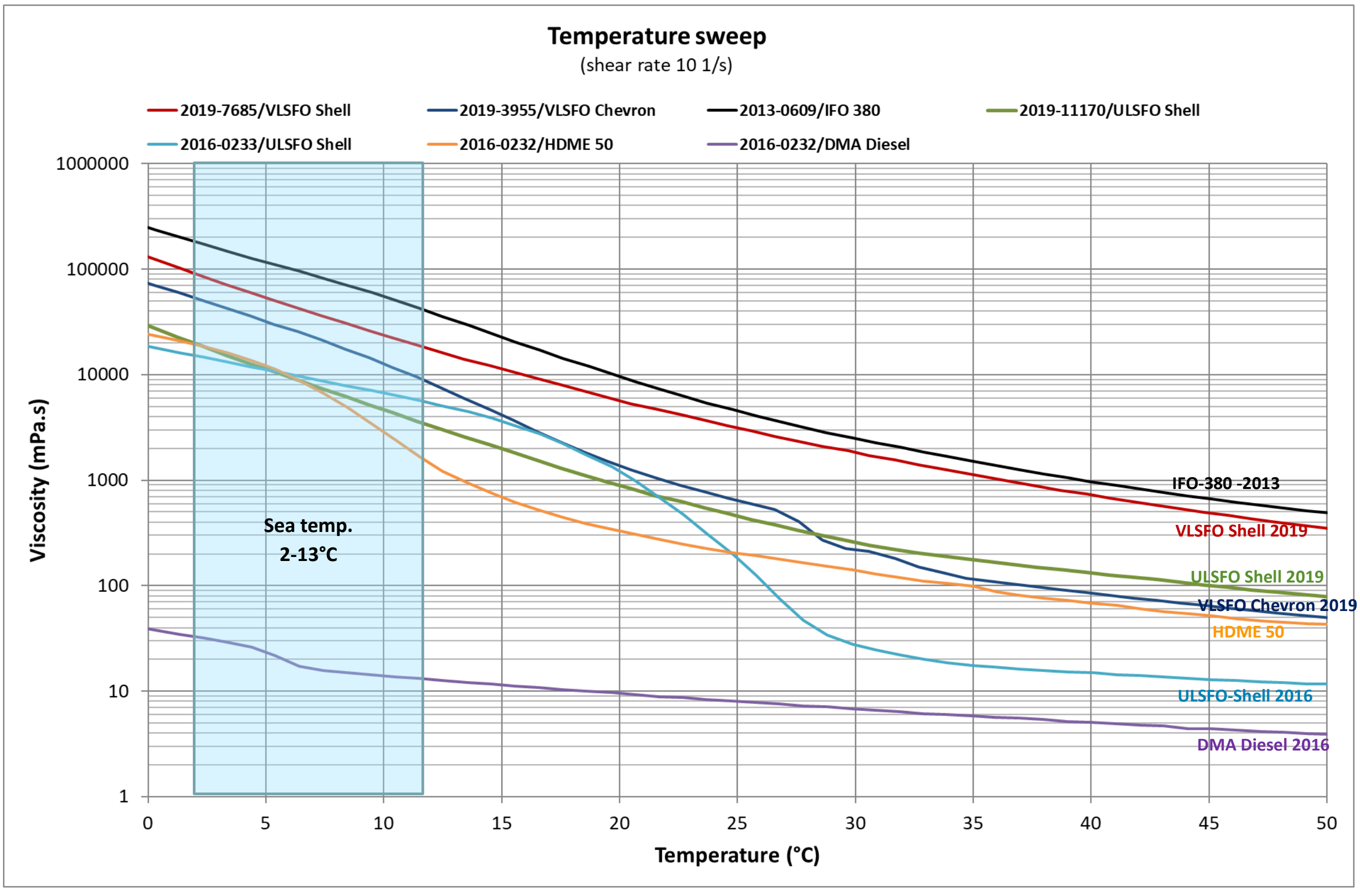


Figure 5-3 *Temperature sweep measurements (viscosities) of VLSFO Chevron 2019, VLSFO Shell 2019 and ULSFO Shell 2019 in comparison with other fuel oils (ULSFO Shell 2016, HDME50, IFO 380 and DMA diesel)*

5.5 Emulsifying properties

The emulsifying properties were studied using the rotating cylinders method as detailed in Hokstad et al. 1993. The parameters for kinetics (rate of water uptake) and maximum water uptake were studied to define the emulsification characteristics of oils selected for this study as described in Appendix A. The $T_{1/2}$ value derived from kinetics is defined as the consumed time in hours needed to incorporate half of the maximum water uptake.

Due to the very low contents of volatiles below 150°C (see gas-chromatogram in Figure 5-2), the emulsification testing was carried out on the non-evaporated (i.e. fresh) oils, in addition to the evaporated residues (200°C+/250°C+). Experiments of the fresh oils and residues were made to produce data for stability, viscosity, maximum water uptake, kinetics, and the effectiveness of the emulsion breaker application. Four cylinders of fresh oil /residue of each oil were prepared to study in parallel: stability testing and water uptake (rotating cylinder 1); viscosity / water update (rotating cylinder 2); effectiveness of emulsion breaker at dosage of 500 ppm (wt.%) (rotating cylinder 3); and effectiveness of emulsion breaker at dosage of 2000 ppm (wt.%) (rotating cylinder 4).

5.2.1 Water uptake and maximum water content

The VLSFO Chevron 2019, VLSFO Shell 2019 and ULSFO Shell 2019 showed all varying water uptake, but the water uptake was relatively low at both 2 and 13 °C. See images (figures) and tabulated results, below.

VLSFO Chevron 2019

Figure 5-4 shows the emulsification of the VLSFO Chevron 2019 (fresh oil) after 24-hour rotating at 2 and 13 °C. The tabulated water uptake as a function of time and the calculated $T_{1/2}$ are shown in Table 5-3. The maximum water uptake was lower at 2 °C compared with 13 °C.

Figure 5-4 ***The rotating cylinders of water-in-oil emulsion of VLSFO Chevron 2019 after 24 hours of rotation at 2 °C (left) and 13 °C (right)***

Table 5-3 ***Water uptake of the fresh oil of VLSFO Chevron 2019 at 2 and 13 °C***

Mixing time	Fresh oil, 2 °C (vol. % water)	Fresh oil, 13 °C (vol. % water)
Start	0	0
5 min	0	3
10 min	2	3
15 min	4	3
30 min	6	3
1 hour	7	3
2 hours	13	15
4 hours	19	27
6 hours	19	31
24 hours	31	49
T ½	**3.0**	**4.0**

VLSFO Shell 2019

VLSFO Shell 2019 formed emulsions of fresh and 250°C+ residue mixing with seawater at 2 and 13 °C. Figure 5-5 shows example of the emulsification of the fresh oil after 24 hours rotating time at both temperatures. Table 5-4 shows the tabulated water uptake by time and the $T_{1/2}$ values.

Figure 5-5 The rotating cylinders of water-in-oil emulsion of VLSFO Shell 2019 (fresh oil) after 24 hours of rotation at 2 °C (left) and 13 °C (right)

Table 5-4 Water uptake of the fresh oil and evaporated residue of VLSFO Shell 2019 at 2 and 13 °C

Mixing time	**Fresh oil, 2 °C (vol. % water)**	**250°C+, 2 °C (vol. % water)**	**Fresh oil, 13 °C (vol. % water)**	**250°C+, 13 °C (vol. % water)**
Start	0	0	0	0
5 min	6	0	3	3
10 min	6	0	5	5
15 min	6	0	8	5
30 min	8	0	10	5
1 hour	10	3	19	10
2 hours	10	6	32	12
4 hours	10	9	40	14
6 hours	13	10	45	21
24 hours	13	23	57	52
T ½	**0.26**	**5.6**	**2.0**	**6.6**

ULSFO Shell 2019

Figure 5-6 shows examples from emulsification of ULSFO Shell 2019 fresh oil after 24 hours rotating time at 2 and 13 °C. At 2 °C, the emulsion formed had irregular shapes and solidified, and the total water-uptake was low. For 200 and 250°C+ residues the emulsion at 2 °C became more a solid ("ball" shaped), as shown in Figure 5-7 (left). Similar, but less extreme behaviour was observed at 13 °C. Emulsions formed did not have an even layer on the top of the water phase due to the high emulsion viscosity and high wax content. At both temperatures, the maximum water incorporated in the oil were quantified by measuring the volume of free water after mixing time. The high wax content also caused formation of waxy /non-emulsified lumps, and an example of such lump is shown in Figure 5-7 (right) of the 250°C+ residue at 13 °C. Moreover, the emulsions at 2 °C were less sticky on the glass interior than at 13 °C.

Figure 5-6 The rotating cylinders of water-in-oil emulsion of ULSFO Shell 2019 after 24 hours of rotation at 2 °C (left) and 13 C (right)

Figure 5-7 Left: Water uptake of 200 and 250 °C+ residues after 24 hours weathering at 2°C.
Right: Waxy lump (red circle) formed form the 250°C+ residue of ULSFO Shell 2019 at 13 °C

Table 5-5 Water uptake of the fresh oil and evaporated residue of ULSFO Shell 2019 at 2 and 13 °C

Mixing time	Fresh oil, 2 °C (vol. % water)	200°C+, 2 °C (vol. % water)	250°C+, 2 °C (vol. % water)	Fresh oil, 13 °C (vol. % water)	200°C+, 13 °C (vol. % water)	250°C+, 13 °C (vol. % water)
Start	0	0	0	0	0	0
5 min	0	4	0	3	3	0
10 min	5	5	0	5	6	0
15 min	8	5	0	5	6	0
30 min	8	5	2	13	9	3
1 hour	8	5	3	38	20	6
2 hours	9	5	2	42	23	13
4 hours	17	5	2	51	24	23
6 hours	24	5	2	52	31	28
24 hours	35	6	2	67	38	44
T ½	**3.6**	**0.06**	**0.27**	**1.4**	**1.5**	**4.1**

5.2.2 Efficiency of emulsion breaker and stability of emulsion

Generally, the findings of stability and the efficiency of the use of emulsion breakers can be important in a mechanical recovery situation because separating the oil from water enables optimal use of available storage facilities/tankers. The emulsion stability of the tested oils was studied by quantifying the amount of water released from the emulsion for 24 hours settling time. In addition, the efficiency of adding emulsion breaker (Alcopol O 60 %) to each emulsion was evaluated.

VLSFO Chevron 2019

The results stability and effect of emulsion breaker for VLSFO Chevron 2019 are shown in Table 5-6. The emulsion formed from the fresh oil were nearly or completely stable when left to stand still for 24 hours at 2 and 13 °C. No significant effects were observed resulting from the addition of emulsion breaker to the emulsified oil.

Table 5-6 Stability of VLSFO Chevron 2019 emulsions (no emulsion breaker) and efficiency of emulsion breaker at 2 and 13 °C. Emulsion prepared from the fresh oil

Temperature	Residue	Emulsion breaker	Water-in-oil emulsion (vol. %)		Stability ratio**
			Reference	24 hours *	
2 °C	Fresh	None	31	30	0.98
	Fresh	Alc. O 60 % 500 ppm	31	30	0.98
	Fresh	Alc. O 60 % 2000 ppm	31	31	1.00
13 °C	Fresh	None	49	44	0.82
	Fresh	Alc. O 60 % 500 ppm	49	45	0.85
	Fresh	Alc. O 60 % 2000 ppm	49	47	0.92

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

** *Stability ratio of 1 implies a totally stable emulsion for 24 hours settling. Stability ratio of 0 (zero) implies a totally unstable emulsion; all the water is settled out for 24 hours settling.*

VLSFO Shell 2019

The results indicating stability and effect of emulsion breaker for VLSFO Shell 2019 is shown in Table 5-7. Overall, the emulsion of 250°C+ residue seemed to be less stable compared to emulsion from the fresh oil, and partly broke the emulsion by adding emulsion breaker at 2 and 13 °C.

At 2 °C, the emulsion of the fresh oil and 250°C+ residue was stable, i.e. no or minor released water was observed after 24 hours stand still. For the 250°C+ residue, the emulsion breaker (2000 ppm) partly broke the emulsion, but this was not observed for the emulsion prepared from the fresh oil. However, the water uptake was low, and uncertainties are therefore expected in evaluating the results.

At 13 °C, the emulsion prepared from the fresh oil was completely stable after 24 hours stand still, and only minor effect of adding emulsion breaker was observed. However, the emulsion from the 250°C+ residue partly released water after 24 hours stand still, and similar effect was also observed after treatment of emulsion breaker.

Table 5-7 Stability of VLSFO Shell 2019 emulsions (no emulsion breaker) and efficiency of emulsion breaker at 2 and 13 °C. Emulsions prepared from fresh oil and the 250°C+ residue

Temperature	**Residue**	**Emulsion breaker**	**Water-in-oil emulsion (vol. %)**		**Stability ratio****
			Reference	**24 hours ***	
2 °C	Fresh	None	13	13	1.00
	Fresh	Alc. O 60 % 500 ppm	13	9	0.67
	Fresh	Alc. O 60 % 2000 ppm	13	13	1.00
2 °C	250°C+	None	23	19	0.76
	250°C+	Alc. O 60 % 500 ppm	23	23	1.00
	250°C+	Alc. O 60 % 2000 ppm	23	8	0.27
13 °C	Fresh	None	57	57	1.00
	Fresh	Alc. O 60 % 500 ppm	57	50	0.75
	Fresh	Alc. O 60 % 2000 ppm	57	53	0.85
13 °C	250°C+	None	52	27	0.34
	250°C+	Alc. O 60 % 500 ppm	52	17	0.19
	250°C+	Alc. O 60 % 2000 ppm	52	-	-

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

** *Stability ratio of 1 implies a totally stable emulsion for 24 hours settling. Stability ratio of 0 (zero) implies a totally unstable emulsion; all the water is settled out for 24 hours settling.*

-: *No data due high uncertainty in the measurement*

ULSFO Shell 2019

The results indicating stability and effect of emulsion breaker for ULSFO Shell 2019 are shown in Table 5-8. Overall, the emulsions formed were nearly or completely stable when left stand still for 24 hours at 2 and 13 °C. Neither significant effect of adding emulsion breaker to the emulsified fresh oil nor emulsified residues 200 and 250°C+.

Table 5-8 *Stability of ULSFO Shell 2019 emulsions (no emulsion breaker) and efficiency of emulsion breaker at 2 and 13 °C for fresh oil, 200 °C+ and 250°C+ residue*

Temperature	**Residue**	**Emulsion breaker**	**Water-in-oil emulsion (vol. %)**		**Stability ratio****
			Reference	**24 hours ***	
2 °C	Fresh	None	35	30	0.81
	Fresh	Alc. O 60 % 500 ppm	35	30	0.81
	Fresh	Alc. O 60 % 2000 ppm	35	35	1.00
2 °C	200°C+	None	6	6	1.00
	200°C+	Alc. O 60 % 500 ppm	6	6	1.00
	200°C+	Alc. O 60 % 2000 ppm	6	6	1.00
2 °C	250°C+	None	2	2	1.00
	250°C+	Alc. O 60 % 500 ppm	-	-	-
	250°C+	Alc. O 60 % 2000 ppm	-	-	-
13 °C	Fresh	None	67	67	1.00
	Fresh	Alc. O 60 % 500 ppm	67	67	1.00
	Fresh	Alc. O 60 % 2000 ppm	67	63	0.85
13 °C	200°C+	None	38	33	0.83
	200°C+	Alc. O 60 % 500 ppm	38	38	1.00
	200°C+	Alc. O 60 % 2000 ppm	38	38	1.00
13 °C	250°C+	None	44	41	0.88
	250°C+	Alc. O 60 % 500 ppm	44	39	0.79
	250°C+	Alc. O 60 % 500 ppm	44	43	0.96

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

** *Stability ratio of 1 implies a totally stable emulsion for 24 hours settling. Stability ratio of 0 (zero) implies a totally unstable emulsion; all the water is settled out for 24 hours settling.*

-: *No data due to negligible water uptake*

5.6 Viscosity of water-free and emulsified fresh oils and residues

As non-Newtonian fluids, the viscosities of both the water-free and emulsified fuel oils tested in this project are dependent on the shear rate; i.e. the viscosities are higher at a lower share rate (10 s^{-1}) compared to 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. All the tested oils show an increasing emulsion viscosity with increasing degree of weathering (evaporating and water uptake). The results are summarized in the tables below for VLSFO Chevron 2019, VLSFO Shell 2019 and ULSFO Shell 2019.

VLSFO Chevron 2019

Table 5-9 gives the viscosities of water-free fresh oil and emulsified fresh oil of VLSFO Chevron 2019 at 2 and 13 °C. The water contents are based on max. water emulsification.

Table 5-9 Viscosity of VLSFO Chevron 2019 water-free and emulsified fresh oil

Temp.	Residue	Water content (vol. %)	Viscosity (mPa.s)	
			$10\ s^{-1}$	$100\ s^{-1}$
2 °C	Fresh	0	71 236	28 399
	Fresh	27	80 274	9563
13 °C	Fresh	0	5550	3948
	Fresh	54	35 468	1124

VLSFO Shell 2019

Table 5-10 gives the viscosities of water-free fresh oil and residue, and emulsified fresh oil and emulsified residue of VLSFO Shell 2019 at 2 and 13 °C. The water contents are based on max. water emulsification.

Table 5-10 Viscosity of VLSFO Shell 2019 water-free and emulsified fresh oil and residue

Temp.	Residue	Water content (vol. %)	Viscosity (mPa.s)	
			$10\ s^{-1}$	$100\ s^{-1}$
2°C	Fresh	0	132 460	77 638
	Fresh	13	141 820	29 982
2°C	250°C+	0	878 540	136 400
	250°C+	16	773 050*	134 280
13°C	Fresh	0	19 450	16 507
	Fresh	57	76 348	11 935*
13°C	250°C+	0	106 130	68 041
	250°C+	52	321 340	5951*

**Reduced viscosities due glance off the incorporated water*

ULSFO Shell 2019

Table 5-11 gives the viscosities of water-free fresh oil and residue, and the emulsified fresh oil and emulsified residues of ULSFO Shell 2019 at 2 and 13 °C. The water contents are based on max. water emulsification, and 50 vol % at 13 °C.

Table 5-11 Viscosity of ULSFO Shell 2019 water-free and emulsified fresh oil and residue

Temp.	Residue	Water content (vol. %)	Viscosity (mPa.s)	
			$10\ s^{-1}$	$100\ s^{-1}$
2°C	Fresh	0	111 800	21 017
	Fresh	39	64 521	2370
2°C	200°C+	0	205 220	15 567
	200°C+	21	101 610	12 362
2°C	250°C+	0	350 250	18 125
	250°C+	2	205 510	25 390
13°C	Fresh	0	33 564	5986
	Fresh	50	33 143	1734
	Fresh	67	38 194	2084
13°C	200°C+	0	53 251	9903
	200°C+	38	36 420	4627
13°C	250°C+	0	91 496	14 826
	250°C+	44	60 024	2567

6 Dispersibility study

The main purpose of using oil spill dispersants is to transfer the oil from the sea surface to the water column by breaking up the surface slick into small oil droplets. The use of dispersants enhances the rate and extent of the natural dispersion process. The dispersibility study was performed to document the relative effect of chemical dispersants on VLSFO Chevron 2019, VLSFO Shell 2019 and ULSFO Shell 2019. The testing was performed at 2 and 13 °C, as described below. Three dispersants were used for testing: Corexit 9500A, Dasic NS and OSR-52. These dispersants are commonly well-known word-wide and are relevant for use elsewhere in Europe. Dasic NS is also included in oil spill contingency in on the Norwegian shelf.

Several methods exist for effectiveness testing of chemical dispersants on oils. The results from different test methodologies may vary in the terms of applied energy, testing on weathered oils /emulsions vs. fresh oils etc. SINTEF uses the low-energy test (IFP) reflecting non-breaking waves conditions (< 5 m/s wind speeds), and the high-energy test (MNS) reflecting breaking waves conditions (> 5 m/s wind speeds). These methods are also in accordance with the currently Norwegian regulations for dispersant testing. The IFP (Bocard et al. 1984) and MNS (Mackay and Szeto, 1980) methods are also further describes in Appendix A. For MNS test, the standard dynamic sampling was conducted when there was still applied energy to the system (waves). However, for some of the tests static samplings after 5 minutes settling time without energy (the wave was stopped) were taken to demonstrate whether the dispersion effectiveness was obtained not necessarily caused by the formation of small oil droplets (< 70-100 µm) but rather due to formation of larger lumps / threads of oil that rise quickly to the surface after settling.

6.1 VLSFO Chevron 2019

Screening and dosage testing of dispersants Corexit 9500A, Dasic NS and OSR-52 were conducted on emulsified fresh oil of VLSFO Chevron 2019 at 13 °C. The testing was conducted by use of IFP and MNS with dispersant-to oil (DOR) ratios 1:10 and 1:25. The results is given in Table 6-1 and Figure 6-1. The emulsions were not dispersible by use of the low-energy test (IFP). For MNS (high-energy test), Corexit 9500A and OSR-52 expressed slightly higher dispersibility effectiveness than Dasic NS, and the effectiveness slightly increased with DOR 1:10 compared with DOR 1:25, but still low effectiveness.

Both dynamic sampling and static sampling of the waterfree fresh oil was conducted (MNS test), and the results are given Table 6-2 and Figure 6-2. Corexit 9500A showed higher effectiveness on the fresh oil (dynamic and static sampling) than OSR-52 and Dasic NS. The lower efficiency from static sampling vs. dynamic sampling also emphasised reduced dispersibility effectiveness after treatment of dispersants. The higher effectiveness from dynamic sampling is due to generation of lager droplets / small lumps, whilst the static sampling is more reflecting the fraction of dispersed small oil droplets.

The fresh VLSFO Chevron 2019 was not found dispersible for any of the dispersants tested at 2 °C (Figure 6-3) due to high viscosity at low temperature (71 236 mPa.s at 10 s^{-1}), and emulsions were therefore not tested.

All over, VLSFO Chevron 2019 was shown to be reduced dispersible at 13 °C and not dispersible at 2 °C. Based on an overall evaluation, the oil is estimated to be reduced dispersible with viscosities > 4000 mPa.s, whilst the oil is considered not dispersible with viscosities > 25 000 mPa.s.

Table 6-1 Screening and dosage testing VLSFO Chevron 2019 emulsion (34-42 vol. %). Viscosities: 21 698 - 21 792 mPa.s ($10s^{-1}$, 13 °C)

Dispersants	IFP (wt.%) DOR 1:25	MNS (wt.%) DOR 1:25	MNS (wt. %) DOR 1:10
Corexit 9500A	3	15	24
OSR-52	2	13	23
Dasic NS	3	4	5

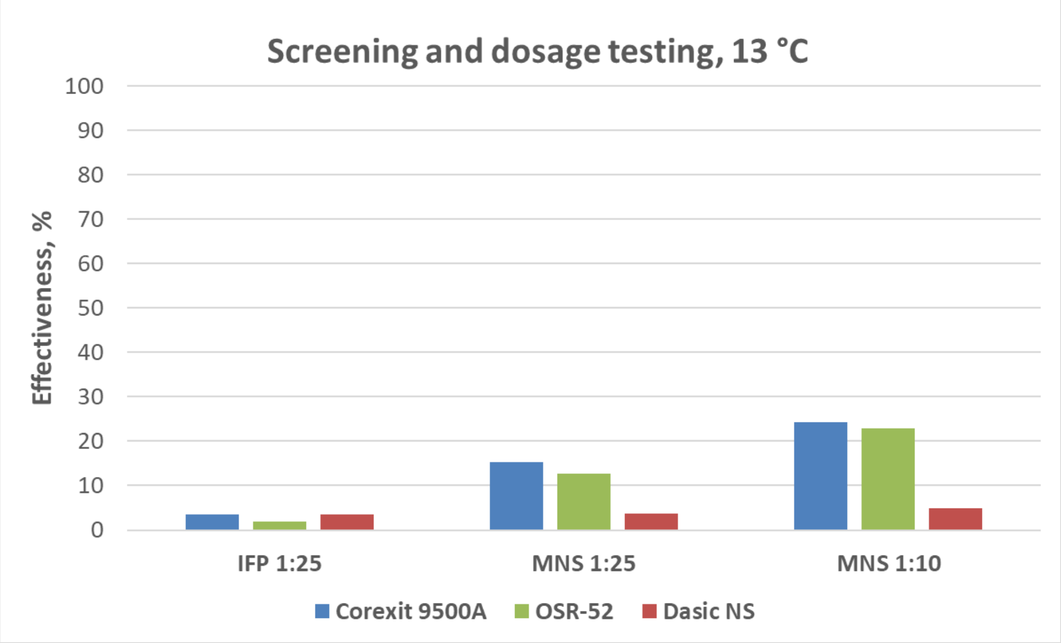


Figure 6-1 Screening and dosage testing on emulsified fresh oil (34-42 vol.%) of VLSFO Chevron 2019 at 13 °C. Viscosities: 21 698-21 792 mPa.s ($10s^{-1}$)

Table 6-2 Dynamic vs. static sampling (MNS) of fresh water-free VLSFO Chevron 2019 at 13 °C Viscosity: 5550 mPa.s ($10s^{-1}$)

Dispersants	MNS, Effectiveness (weight %)	
	Dynamic sampling (DOR 1:25)	Static sampling (DOR 1:25)
Corexit 9500A	83	21
OSR-52	74	11
Dasic NS	58	7

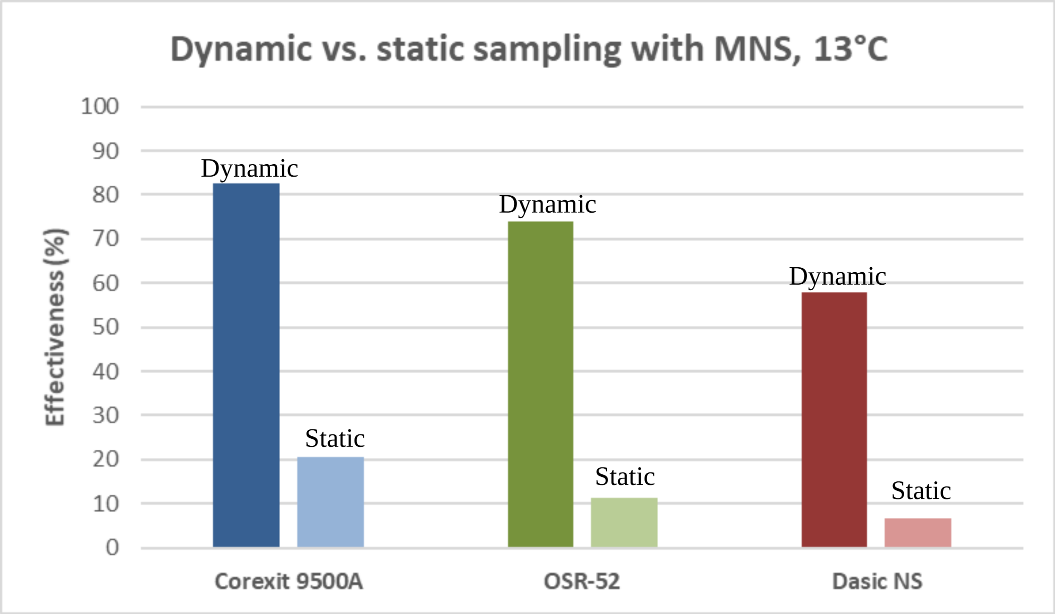


Figure 6-2 *Dynamic vs. static sampling (MNS test) of waterfree (non-emulsified) fresh oil of VLSFO Chevron 2019 at 13 °C (DOR 1:25). Viscosity:5550 mPa.s (10s^{-1})*

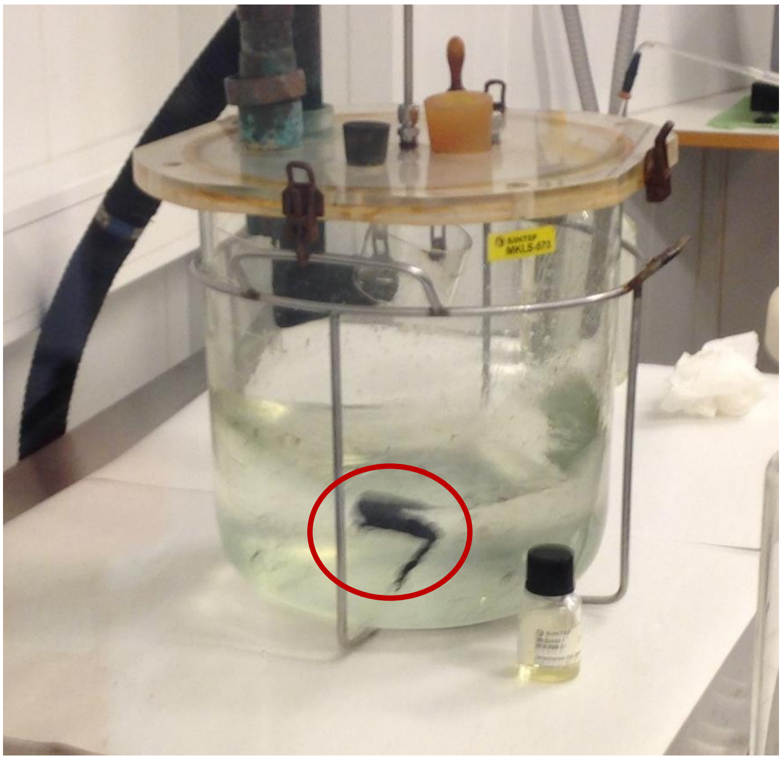


Figure 6-3 *Fresh water-free VLSFO Chevron 2019 (MNS test) after treatment of Corexit 9500A (no efficiency) at 2°C (viscosity: 71 236 mPa.s at 10 s^{-1})*

6.2 VLSFO Shell 2019

Screening and dosage testing of dispersants Corexit 9500A, Dasic NS and OSR-52 were conducted on emulsified fresh oil and emulsified residue (250°C+) oil of VLSFO Shell 2019 at 13 °C. For emulsified fresh oil (27 vol.% water, viscosity 34 537 mPa.s), the screening and dosage testing were conducted by use of IFP and MNS with DOR 1:25 and 1:10 (MNS-test). The high-energy MNS test also indicate that the efficiency of dispersants is dependent on the DOR, as shown in Table 6-3 and Figure 6-4. This phenomenon was particularly pronounced for Dasic NS where the efficiency increased from 10 % (DOR 1:25) to 85 % (DOR 1:10). Moreover, Corexit 9000A showed somewhat better efficiency compared to OSR-52 and Dasic NS on the emulsified fresh oil. However, the low efficiencies obtained by use of the IFP (low-energy test) clearly demonstrated the need for presence of energy in terms of breaking waves and/or artificial energy to enhance the dispersibility effectiveness by dispersant application.

Results from dynamic and static sampling at 13 °C (MNS test, DOR 1:25) of both the water-free fresh oil and 250°C+ residue are shown in Table 6-4 and Figure 6-5, and illustrated (images) in Figure 6-6 and Figure 6-7. For the fresh oil (19 450 mPa.s at $10s^{-1}$), the dispersants could easily break up the slick, and Corexit 9500A and OSR-52 showed a relatively good effectiveness (50 %, static sampling). Figure 6-6 also shows that no dispersant added (only wave energy) had no effect on the water-free fresh oil. For the 250°C+ residue, no efficient dispersion due to the high viscosity (106 130 mPa.s at $10s^{-1}$), and the artificial high efficiency from dynamic sampling is caused by formation of large lumps /threads.

At 2 °C, the fresh oil of VLSFO Shell 2019 was shown not dispersible as the dispersion effectiveness on MNS was lower than 5 % due to high viscosity (132 469 mPa.s at $10s^{-1}$). Dispersibility testing on emulsion were therefore not performed.

The fresh oil VLSFO Shell 2019 showed to have a potential for dispersant use at 13 °C, however the dispersion efficiency requires breaking waves conditions (> 5 m/s wind speed) and /or supplement from artificial energy. Increasing DOR and/or successively application of dispersants may be beneficial to enhance the dispersion efficiency.

The dispersibility limits based on viscosities when the oil is considered as dispersible is estimated up to 20 000 mPa.s. The dispersible limit when the oil is considered not dispersible is estimated to 40 000 mPa.s due to limited data points and similarities with IFO 180-380 grades.

Table 6-3 Screening and dosage testing VLSFO Shell 2019 emulsion of fresh oil (27 vol. %). Viscosity: 34 357 mPa.s ($10s^{-1}$, 13 °C)

Dispersants	IFP (wt.%) DOR 1:25	MNS (wt.%) DOR 1:25	MNS (wt. %) DOR 1:10
Corexit 9500A	7	55	88
OSR-52	13	35	82
Dasic NS	7	10	85

Table 6-4 Dynamic and static sampling of water-free fresh oil and 250°C+ residue at 13 °C. Viscosity fresh oil: 19 450 mPa.s ($10s^{-1}$), viscosity 250°C+: 106 130 mPa.s ($10s^{-1}$)

Dispersants	Fresh Water-free (DOR 1:25)		250°C+ waterfree (DOR 1:25)	
	Dynamic (%)	Static (%)	Dynamic (%)	Static (%)
Corexit 9500A	>100*	52	>100*	2
Dasic NS	86	18	>100*	6
OSR-52	74	52	3	0

**Dispersant effectiveness > 100 % due to entrainment of lumps/threads of the treated oil*

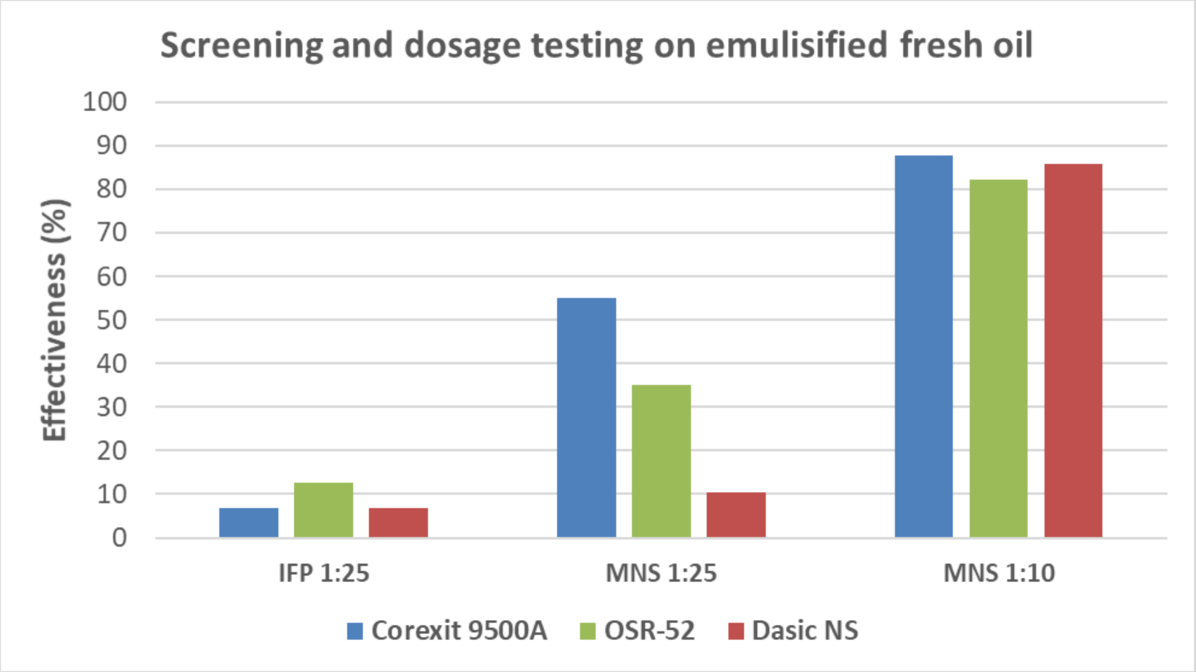


Figure 6-4 *Screening and dosage testing (MNS) on emulsified fresh oil of VLSFO Shell 2019 on emulsified fresh oil (27 vol.% water and viscosity: 34 357 mPa.s (10s^{-1}) at 13 °C*

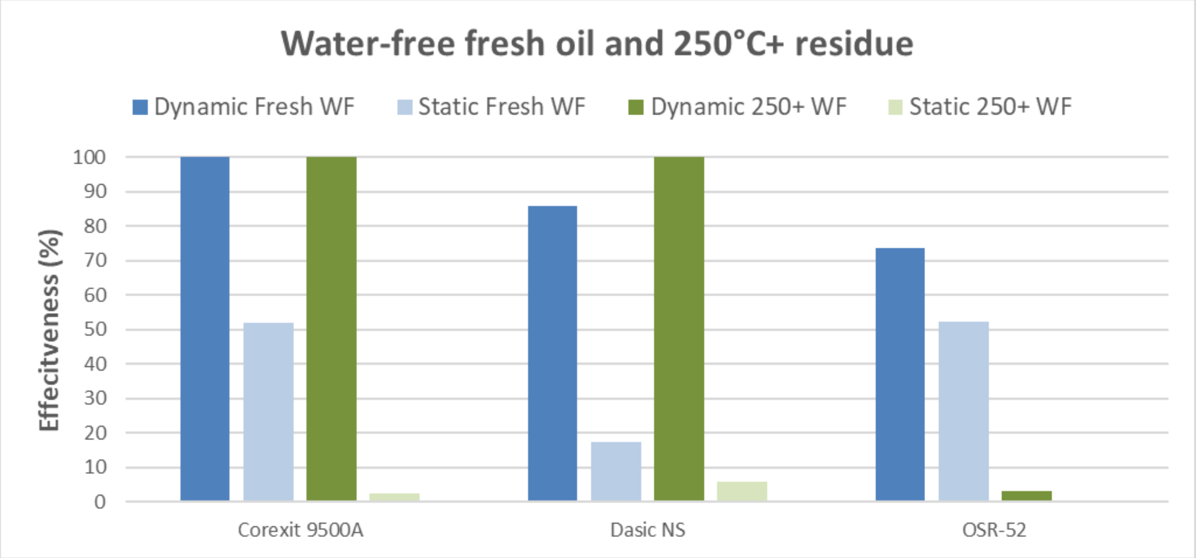


Figure 6-5 *Dynamic (dark blue) and static (light blue) of fresh oil (viscosity: 19 450 mPa.s at 10s^{-1}) . Dynamic (dark green) and static (light green) sampling of 250°C+ residue (viscosity: 106 130 mPa.s at 10s^{-1}). MNS testing at 13 °C (DOR: 1:25)*

Figure 6-6 VLSFO Shell 2019 (MNS test). Fresh oil (water-free, viscosity 19 450 mPa.s at 10s^{-1}, 13 °C) after application of Corexit 9500A (DOR 1:25). Left: Dynamic sampling. Middle: Static sampling, larger droplets/lumps on the surface after 5 min. settling. Right: Fresh oil without dispersant (no-disp.)

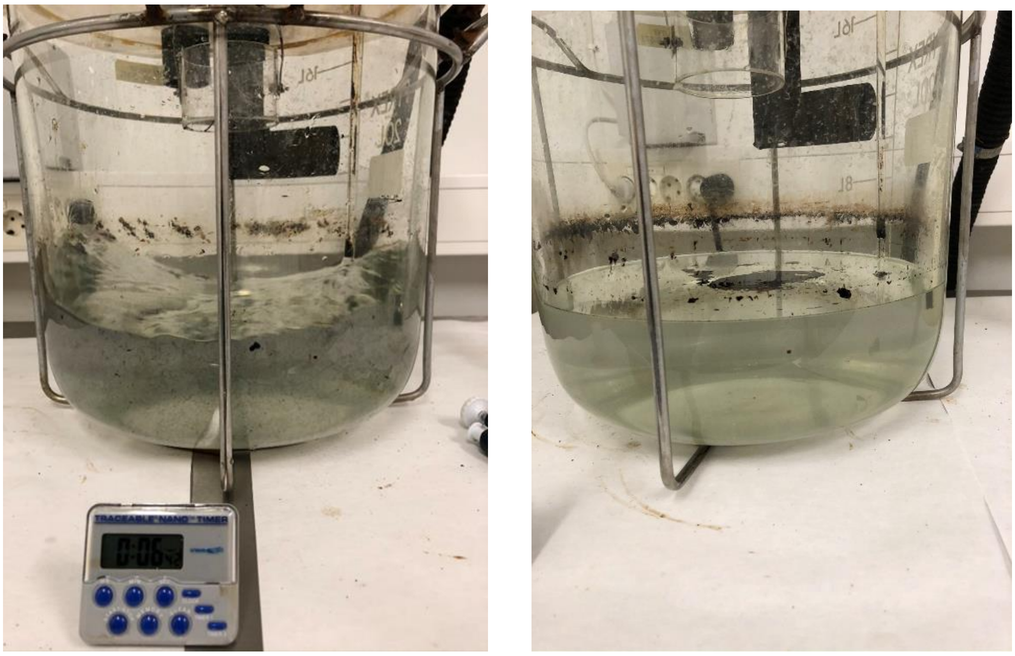


Figure 6-7 Water-free residue 250°C+ of VLSFO Shell 2019 (MNS test) at 13 °C, DOR 1:25. Viscosity: 106 130 mPa.s at 10s^{-1}). Left: Dynamic sampling. Right: Static sampling

6.3 ULSFO Shell 2019

Dispersibility testing was attempted on ULSFO Shell 2019. Testing was conducted both on the emulsified fresh oil (50 vol.%) and the water-free fresh oil at 13 °C (high-energy MNS test), DOR 1:25 by use of the three dispersants Corexit 9500A, Dasic NS and OSR-52. The low-energy test (IFP) had no effect on this oil. For the MNS test, the dispersibility effectiveness were minor (< 5%) on the 50 % emulsion (viscosity 33 143 mPa.s at 10s^{-1}). This is illustrated in Figure 6-8 for Corexit 9500A and OSR-52 (similar observed for Dasic NS). For the non-emulsified fresh oil at 13 °C, the dispersants showed to have some effect (MNS-test), as the slick was broken up into smaller patches, see Table 6-5, Figure 6-9 (Corexit 9500A) and Figure 6-10 (OSR-52). No effect was however observed when no dispersant was added to the fresh oil (Figure 6-11). The very low dispersant efficiency based on static sampling vs. dynamic sampling also emphasized that the dispersants did not enhance dispersion with formation of smaller droplets but formed lager lumps/threads that easily rise to the surface after stand still.

At 2 °C, no observed effect of adding dispersants on the fresh oil due to solidification by high pour point (+24 °C) and high viscosity (111 800 mPa.s at $10s^{-1}$). Example with Corexit 9500A is shown in Figure 6-12. Testing on weathered residues and emulsions were therefore not performed.

Overall, adding dispersants to emulsified fresh oil of ULSFO Shell 2019 has very limited effect, and show low/reduced efficiency on the water-free fresh oil at 13 °C. However, the fresh oil was found not dispersible at 2 °C and expects similar results for emulsions. Moreover, ULSFO Shell 2019 exhibits very high pour point that prevents the dispersant to diffuse into the surface slick and excess dispersant was washed off with the wave activity during the MNS-test. Based on the results, no dispersibility (viscosity) limits where estimated ULSFO Shell 2019, as the high pour point is the main limited factor for dispersant use.

Table 6-5 *Efficiency of dispersant of water-free fresh oil of ULSFO Shell 2019 at 13 °C. Dynamic and static sampling, viscosity fresh oil: 33 564 mPa.s ($10s^{-1}$)*

Dispersants	**Fresh Water-free (13°C), DOR 1:25**	
	Dynamic (%)	**Static (%)**
Corexit	75	4
OSR52	51	2
Dasic NS	9	2

Figure 6-8 *MNS test of ULSFO Shell 2019 emulsified fresh oil (50 vol.%) at 13 °C (viscosity: 33 143 mPa.s at $10s^{-1}$). DOR 1:25. Left: Corexit 9500A. Right: OSR-52*

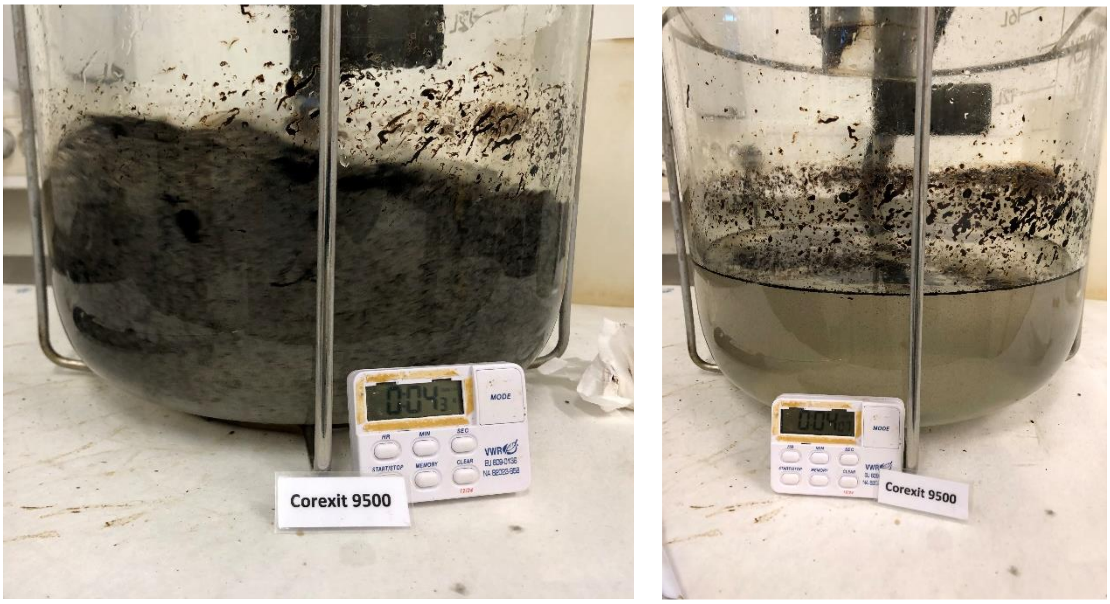


Figure 6-9 *MNS test of water-free fresh ULSFO Shell 2019 at 13 °C (Corexit 9500A). Viscosity: 33 564 mPa.s ($10s^{-1}$). DOR 1:25. Left: Dynamic sampling. Right: Static sampling*

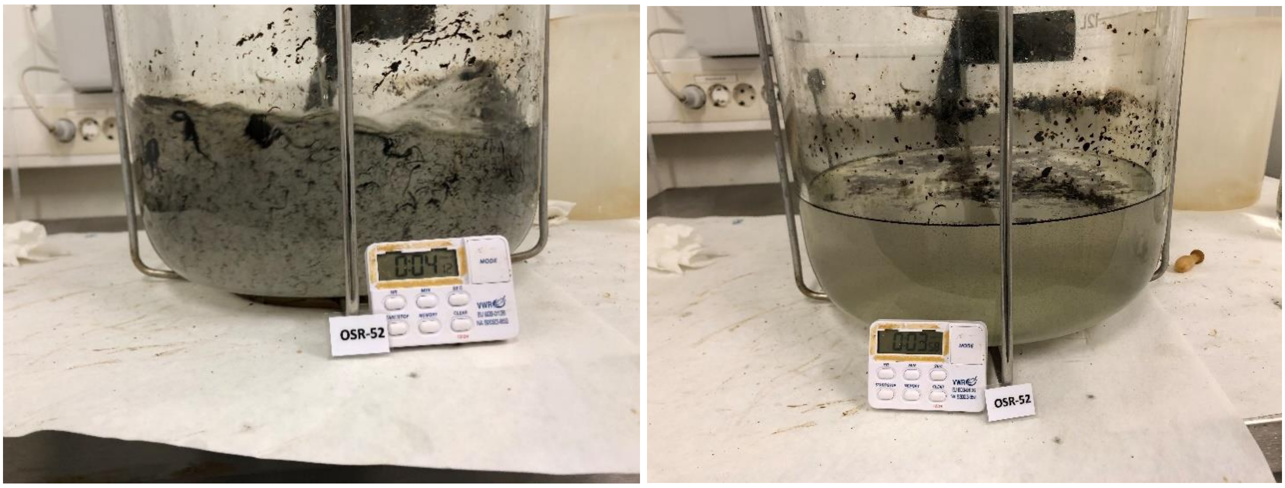


Figure 6-10 *MNS test of water-free fresh ULSFO Shell 2019 at 13 °C (OSR-52). Viscosity: 33 564 mPa.s ($10s^{-1}$). DOR 1:25. Left: Dynamic sampling. Right: Static sampling*

Figure 6-11 No dispersant added to fresh ULSFO Shell 2019, 13 °C. (No effect observed)

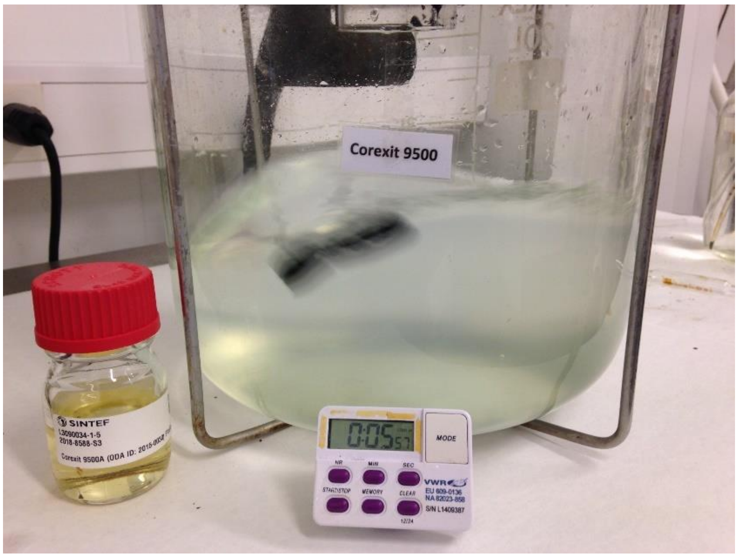


Figure 6-12 Corexit 9500A added to the fresh ULSFO Shell 2019 at 2 °C. (No effect observed)

6.4 Summary dispersibility

Results from the dispersibility study on the VLSFO Chevron 2019, VLSFO Shell 2019 and ULSFO Shell 2019 are summarized in Table 6-6. The testing was conducted at 2 and 13 °C. The dispersibility testing were conducted by use of IFP (low-energy test, reflecting non-breaking waves < 5 m/s wind speeds) and MNS (high-energy test, reflecting breaking waves > 5 m/s wind speeds). The dispersibility was performed on the water-free fresh oils / water-free residues and emulsified fresh oils /emulsified residues. The dispersants tested on the oils/emulsions were Corexit 9500A, OSR-52 and Dasic NS. Overall, Corexit 9500A was found slightly more efficient than OSR-52 and Dasic NS.

At 2 °C (Cold climate /Arctic conditions):

- No effects after treatment of dispersants were observed for any of the oils.
- Similarly, no addition of dispersants also showed no effects on the surface slick

At 13 °C (North Sea summer temperature):

- Dispersants could break up the slicks into larger droplets/lumps (mm)
- Low formation of small oil droplets (< 100 µm)
- Requires breaking wave conditions (> 5 m/s) or artificial energy to break up the slick
- No addition of dispersants also showed no effects on the surface slick

Table 6-6 Summary dispersibility study of VLSFO Chevron 2019, VLSFO Shell 2019 and ULSFO Shell 2019

Oil Type	Dispersibility at 2 °C	Dispersibility at 13 °C	Comments
VLSFO Chevron 2019 Fresh	Non-dispersible	Reduced dispersibility	2 °C: High viscosity 13 °C: Requires breaking waves/artificial energy. DOR 1:25 or higher. Consider successive application to enhance dispersion.
VLSFO Chevron 2019 Emulsion of fresh oil	*Non-dispersible**	Reduced dispersibility	2 °C: *Not tested. Expecting no effect* 13 °C: Requires breaking waves /artificial energy. High dosage, breaking waves/artificial energy.
VLSFO Shell 2019 Fresh	Non-dispersible	Reduced dispersibility	2 °C: High viscosity 13 °C: Requires breaking waves /artificial energy. Consider successive application and/ or higher dosage to enhance dispersion
VLSFO Shell 2019 250°C+ residue	*Non-dispersible **	Non-dispersible	*2 °C: Not tested. Expecting no effect* 13 °C: High viscosity
VLSFO Shell 2019 Emulsion of fresh oil	*Non-dispersible**	Reduced dispersibility	*2 °C: Not tested. Expecting no effect* 13 °C: Requires breaking waves /artificial energy. High dosage (DOR 1:10). Consider successive application
ULSFO Shell 2019 Fresh	Non-dispersible	Limited / non-dispersible	2 °C: Solidifying properties – high pour points 13 °C; Break up oil slick into patches. Requires breaking waves but very limited dispersion
ULSFO Shell 2019 Residue 200°C+/250°C+	*Non-dispersible**	*Non-dispersible**	*2 and 13 °C: *Not tested. Expecting no effect*
ULSFO Shell 2019 Emulsion of fresh oil	*Non-dispersible**	Limited / non-dispersible	2 °C: *Not tested. Expecting no effect* *13 °C.* Broke up oil slick into large patches (very limited dispersion)

**: Not tested, expecting no effects*

7 SINTEF Oil Weathering Model (OWM)

The SINTEF Oil Weathering Model (OWM) relates oil properties to a chosen set of conditions (oil/emulsion film thickness, wind speeds and sea temperature) and predicts the change rate of the oil's properties on the sea surface with time. The SINTEF OWM is schematically shown in Figure 7-1. 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. The SINTEF OWM is described in more details in e.g. Johansen (1991), and in the user's guide for the model.

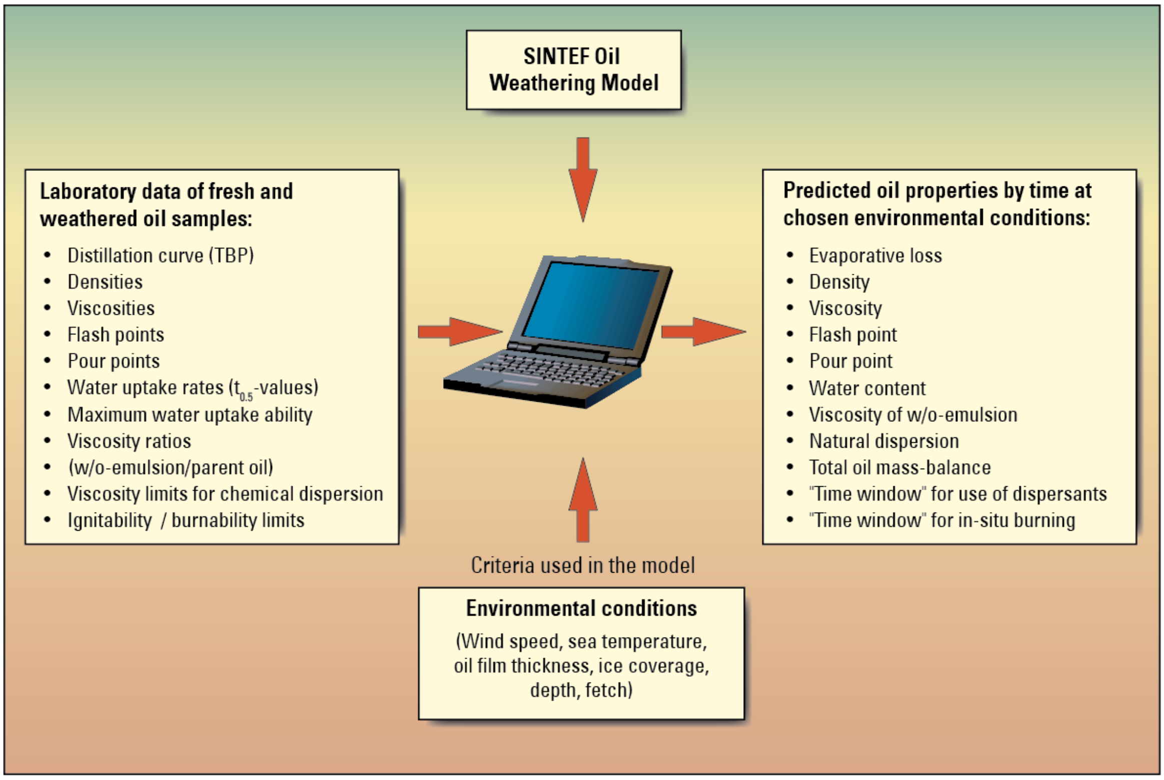


Figure 7-1 Schematic input data to the SINTEF OWM and the predicted output oil weathering properties

Oil weathering predictions

In this report, the presented OWM predictions span a period from 15 minutes to 5 days after an oil spill has occurred. The input laboratory data of the oils tested in this project are summarized in Appendix B, and the OWM predictions of each of the oils are summarized in Appendix C. A comparison of OWM predictions are given in section 8.

Spill scenario

A standard surface release was chosen to give OWM predictions of the weathering properties of the tested oils. The residual marine fuel oils are expected to reach a terminal oil film thickness of 2 mm from a surface (batch) release. The seawater temperatures chosen for the OWM predictions were 2 and 15 °C reflecting relevant sea temperatures from the laboratory testing. The relationship between the wind speeds and significant wave heights used in the oil weathering predictions are given in Table 7-1. An overview of the input OWM parameters is given in Table 7-2.

Table 7-1 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

Table 7-2 Scenario input parameters to SINTEF OWM

Parameters	Value
Release scenario	Surface release
Release rate (m^3/h)	80
Duration of spill (minutes)	15
Volume spilled (metric tons)	20
Terminal oil film thickness (mm)	2
Wind speed (m/s)	2, 5, 10 and 15
Seawater temperature (°C)	2 and 15°
Prediction period	15 min. to 5 days

8 Comparison of OWM predictions

In this section, the predicted weathering properties of the three tested fuel oils; VLSFO Chevron 2019, VLSFO Shell 2019 and ULSFO Shell 2019 were compared, in addition to the previously study on ULSFO Shell 2016 (denoted as ULSFO 13C 2017 in the prediction figures) and two IFOs (IFO 180 and 380). The presented comparisons are based on predictions limited to a standard temperature of 15 °C and wind speed of 10 m/s, reflecting breaking waves conditions.

8.1 Evaporative loss

The predicted evaporative loss is shown in Figure 8-1. Evaporation is one of the natural process that promotes removing spilled oil from the sea surface. The low sulfur marine fuel oils tested in this project have low evaporative loss (< 10 wt. %) after 5 days of weathering, reflecting low content of light components in the oils similar as for the other oils in comparison. However, the behaviour of ULSFO Shell 2016 exhibits slightly higher evaporative loss of 20 % after 5 days compared to the recent study of ULSFO Shell 2019.

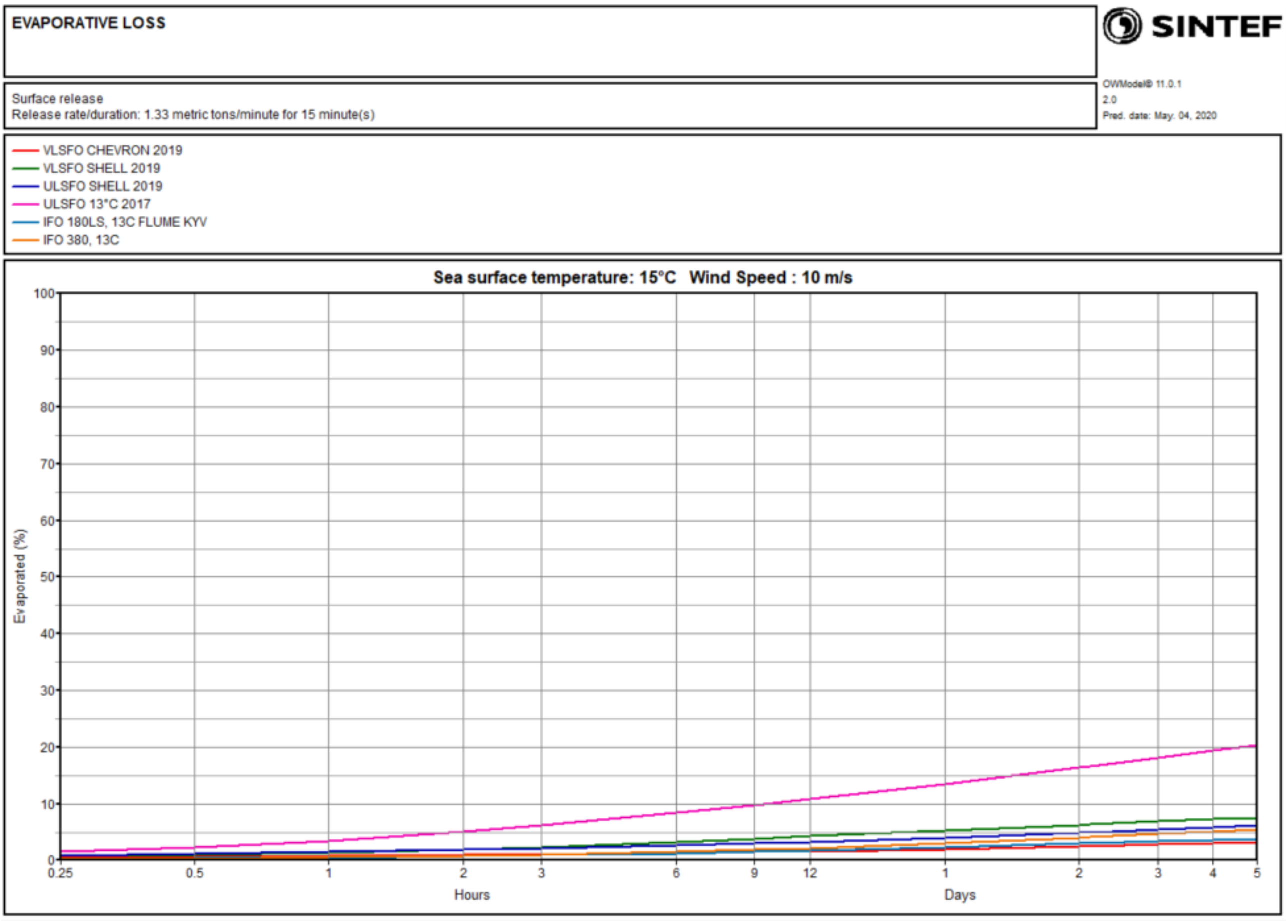


Figure 8-1 *Comparison of predicted evaporative loss at 15 °C and 10 m/s VLSFO Chevron 2019, VLSFO Shell 2019, ULSFO Shell 2019, ULSFO Shell 2016, IFO 180, and IFO 380*

8.2 Water uptake

The predicted water uptake of VLSFO Chevron 2019, VLSFO Shell 2019 and ULSFO Shell 2019 in comparison with ULSFO Shell 2016, IFO 180 and IFO 380 is shown in Figure 8-2. The previously batch of ULSFO 2016 has the highest water uptake reaching as much as 80 vol.% after 1 day of weathering. IFO180 also reach a relatively high-water uptake of 65 vol. %. VLSFO Chevron 2019 and VLSFO Shell 2019 exhibit very similar water uptake reaching up to 55 vol. % after 5 days, whilst ULSFO Shell 2019 and IFIO 380 have the lowest water uptake (20-35 vol.%). The predicted emulsification rate (kinetics) is however slow for all the oil tested in this project, as shown in Figure 8-2.

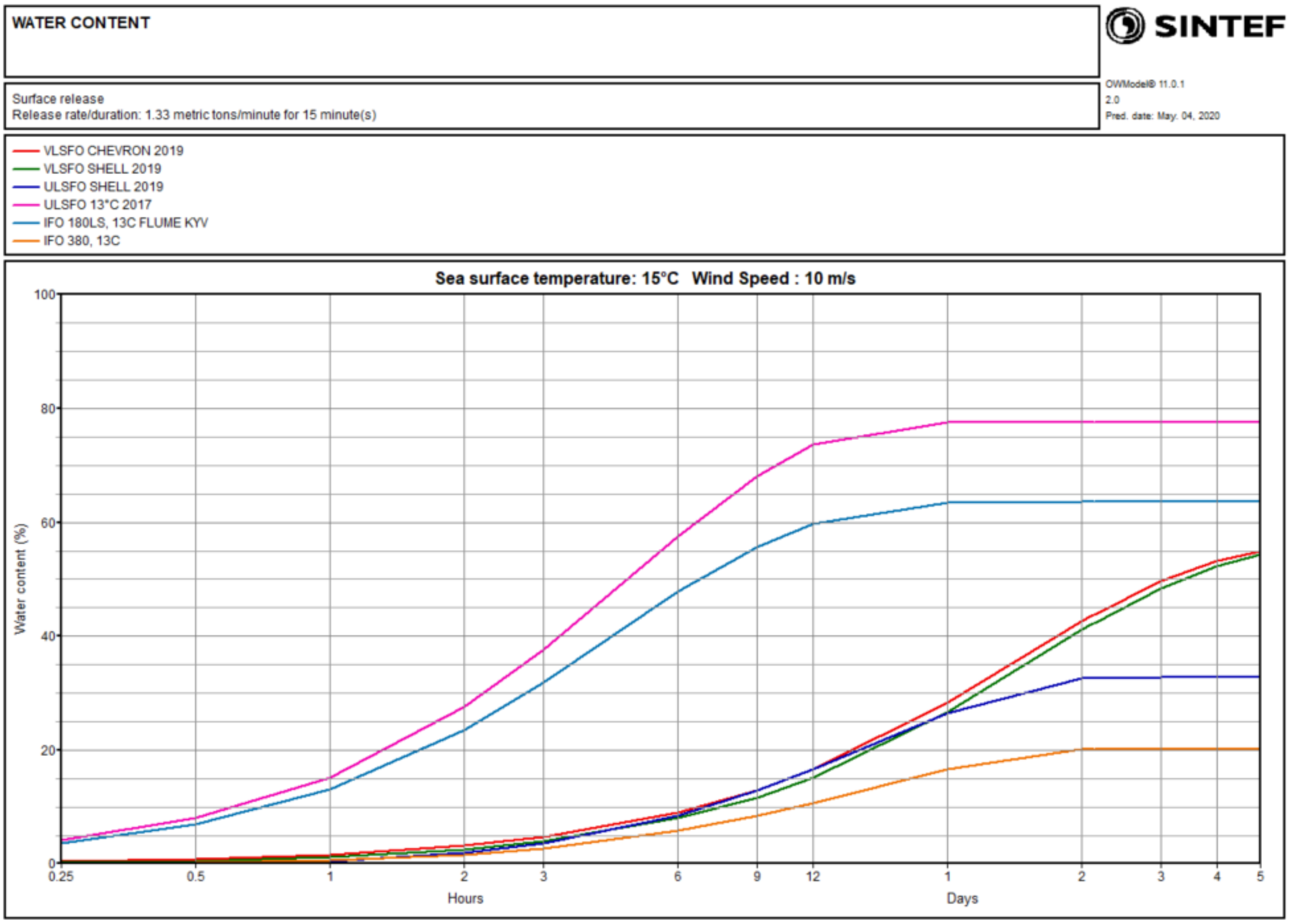


Figure 8-2 *Comparison of predicted water uptake at 15 °C and 10 m/s VLSFO Chevron 2019, VLSFO Shell 2019, ULSFO Shell 2019, ULSFO Shell 2016, IFO 180, and IFO 380*

8.3 Emulsion viscosity

The predicted emulsion viscosities of the rested fuel oils are shown in Figure 8-3, at 15 °C. VLSFO Shell 2019 has high emulsion viscosities and can reach >200 000 mPa.s after 5 days of weathering. The viscosities of VLSFO Shell 2019 is comparable with viscosities of the IFO 380. The other oils have significantly lower viscosities. VLSFO Chevron 2019 and ULSFO Shell 2016 follow quite similar predictions and reach viscosities up to 40 000 mPa.s (5 days), whilst ULSFO Shell 2019 from this project has higher viscosities and reach about 60 000 mPa.s It should be emphasized that the oils will reach higher viscosities at lower sea water temperatures (2 °C, see induvial predictions in Appendix C). High viscosities will influence of strategy for oil spill response.

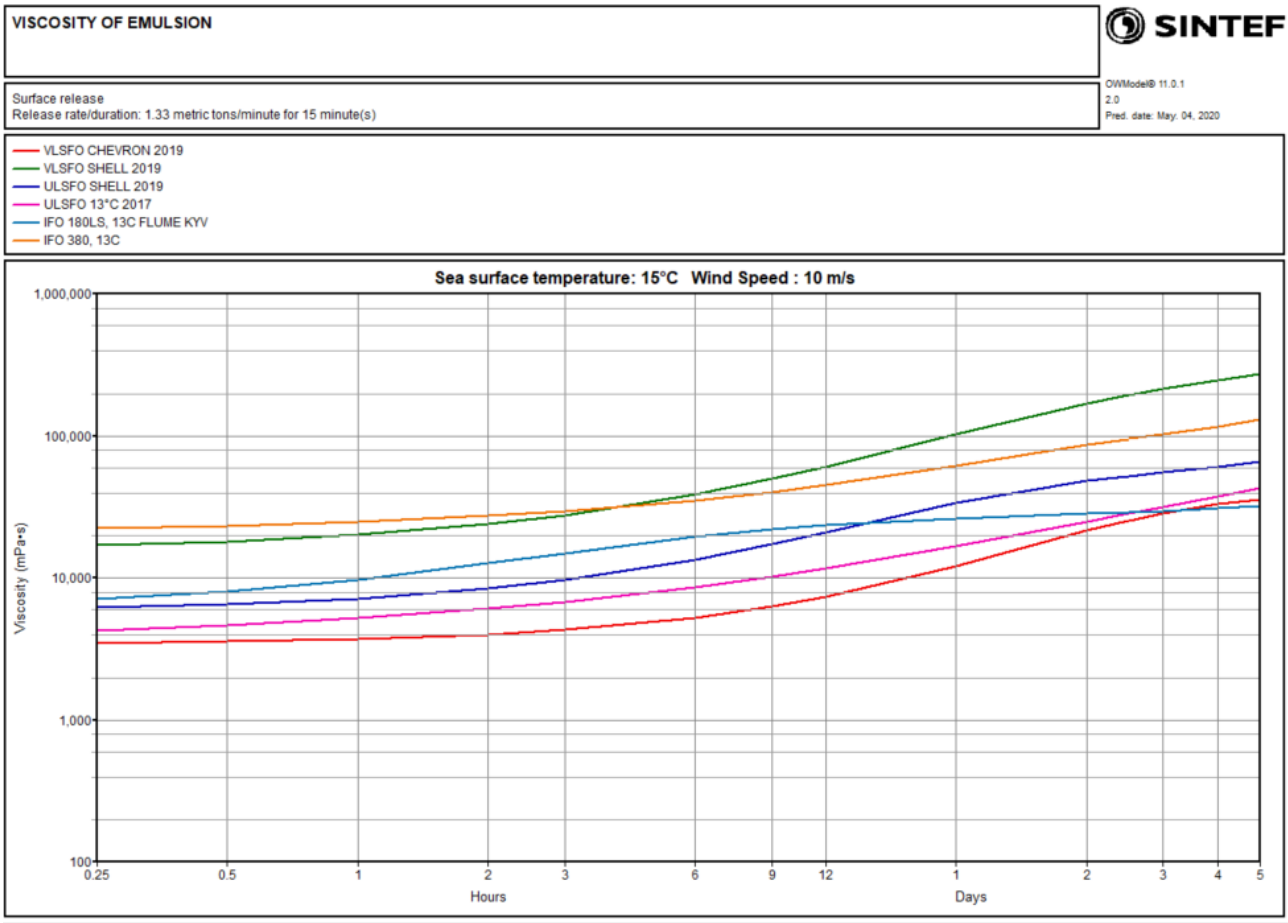


Figure 8-3 ***Comparison of predicted emulsion viscosity at 15 °C and 10 m/s VLSFO Chevron 2019, VLSFO Shell 2019, ULSFO Shell 2019, ULSFO Shell 2016, IFO 180, and IFO 380***

8.4 Flash point

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

The flash points of VLSFO Chevron 2019, VLSFO Shell 2019, ULSFO Shell 2019 and ULSFO Shell 2016 are shown in Figure 8-4. The fuel oils have initially high flash points and no fire or exploration hazard occurs after a release, as the flash points are well above sea temperature, and above 60 °C as limit for vessels not permitted as cargo for flashpoint < 60 °C. The slow increase of flash points reflects the low evaporative loss.

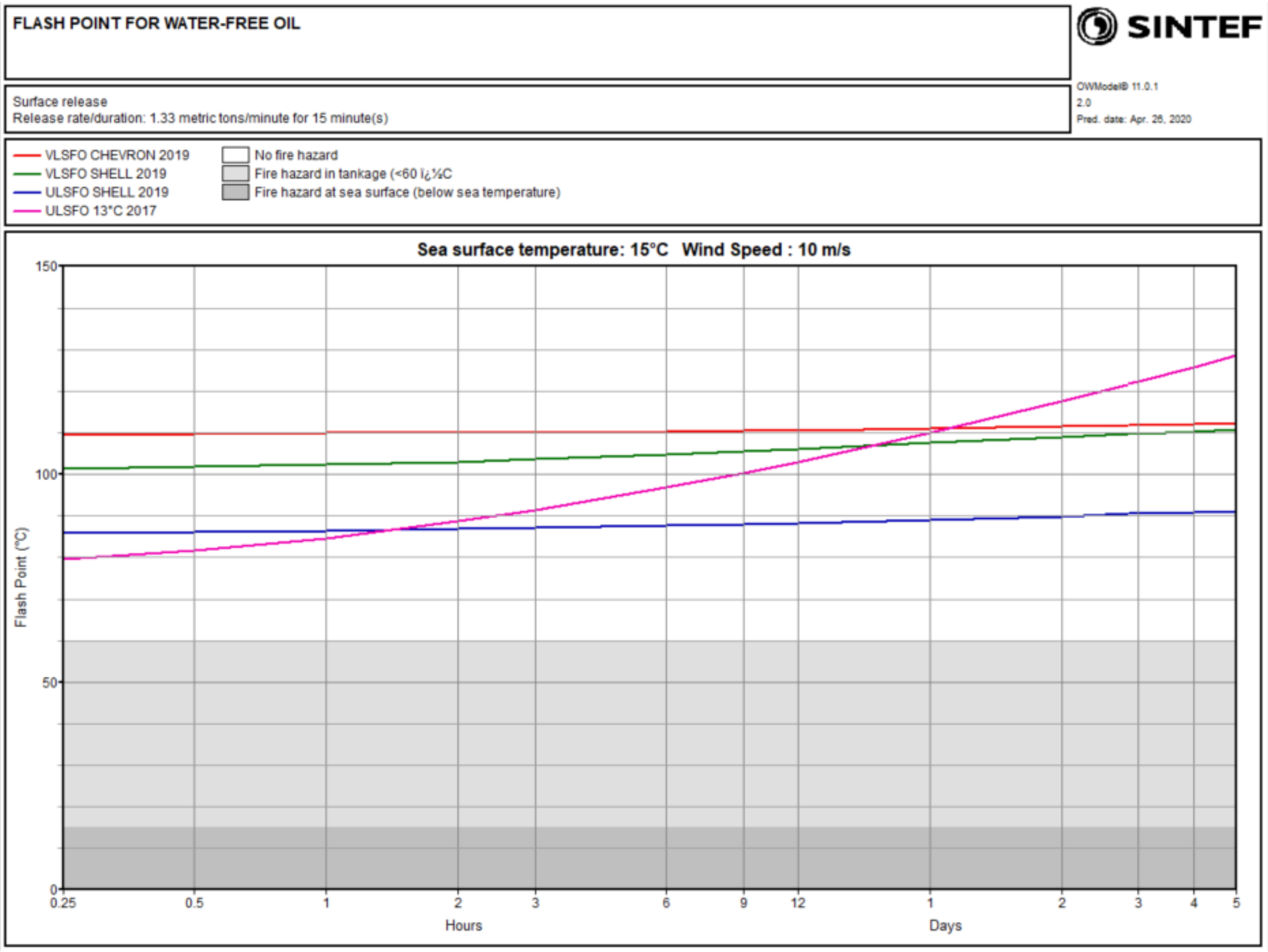


Figure 8-4 Comparison of predicted flash point at 15 °C and 10 m/s VLSFO Chevron 2019, VLSFO Shell 2019, ULSFO Shell 2019 and ULSFO Shell 2016

8.5 Pour point

Pour point depends on the oil's wax content and the amounts of light components that can keep the wax components dissolved in the oil phase. In addition, contents of asphaltenes prevent or reduce precipitation and lattice formation and hence lowers the pour point. High pour points may prevent the dispersant to soak into the oil slick and influence the dispersant effectiveness and may also reduce the potential for flowability towards weir skimmers. High pour points may cause solidification (elastic properties) when oil is spilled on the sea surface. High pour point may therefore imply solidification on the sea surface immediately after the release, and this is pronounced when the pour point is typically 5-15 °C above sea temperature and in cold temperatures (Daling et al. 1990). High pour point may reduce the dispersant effectiveness.

The predicted pour points of the tested oils are given in Figure 8-5. The two ULSFOs show a very similar and high pour points, reflecting the reduced to low dispersibility (i.e. dispersant effectiveness). The VLSFO Chevron 2019 and VLSFO Shell 2019 have lower pour points, similar as the IFO 180, and dispersant effectiveness are dependent on their viscosities. This batch of IFO 380 exhibits the lowest predicted pour points.

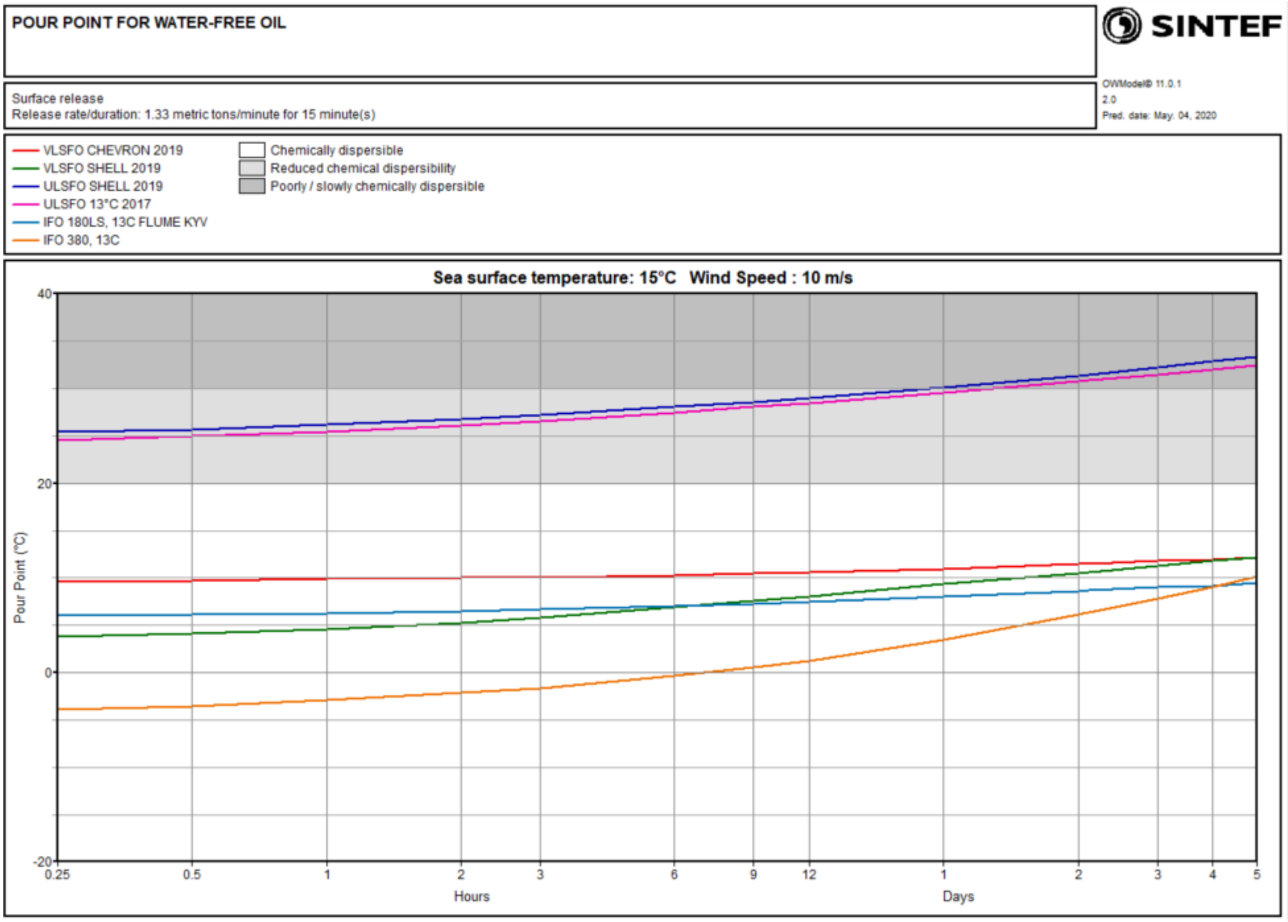


Figure 8-5 *Comparison of predicted pour point at 15 °C and 10 m/s VLSFO Chevron 2019, VLSFO Shell 2019, ULSFO Shell 2019, ULSFO Shell 2016, IFO 180, and IFO 380*

8.6 Volume of surface emulsion

In general, the total volume of surface oil will for most oil types (e.g. crude oils) be reduced with time due to evaporation and natural dispersion in the initial stages of weathering. However, the volume of water mixed into the oil may increase the total volume of the surface emulsion considerably. Increasing surface emulsions should be considered in a spill operation, for example, when evaluating skimmer capacity based on the total volume of emulsified oil. For the residual marine fuel oils studied in this project, the evaporation is very low.

The predicted volumes of oil emulsion on the sea surface (relative to the amount of oil released) are shown in Figure 8-6 for VLSFO Chevron 2019, VLSFO Shell 2019 and ULSFO Shell 2019 in addition to a previously batch of ULSFO Shell 2016, and two IFOs (IFO 180 and 380). The oils tested in this project exhibit all low and slow emulsification rate (water uptake) that reflect the low increase of the total volume after 5 days of weathering. Among the oils tested, VLSFO Shell 2019 has slightly higher increase in surface volume compare to VLSFO Chevron 2019 and ULSFO Shell 2019. In comparison, the ULSFO Shell 2016 and IFO 180 have both a much higher water uptake and the oil volume is predicted to increase about 2.5-3.5 times. as shown in the figure, below.

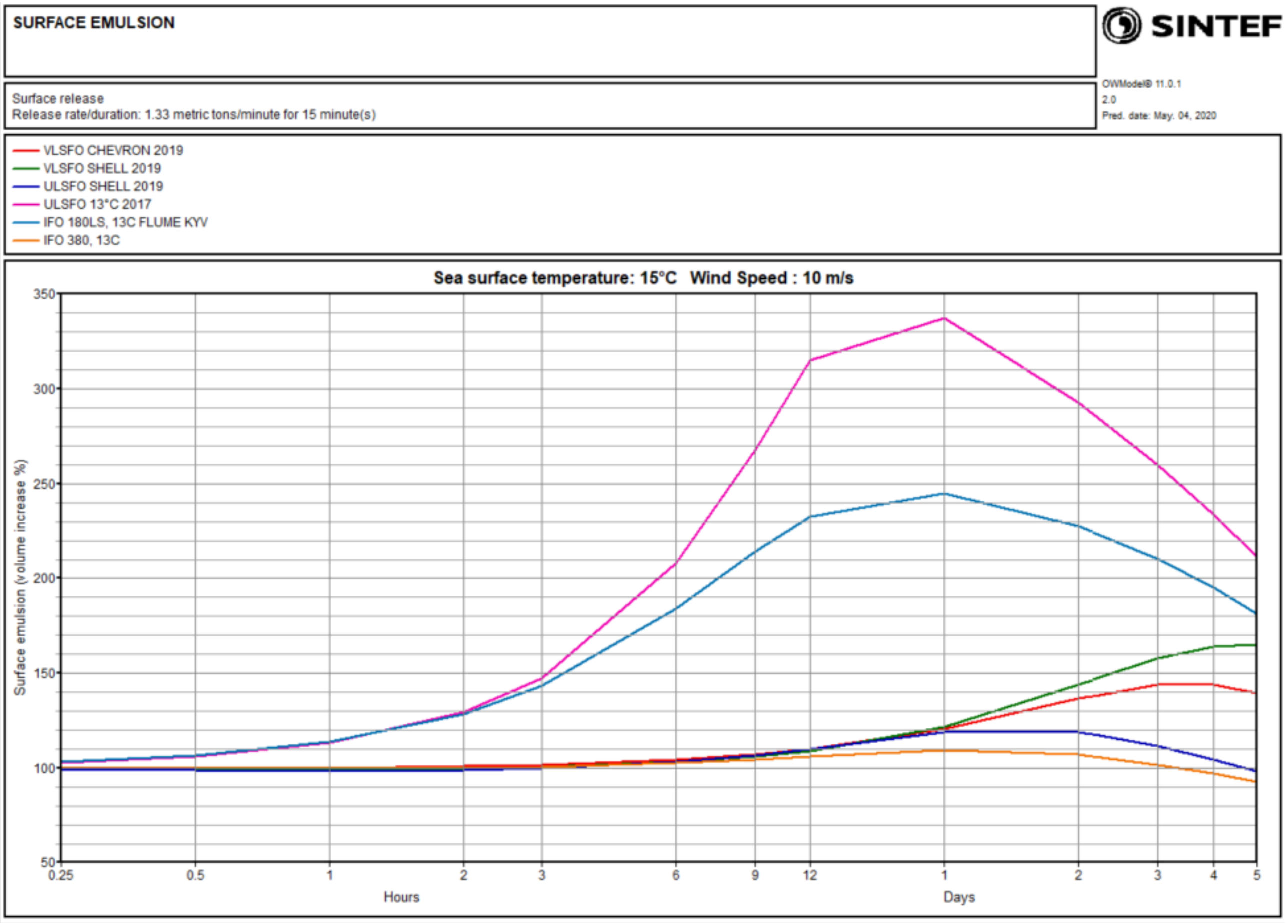


Figure 8-6 *Comparison of predicted surface emulsion (emulsification) at 15 °C and 10 m/s VLSFO Chevron 2019, VLSFO Shell 2019, ULSFO Shell 2019, ULSFO Shell 2016, IFO 180, and IFO 380*

9 Ignitability of the oils (*in-situ* burning experiments)

The purpose with the ignitability testing was to check the potential for using ISB as a response option for the three LSFO oils. The ignitability potential was characterized by following a "progressive" ignition strategy in igniting the oils. Totally 5 burning experiments were performed:

1. ULSFO Shell 2019 (non-weathered, waterfree), density: 0.917 kg/l
2. VLSFO Shell 2019 (non-weathered, waterfree), density: 0.989 kg/l
3. VLSFO Chevron 2019 ((Waterfree), density: 0.988 kg/l
4. ULSFO Shell 2019 (30 % w/o-emulsion). Density emulsion: 0.949 kg/l
5. ULSFO Shell 2019 (50 % w/o-emulsion). Density emulsion: 0.971 kg/l

A separate memo outlined by SINTEF from the ignitability study is available for more details. Additionally, to the SINTEF ISB, an interlaboratory comparison of test methodologies and ISB results of the ULSFO oil testing at SINTEF and SL Ross Laboratories are briefly discussed in the interlaboratory comparison in section12.

9.1 Experimental

Weather conditions:

Perfect weather conditions during the experiments:

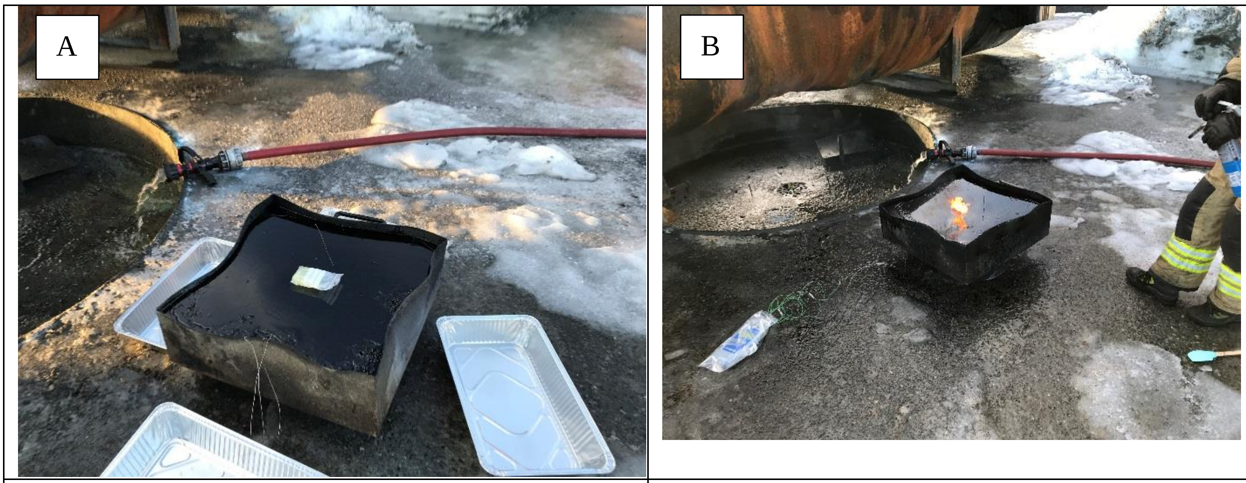
- Wind: < 2-3 m/s
- Air temp: 0-1 ºC
- Seawater temp: 5- 6 ºC
- No fall of rain / snow

Experimental setup:

- Test tank. Standard burning tray at RelyOn Nutec (0.6m x 0.6m x 0.2 m, see Figure 9-1A), i.e. surface area: 0.36 m^2.
- 60 L water, and 6 L oil (ca. 17 mm thickness) added gently on the top of the water surface
- Ignitor source: Gelled gasoline /diesel mixture (20/80 added 3 -4% gelling agents, Surfire). The gel was packed in 100 mL plastic bags. The bag was placed in the middle of the tray (see Figure 9-1 A/B).
- Gelled gasoline/diesel was ignited immediately by a propane torch (see Figure 9-1 B)
- Temperature logging: Three sensors: 1): placed in the flame (10-15 cm above oil surface), 2): in the oil phase and 3): in water 1-2 cm beneath the oil layer) (see Figure 9-1A/B)
- Ignition time: Time from igniting the gel until the flame has spread to the total (100 %) oil area
- Burning time: Time from the flame has spread to the total oil area until the burn extinguished
- Recovery and quantification of burned residue
- Sampling of residue for aftermath physico-chemical characterization in the laboratory

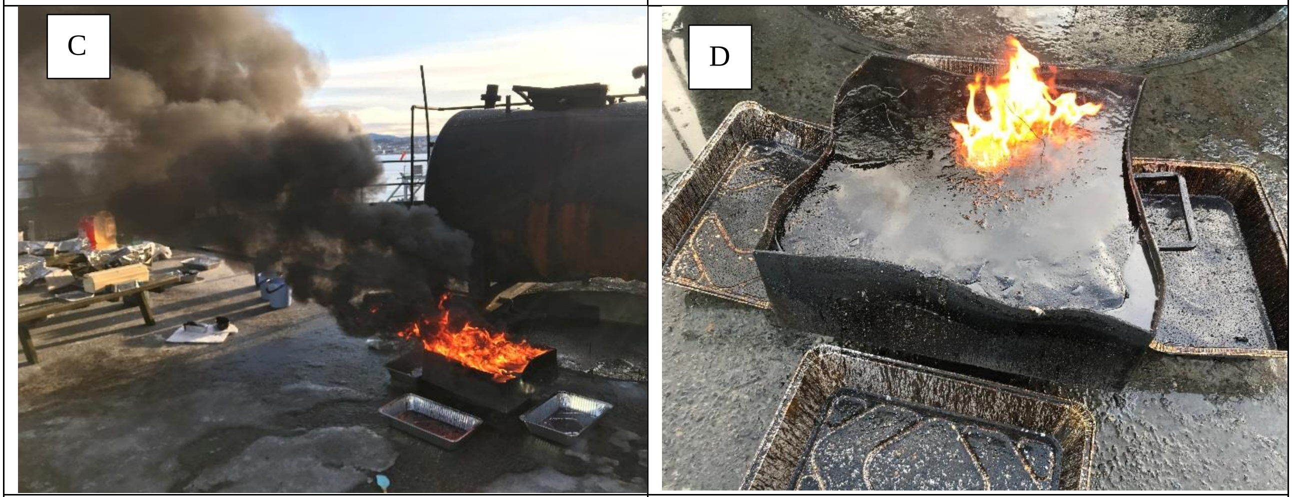
Ignition strategy:

- The effective burning time of a 100 mL gel bag is 10-12 min.
- If the burn has not spread to the oil area within 10 min., another 100 mL gel bag is applied (same position) and ignited
- If the burn still has not spread to the oil area within another 10 min., suffocate the burning gel, and add 300 ml diesel fuel as a primer (equivalent to a 1 mm slick) on the top of the oil. And ignite a third gel bag
- If the burn still has not spread to the oil area within another 10 min., suffocate the burning gel, and add 600 ml diesel fuel as a primer (equivalent to a 2 mm slick) on the top of the oil. And ignite a fourth gel bag
- If this fails, the oil is designated as being "unignitable"



1A): Start experiment: Burning tray filled with oil (6L) on water. Plastic bag (100ml) with gelled ignitor placed on top of the oil (middle of tray)

1B): Ignition of plastic bag with gelled gasoline/diesel mix. by a propane torch



During burning

Just before the burn extinguish in experiment 4 (30% emulsified ULSFO Shell 2019. Minimal loss of oil outside the tray due to "splashing"

Figure 9-1 **_Selection of pictures taken at different stages during the experiments_**

9.2 Resumé of log from each experiment

All images (photos) and videos taken during the burns are archived and available upon request.

9.1.1 Exp. 1 ULSFO Shell 2019

- Oil applied: 5.455 kg
- Water temp.: 9 °C
- 09:25: Gel ignited
- 09:26: (1 min) flame start to spread to the oil (10 % of the surface area burn)
- 09:27: 50 % of surface area burn (2 min. after ignition)
- 09:28: 100 % of surface area burn (3 min. after ignition)
- 09:34: Flame extinguish, i.e. 6 min. burning time (time after 100 % burn area started)
- Minimal splash-over: Total 80 gram in the recovery trays
- 5 min after burn: Start recovery of residue
- Amount residue: 3.115 kg (i.e. 58 wt.% of oil applied)

- Burning effectiveness (BE): 42 wt.%

9.1.2 Exp. 2 VLSFO Shell 2019

- Oil applied: 6.287 kg
- Water temp. 13 °C (water not replaced)
- 10:28: Gel ignited
- 10:34: (6 min.) flame start to spread to the oil (10 % of the surface area burn)
- 10:36: 40 % of surface area burn (8 min after ignition)
- 10:38: 100 % of surface area burn (10 min after ignition)
- 10:48: Flame extinguish, i.e. 10 min. burning time (time after 100 % burn area). Top layer of water boiled (i.e. must check water content if the burned residue had incorporated water)
- Some oil residue overflow (373 g), recovered in recovery trays. Good control of residue
- 5 min. after burn: Start recovery of residue:
- Amount residue: 4.016 kg (i.e. 64 wt.% of oil applied), (incl. the residue flew over)
- Burning effectiveness (BE): 36 wt.%

9.1.3 Exp. 3 VLSFO Chevron 2019

- Oil applied: 5.306 kg
- Water temp. 14 °C (water replaced)
- 12:15: Gel bag ignited
- 12:25: (10 min.) still no spreading of burn to the oil area
- 12:26: (11 min.). second gel bag ignited
- 12:31 (16 min.) Flame start to spread to the oil (10% of the surface area burn)
- 12:32: 40 % of surface area burn (17 min. after ignition)
- 12:33: 100 % of surface area burn (18 min. after ignition)
- 12:40: Flame extinguish, i.e. 7 min. burning time (time after 100% burn area). Top layer of water boiled (i.e. must check water content if the burned residue had incorporated water)
- Minimal splash-over. Good control of residue
- 5 min after burn: Start recovery of residue:
- Amount residue: 4.002 kg (i.e. 55 wt.% of oil applied)
- Burning effectiveness (BE): 45 wt.%

9.1.4 Exp. 4 ULSFO Shell 2019 (30 % w/o-emulsion)

- Emulsion applied: 5.770 kg (i.e. 4.039 kg water-free oil)
- Water temp. 14 °C (water replaced)
- 13:24: Gel bag ignited
- 13:31: Emulsion is "boiling" around the burning gel bag. Still no spreading of burn
- 13:33: (9 min). second gel bag ignited
- 13: 37: (4 min. after 2nd. Gel bag) < 5-10 % of area around gel bag is boiling.
- 13:40 (7 min. after 2nd. Gel bag) < 5-10 % of area around gel bag is boiling. Still no spreading of burn. Suffocate the burning gel
- 13:48: 300 ml (1 mm) diesel applied on the top of the emulsion
- 13:50 Ignite a new gel-bag. Flame start to spread over the entire emulsion (100 % of the surface area burn).
- Low intensity of the burn
- 14:03: Flame extinguish, i.e. 13 min. burning time (time after 100% burn area)
- Minimal splash-over. Good control of residue

- 5 min after burn: Start recovery of residue:
- Amount residue: 3.200 kg (i.e. 75 wt.% of emulsion applied)
- Burning effectiveness (BE): 25 wt.%

9.1.5 Exp. 5 ULSFO Shell 2019 (50 % w/o-emulsion)

- Emulsion applied: 5.570 kg (i.e. 2.785 kg water-free oil)
- 300 mL (1 mm) diesel applied on the emulsion
- Water temp. 14 °C (water not replaced)
- 14:23: Gel bag ignited
- 14:30: Fire not spread on the surface. (Suffocate the burning gel)
- 14:33: Additional 600 mL (2 mm) diesel applied on the top of the emulsion
- 14:34 Ignite a new gel-bag. → Flame start to spread to the oil area
- 14:35 Burn spread over the entire emulsion (100 % of the surface area burn)
- Very low intensity of the burn
- 14:41: Flame extinguish, i.e. 6 min. burning time (time after 100 % burn area)
- Minimal splash-over. Good control of residue
- 5 min. after burn: Start recovery of residue:
- Amount residue: 4.655 kg (i.e. 84 wt.% of emulsion applied)
- Burning effectiveness (BE): 16 wt.% of the emulsion applied

9.3 Summary ignitability

The primary goal with the SINTEF burning testing performed in the meso-scale trays at RelyOn Nutec, was to study the ignitability potential for the three residual fuel oils. The outcome of the burning effectiveness (BE, i.e. the mass loss after a burn) will have limited operative value as it is impossible to simulated in small scale the burning conditions and burning efficiency that happen at a large scale in the field. The SINTEF experimental set-up by using trays with the oil layer on a "static" reservoir of water, is an attempt to mimic the burn of a "free" drifting oil slick in open or ice-infested water, where the upper water layer beneath the burn will be heated up and eventually start to boil. This will generate turbulence, which will influence on the burn intensity, and promote termination of the burn. However, small-scale ISB system may give reliable understanding and documentation of the ignitability potential of different oil products - both non-weathered and at different weathering stages (evaporated and emulsified).

The water-free (non-emulsified) oils were all ignitable, however, due to the low content of volatiles, the oils required a prolonged time to be heated by a burning gelled gasoline/diesel mixture before the burn spread to the oil layer. Among the three oils, ULSFO Shell 2019 was the easiest to ignite, where the gel needed to burn for 3 min. before the burn was spread to the surrounding oil. For the VLSFO oils this "heating time" was even longer i.e.10 min for the VLSFO Shell 2019, and 18 min for the VLSFO Chevron 2019. The ignitability results are comparable and give complementary information to previous similar tests with different marine fuels (Hellstrøm et al. 2017). SINTEFs attempted to ignite 30 and 50 % w/o-emulsions of the ULSFO Shell 2019, were not possible with burning gels without adding significant amount (1 mm and 3 mm) of diesel on the top of the emulsions. The findings from these ignitability tests indicate therefore that even low content of water incorporation (w/o-emulsification) at sea for these new generations of marine residual fuel oils are exceedingly difficult to ignite by use of present operative ignition methodology (i.e. gelled gasoline/diesel) without application of significant amount of primer (e.g. diesel) on the emulsified oil.

10 Summary oil properties related to oil spill response

In general, the oil weathering properties will influence the evaluation of response options (mechanical recovery, dispersant use and *in-situ* burning) in a spill situation. This section the results from the experiments are discussed in relation to the different response options for the tested oils.

10.1Mechanical recovery

In general, experiences from Norwegian field trials with oil spill booms have demonstrated that the effectiveness of various mechanical clean-up operations may be reduced due to the high degree of leakage of the confined oil or emulsion from the oil spill boom. Boom leakage is particularly pronounced if the viscosity of the oil or the w/o-emulsion is lower than 1000 mPa.s (Nordvik et al. 1992). However, due to high viscosities none of the tested oils are expected to be subjected to boom leakage due to this predicted lower viscosity limit. Previously studies at SINTEF have shown that weir skimmers may reduce recovery rates (m^3/h) when skimming oils with viscosities in the range 15-20 000 mPa.s (Leirvik et al. 2001). Moreover, NOFO (Norwegian Clean Seas Association for Operating Companies) is operating with viscosity limits for skimmer efficiency as followed: primary use of weir skimmers (< 20 000 mPa.s), combination of weir and high-visc. skimmer (20-50 000 mPa.s), and primary high visc. skimmer (> 50 000 mPa.s). The NCA, however, have other skimmer types in their stock that are suitable for a range of emulsion viscosities, as mentioned: Low viscous oils/emulsions < 10 000 mPa.s, Medium viscous oil/emulsions: 10-50 000 mPa.s and high viscous oils/emulsions > 50 000 mPa.s. Other oils spill responders may have other skimmer /equipment in stock.

VLSFO Chevron 2019

Mechanical recovery is expected to be an option for VLSFO Chevron 2019, both in cold climate conditions and in higher temperatures. The predicted oil/emulsion viscosities are in the range of 10 000-60 000 mPa.s (2 °C) and 4000 to 40 000 mPa.s (15 °C), see prediction chart in Figure C-3 (Appendix C).

VLSFO Shell 2019

The predicted viscosities of VLSFO Shell 2019 at 2 °C, are in the range of 80 000 to 800 000 mPa.s, see prediction chart in Figure C-12 (Appendix C). This means that in cold climate regions/arctic conditions, mechanical recovery can be challenging for weathered oils due to the very high viscosities (risk for solidification). At higher temperatures, the viscosities are lower, however at 1 days of weathering e.g. at 10 m/s wind speed, the viscosity may reach 100 000 mPa.s.

ULSFO Shell 2019

Based on the predicted viscosities, mechanical recovery is expected to be an option both in cold climate regions and higher seawater temperatures for ULSFO Shell 2019, see prediction chart in Figure C-21 (Appendix C). However, viscosities may surpass > 100 000 mPa.s at 2 °C by weathering that may influence on the choice of skimmer system. Moreover, this oil has also very high pour points, see predictions chart in Figure C-23 (Appendix C), and solidification (pour point typically 5-15 °C higher than the sea temperature) is a likely scenario, particularly at 2 °C. Solidification of oil at sea can result in limited flowability towards traditional skimmer (e.g. weir skimmers, adhesion skimmers) in in a spill operation, but this oil requires specific "active" skimmer systems designated for solidified oils (e.g. belt-skimmers, grabs).

10.2Dispersibility

The results from the performed dispersibility studies is presented in section 6.

VLSFO Chevron 2019

The use of dispersants on VLSFO Chevron 2019 proved to be ineffective, based upon the laboratory testing at 2 °C, reflecting cold climate regions /arctic conditions. The oil/emulsion was found reduced/good dispersible at higher temperatures (13 °C). This means that use of dispersants can be an option to break up the surface slick into smaller patches. However, slick break-up requires energy in terms of either breaking waves (> 5 m/s wind speed) and/or artificial energy and high dosage. DOR 1:10 was found more efficient than DOR 1:25. Successive application of dispersants may also be beneficial to enhance dispersion, but this option was not tested in this project. Larger oil droplets / lumps will easily re-surface.

VLSFO Shell 2019

Use of dispersants is not an option at 2 °C, reflecting a cold climate /arctic conditions due to high viscosities. At higher temperature (13 °C) the oil may have the potential (reduced) for dispersants use but requires breaking waves conditions (> 5m/s wind speeds) and /or additional artificial energy. Successive application of dispersants (not tested in this project) and /or increased dosage (> DOR 1:25) may also enhance dispersion.

ULSFO Shell 2019

At 2 °C, ULSFO Shell 2019 was found to be not dispersible due to high pour point and high viscosity. At 13 °C, adding dispersants showed also low dispersibility when tested with dispersants. Overall, the use of dispersants is not recommended for this oil.

10.3*In-situ* burning - ignitability

In-situ burning (ISB) is often considered as a primary response operation in arctic and ice-covered areas. The primary goal with the SINTEF burning testing performed in the meso-scale trays, was to study the ignitability potential for the three residual fuel oils. The outcome of the burning effectiveness (BE, i.e. the mass loss after a burn) will have limited operative value as it is not possible to simulate, at the bench-scale, the burning conditions and burning efficiency that happens at the large scale in the field. However, meso-scale ISB systems may give operative relevant documentation and valuable understand about the potential and limitations in igniting different oils at different weathering stages (with respect to both evaporation and emulsification degrees).

The water-free (non-emulsified) oils were all ignitable, however, due to the low content of volatiles, the oils required a prolonged time to be heated by a burning gelled gasoline/diesel mixture before the burn spread to the oil layer. The ignitability results are comparable and give complementary information to previous similar tests with different marine fuels (Hellstrøm et al. 2017).

VLSFO Chevron 2019

Among the three oils, VLSFO Chevron 2019 is the oil with the lowest content of volatiles and the highest flashpoint (109°C). By using the standard SINTEF ignition strategy, it took 18 min. before the burn from the gelled gasoline/diesel ignitor mixture spread to the oil. Due to the very long heating time needed for igniting the waterfree oil, tests on emulsified oil was not considered to be relevant.

VLSFO Shell 2019

VLSFO Shell 2019 had a slightly higher content of volatiles, and a flashpoint of (100 °C). By using the standard SINTEF ignition strategy, it took 10 min. before the burn from the gelled gasoline/diesel ignitor mixture spread to the oil. Due to the very long heating time needed for igniting the waterfree oil, tests on emulsified oil was not considered to be relevant.

ULSFO Shell 2019
Among the three oils ULSFO Shell 2019 was the easiest oil to ignite, where the burning gel needed to burn for 3 min. before the burn was spread to the surrounding oil. The ULSFO has a similar content of volatiles as the VLSFO Shell 2019 (5-8 % with boiling point below 250 °C. 30 and 50 % w/o-emulsions of the ULSFO, were not possible ignite by burning gels without adding significant amount (1 mm and 3 mm) of diesel on the top of the emulsions.

These ignitability tests indicate therefore that even a low amount of water entrainment (w/o-emulsification) likely to occur at sea for these new generation of marine residual fuel oils render them to be very difficult to ignite by the present operative ignition methodologies in an ISB response operation without the application of significant amount of primer (e.g. diesel) on the emulsified oil slick.

11 WAF and toxicity

In acute oil spill, component in the spilled oil that have some solubility in water will migrate from the oil phase to the water phase. Aquatic organism can be exposed to soluble oil compounds, and knowledge of the toxicity of an oil is therefore important for evaluation of response options and evaluation of effects on the environment resulting from an acute oil spill. Low-energy water accommodated fraction (LE-WAF) of the fresh low sulfur fuel oils were characterised with emphasis on chemistry and acute toxicity. Two pelagic species representing primary producers (the marine algae *Skeletonema pseudocostatum*) and invertebrates (the marine copepod *Calanus finmarchicus*) were tested.

11.1Materials and methods

Description of the tested oils are given in Table 11-1. Details about the oils physical properties are given in Section 5, Table 5-2, and GC-chromatograms in Figure 5-2.

Table 11-1 Description of oil names used in figures and tables

SINTEF ID	Oil type	Name used in figures and tables
2019-3955	VLSFO Chevron 2019	VLSFO
2019-7685	VLSFO Shell 2019	VLSFO Shell
2019-11170	ULSFO Shell 2019	ULSFO

11.2 WAF preparation

Preparation of low energy WAF (LE-WAF) was performed under controlled conditions following the guidelines established by the Chemical Response to Oil Spills: Ecological Research Forum (CROSERF). These guidelines were developed to standardize WAF preparation, laboratory exposures to aquatic organisms, and analytical chemistry measurements used to determine the acute toxicity of the water-soluble components in the oil (Aurand and Coelho, 2005). LE-WAF can be defined as a water solution of dissolved oil components prepared in closed vessels, with calm mixing of oil and water without the formation of any vortex. LE-WAFs were chosen to avoid generation of oil droplets. The WAFs were prepared with the oil-to-water loadings of 1 to 40 (25 g oil/L water) at 13 °C. The oil-to-water ratio of 1:40 is assumed to be "saturated" and therefore represents a "conservative" estimate of the concentrations foreseeable during an oil spill. The WAFs were generated with a contact time between water and oil for three days before the water was collected for chemical characterization and toxicity tests.

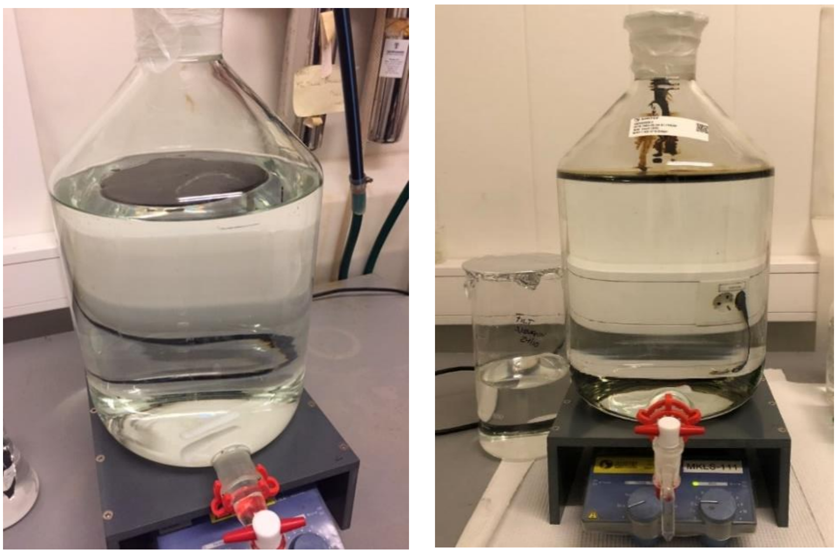


Figure 11-1 WAF of VLSFO Chevron 2019 and VLSFO Shell 2019

11.3 Chemical composition of the oils and the WAFs

GC chromatograms of the WAFs are provided in Appendix D (Figure D1-D3). There are no indications of the presence of oil droplets in any of the WAFs according to the GC chromatograms; solely the water-soluble fractions are detected. Figure 11-2 summarizes the composition of the main groups of the aromatics in the oil products. The data are also provided in Table D-1. According to the results, the contents of volatiles were low in all oils. The ULSFO Shell 2019 contains less 2-6 ring PAHs than the VLSFO oils (15 g/kg oil vs. 66 and 24 g/kg oil in VLSFO Chevron 2019 and VLSFO Shell 2019, respective).

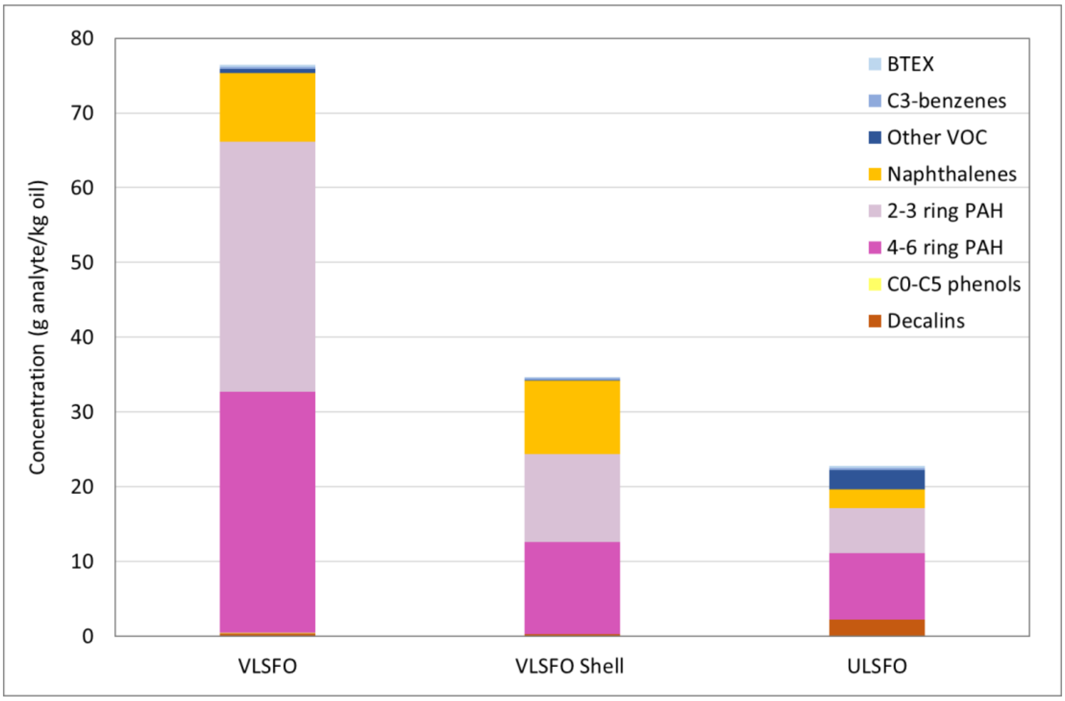


Figure 11-2 Chemical composition of selected component groups (aromatics) in the oil products studied. The component groups are described in Appendix D

The "chemical profile" of a WAF is unlike that of its parent oil due to the different water solubilities of the various oil components. Figure 11-3 and Table D-1 (Appendix D) show the concentration of the water-soluble components of the WAFs prepared, including unresolved complex materials (UCM). The UCM was calculated by subtracting the SVOC concentration from the TPH concentration.

Total WAF concentration is based on the sum of total petroleum hydrocarbon (TPH) and volatiles (C_5-C_9, including BTEX). The VOCs (especially BTEX and C3-benzenes) usually constitute a major part of the WAFs from fresh oils, and the naphthalenes are generally dominating the semi-volatile organic components (SVOC) as they have relatively high solubility in water. This can be seen in these WAFs. The total WAF concentrations are higher in VLSFO Shell 2019 than in VLSFO Chevron 2019, although VLSFO Chevron 2019 oil contains more aromatics in total than VLSFO Shell 2019. This is due to a different distribution of the individual components (with different solubilities) within the same component group. E.g. the VLSFO Chevron 2019 has a higher content of the larger PAHs (2-6 ring) with low solubilities. Furthermore, the total concentration of naphthalenes in these two oils are similar, but the content of most water soluble naphthalenes (naphthalene and C1-naphthalenes) are higher in VLSFO Shell 2019 than in VLSFO Chevron 2019 (see Table D-2, Appendix D). The concentrations of phenols and UCM are also higher in VLSFO Shell 2019.

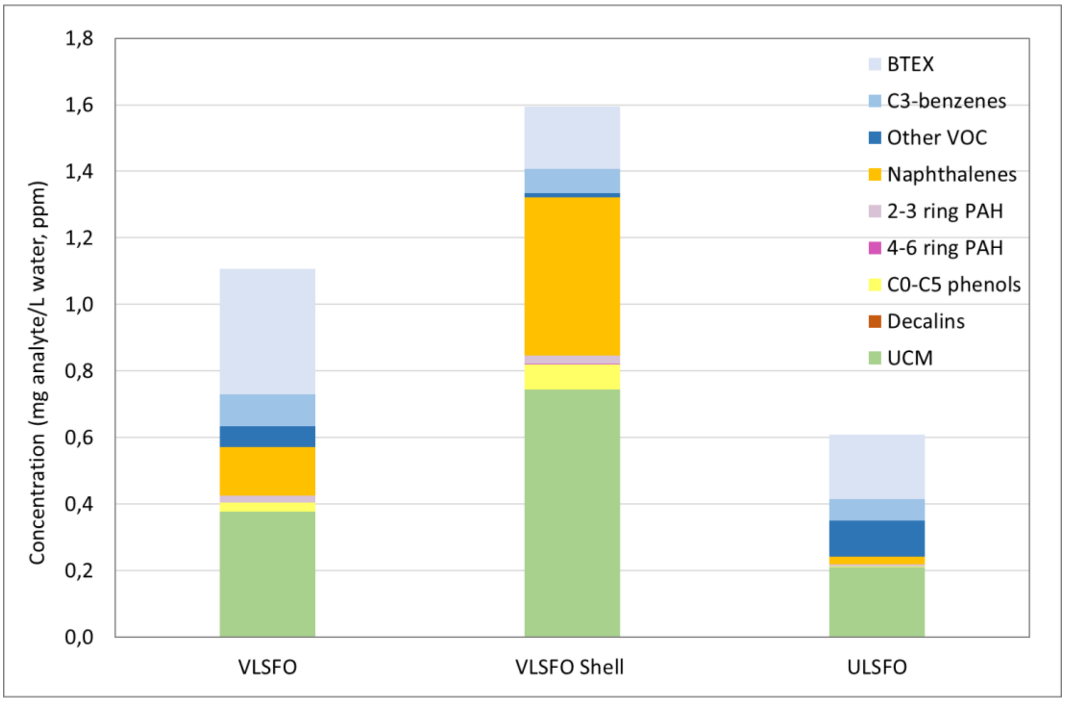


Figure 11-3 ***Chemical composition of selected component groups in the WAF systems. The component groups are described in Appendix D***

11.4Acute toxicity of WAFs to marine organisms

There are several ways to present the toxicity results. The toxicity of a chemical is normally quantified as an LC_{50} or EC_{50} value, defined as the concentration causing 50% of the organisms in a test population to die or to show a significant negative effect when they are exposed to a fixed concentration of the chemical for a defined time period (Rand et al. 1995). LC_{10} and EC_{10} values reflect the concentrations causing 10% of the organisms to die or to show a significant negative effect and can be used if the toxicity is too low to be expressed as EC_{50} or LC_{50}. The EC_{50} and LC_{50} can be given either in percent dilution of the undiluted (or 100 %) WAF (relative toxicity, EC_{50} or LC_{50} (%)), or as normalized to the total WAF concentration (specific toxicity, EC_{50} or LC_{50} (mg/L or ppm)). Low values for LC_{50} or EC_{50} indicates a high toxicity, while a high value for LC_{50} or EC_{50} corresponds to a lower toxicity. A summary of the toxicity results is given in Table D-4 (Appendix D), both EC_{50} or LC_{50} and EC_{10} or LC_{10} are calculated for all systems. LC_{10} indicates similar trends as LC_{50}. In addition, predicted acute toxicity expressed as toxic units is provided in Table D 5.

In Figure 11-4, the relative toxicity (left graph) and the specific toxicity (right graph) to the WAFs are shown. Specific toxicity is normalized to the total WAF concentration and has been the traditional approach for expressing toxicity. The specific toxicity indicates that the WAFs of VLSFO Chevron 2019 and VLSFO Shell 2019 have similar toxicity to *C. finmarchicus*, VLSFO Chevron 2019 being slightly more toxic. WAF of VLSFO Chevron 2019 was more toxic to *S. costatum* than VLSFO Shell 2019. For ULSFO Shell 2019, the LC_{50} for 96 hours exposure of *C. finmarchicus* could not be calculated as the lethal immobilization was too low. *S. costatum* seems to be more sensitive than *C. finmarchicus* to the WAFs of VLSFO Chevron 2019 and ULSFO Shell 2019. The relative toxicity was presented as EC_{50} and LC_{50} given in percent of the diluted WAF. WAF prepared with VLSFO Shell 2019 was most toxic to *C. finmarchicus*, and WAF prepared with VLSFO Chevron 2019 was most toxic to *S. costatum*. The level of toxic effect observed was not high enough to calculate conclusive values for LC_{50} as the effect was less than 50% for *C. finmarchicus* in the WAF of ULSFO Shell 2019.

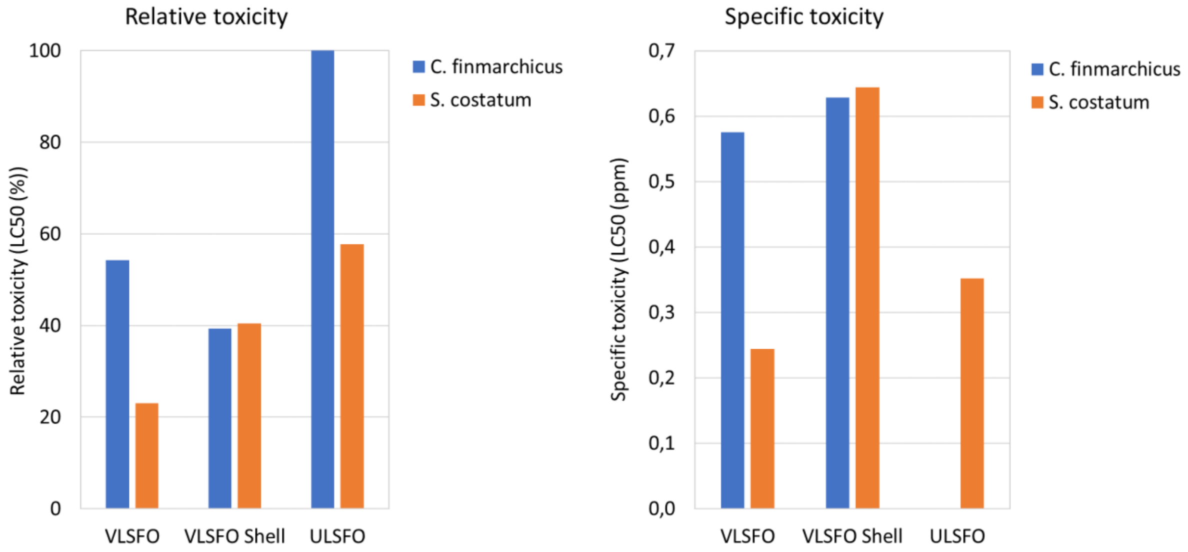


Figure 11-4 ***Acute toxicity (LC$_{50}$ values)expressed as relative toxicity (left figure) and specific toxicity (right figure) to WAF of VLSFO (Chevron), VLSFO Shell (2019) and ULSFO (Shell 2019) for* C. finmarchicus *and* S. costatum. *Lower bars indicate higher toxicity. Absence of observed effect (no bar) on WAF of ULSFO (Shell 2019) for* C. finmarchicus *(no mortality observed)***

Figure D-5 (Appendix D) presents toxicity as percent reduction in growth rate and biomass production for *Skeletonema* sp. after 72 hours to different dilutions of the WAFs. Figure D-6 (Appendix D) gives the toxicity in percent mortality for *C. finmarchicus* after 24, 48, 72, and 96 hours. The graphs show that the toxicity increases with time and concentration.

Acute toxicity expressed as toxic unit (TU) was predicted based on the chemical composition of the WAFs and the K_{ow} for the individual components (DiToro et al. 2007, see Appendix D). A TU>1 for the total WAF implies that it is expected to cause more than 50% mortality in the test organisms. TU for the WAFs are computed and provided in Table D 5. TU for VLSFO Shell 2019 and ULSFO Shell 2019 was below 1 (0.51 and 0.24, respective). TU for VLSFO Chevron 2019 was 1.02, indicating that the WAF could cause mortality to more than 50% of the test organisms. Decalins, 2-3 ring PAHs and 4-6 ring PAHs contribute more to the TU for WAF of VLSFO than in the other two WAFs.

11.5Comparison with WAFs from other oil products

WAF concentrations and TU for the WAFs were compared with other oil products in Figure 11-5 and Figure 11-6. These marine fuel oils (including marine distillate fuels) are from previous studies at SINTEF reported in Faksness and Altin (2017). WAF of ULSFO has been investigated earlier, "ULSFO 2016" is another batch of ULSFO from the Shell refinery and contained more volatiles than the batch studied here.

Although the total WAF concentration in the WAFs of VLSFO Chevron 2019 was lower than most of the other oil products, its TU was higher. The calculations indicated that especially the larger PAHs (with high K_{ow} values) contributing to the toxicity, resulting in a TU slightly higher than 1 (1.02). UCM is not included in TU calculations.

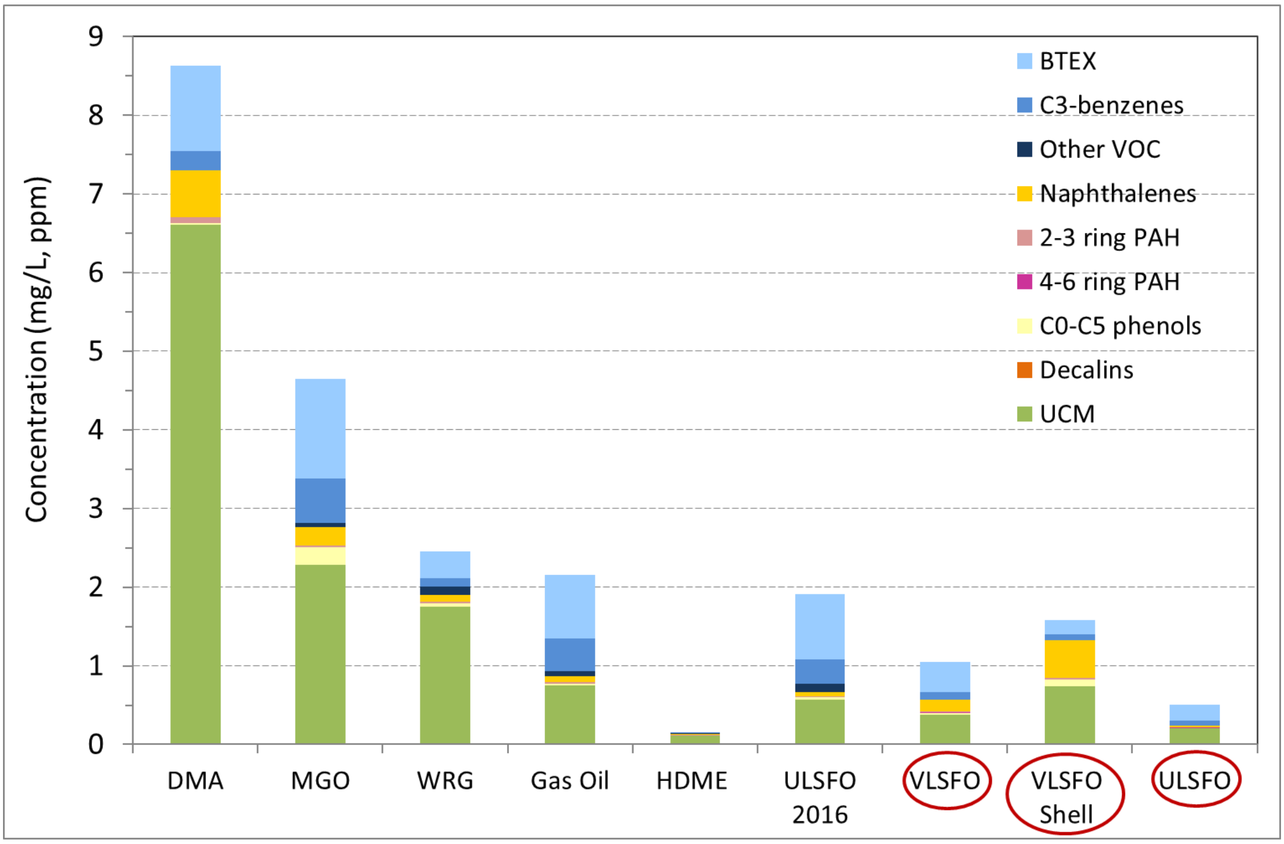


Figure 11-5 *WAF concentrations of oil products tested in previous studies at SINTEF (Faksness and Altin (2017), compared with the WAFs studied here: VLSFO (Chevron), VLSFO Shell (2019), and ULSFO (Shell 2019) in red circles*

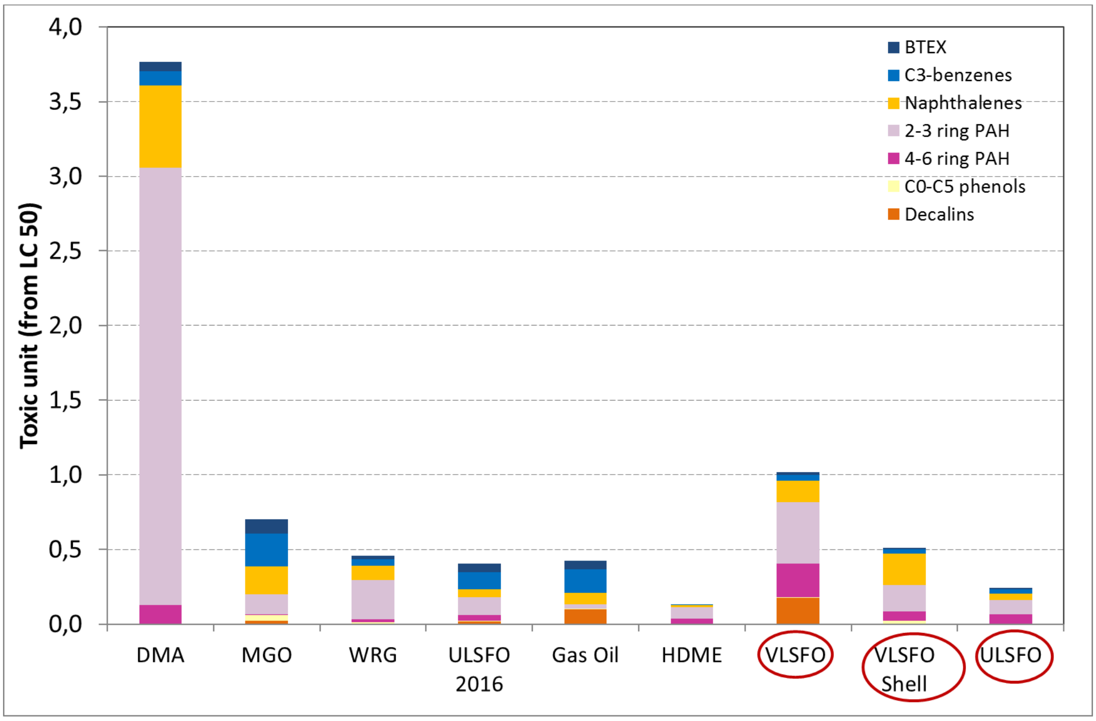


Figure 11-6 *Predicted acute toxicity expressed as TU for WAFs of oil products tested in previous studies at SINTEF compared with the WAFs studied here: VLSFO (Chevron), VLSFO Shell 2019, and ULSFO (Shell 2019) in red circles. A TU>1 indicates mortality of 50% for the tested organisms*

11.6Summary and conclusions WAF

The total WAF concentrations of the three residual fuels were in the lower range compared to the previously tested marine distillate fuels, and were 0.61 ppm for ULSFO, 1.1 ppm for VLSFO Shell 2019, and 1.6 ppm for VLSFO. The relative toxicity was presented as EC_{50} and LC_{50} given in percent of the diluted WAF. WAF prepared with VLSFO Shell 2019 was most toxic to *C. finmarchicus*, and WAF prepared with VLSFO Chevron 2019 was most toxic to *S. costatum*. The level of toxic effect observed was not high enough to calculate conclusive values for LC_{50} as the effect was less than 50% for *C. finmarchicus* in the WAF of ULSFO Shell 2019.

Specific toxicity is normalized to the total WAF concentration and has been the traditional approach for expressing toxicity and indicated that the toxicity to *C. finmarchicus* of WAF prepared of VLSFO Chevron 2019 and VLSFO Shell 2019 were quite similar, VLSFO Chevron 2019 being slightly more toxic. WAF of VLSFO Chevron 2019 was more toxic to *S. costatum* than ULSFO Shell 2019 and VSLFO Shell.

Acute toxicity, expressed as toxic unit (TU), was predicted based on the chemical composition of the WAFs and the K_{ow} for the individual components. A TU> 1 for the total WAF implies that it is expected to cause more than 50% mortality in the test organisms. TU for VLSFO Shell 2019 and ULSFO Shell 2019 was below 1 (0.51 and 0.24, respective). TU for VLSFO Chevron 2019 was 1.02, indicating that the WAF could cause mortality to more than 50% of the test organisms. The calculations indicate that especially 2-3 ring PAHs and 4-6 ring PAHs contribute more to the TU for WAF of VLSFO Chevron 2019 than in the other two WAFs. However, the toxicity of the tested oils are low and is in the same range of the other previously marine distillates fuels (TU<1), except from the DMA Shell diesel that had a significant higher TU value due to the its high content of semi-soluble naphthalenes and PAHs (aromatics).

12 Interlaboratory comparison

As a part of this project, SINTEF and SL Ross have performed some similar bench-scale analysis of ULSFO Shell 2019 for interlaboratory comparison. This included physico-chemical analysis, emulsification, dispersibility and ignitability /ISB on ULSFO Shell 2019. The results are given in following sections, below. Both laboratories at SINTEF and SL Ross have used their standard analytical procedures and methods, i.e. the analytical procedures have not been customized or adapted to one or the other laboratory within this project. A summary of results and methods from SL Ross is given in Appendix E.

12.1Physico-chemical parameters

The physico-chemical parameters analysed at SINTEF and SL Ross are summarized in Table 12-1.

SINTEF and SL Ross are using different procedure for evaporation, that explain the differences in the evaporative loss. However, the evaporative loss of ULSFO Shell 2019 is low despite the method used. As a standard procedure, SINTEF distillate off volatiles up to 150, 200 and 250 °C that reflects an evaporation loss corresponding to approximately 0.5-1-hour, 0.5-1 day and 0.5-1 week of weathering. SL Ross is using a wind tunnel to correlate the Weathering States (WS) as Fresh, (0 days, as received), WS2 (2 days in wind tunnel, and WS3 (2 weeks in wind tunnel). Depending on the conditions at a spill site, the WS would typically correlate to periods from a few hours to a day or two for a spill on water.

ULSFO Shell 2019 is residual fuel oil. The densities measured at 15.5 °C is shown in Table 12-1. The density of the fresh oil measured at SINTEF is 0.917 vs. 0.911 g/mL at SL Ross, which is considered as acceptable due to the nature of this oil. The viscosities (mPa.s) are given as multiple temperatures to provide property information about the oil, as shown in Table 12-1. The unit mPa.s (SI unit) is numerically equivalent to centi-Poise (cP). The viscosities were measured at different temperatures but are likely comparable. The pour points measurements are also comparable (+24 °C vs. +27 °C (analytical uncertainty ±3 °C). The interfacial tension of the fresh oil is very similar 11.7 vs 10.4 mN/m (SI unit) or cm/dynes. The asphaltene and wax contents were measured at SINTEF, only. The precipitations of asphaltene and wax are time-consuming methods and the procedures were therefore not adapted at SL Ross withing this project.

The True Boiling Point (TBP) curve of the fresh ULSFO Shell 2019 was analysed by use of Gas Chromatographic Simulated Distillation analysis (SIMDIS), ASTM D7169. Figure 12-1 shows the results from SIMDIS reported by SINTEF and SL Ross. The TBPs reported are very similar.

Overall, the physical properties as density, viscosities, pour point, and interfacial tension are recognized as comparable results for interlaboratory calibration between SINTEF and SL Ross. The variations are caused by different procedures and methods, but also due to pre-handling and the nature of the oil tested.

The oil type will influence on the results. ULSFO Shell 2019 is not an optimal oil for intercalibration due to its high density, low evaporative loss, and high pour point that make it difficult to get reproducible results. Therefore, a test oil with other properties such as lower pour point, and more Newtonian behaviour would be most appropriate for interlaboratory comparison. It had been preferable to choose an oil with a lower density with higher evaporative loss. The ULSFO Shell 2019 was, however, the test oil that was available in high volumes for interlaboratory comparison within this project.

Table 12-1 Physico-chemical parameters analysed at SINTEF and SL Ross of ULSFO Shell 2019

Analytical parameters	**SINTEF**				**SLRoss**		
	Fresh	**150°C+**	**200°C+**	**250°C+**	**Fresh**	**WS1**	**WS2**
Evap. (vol%)	0	0	2.7	5.1	0	0.3	1
Density (g/mL) @ 15 °C	0.917	0.917	0.92	0.922	0.911	0.919	0.919
Visc. (mPa.s) @ 0 °C, 100s^{-1}	*30000* [a]	NA	NA	NA	42607	58307	59636
Visc. (mPa.s) @ 2 °C, 100s^{-1}	21017	21017	15567	18125	NA	NA	NA
Visc. (mPa.s) @ 13 °C, 100s^{-1}	5986 [a]	5986	9903	14826	NA	NA	NA
Visc. (mPa.s) @ 15 °C, 100s^{-1}	*1820* [a]	NA	NA	NA	4663	5292	5725
Visc. (mPa.s) @ 20 °C, 100s^{-1}	*959* [a]	NA	NA	NA	2103	2391	2562
Visc. (mPa.s) @ 30 °C, 100s^{-1}	*268* [a]	NA	NA	NA	463	532	605
Pour point (° C)	24	24	27	30	27	27	27
Flash point (° C)	*70* [b]	NA	NA	NA	85	87	89
Interfacial Tension (mN/m) [c]	11.7	NA	NA	NA	10.4	10	9.2
Asph. (wt.%)	0.14	0.14	0.15	0.15	NA	NA	NA
Wax (wt.%)	20.7	20.7	21.1	21.6	NA	NA	NA

a: Data from temperature sweep (50-0 °C, 10s^{-1}); b: COA; c: mN/m (SI unit) = dyne/cm; NA: Not analysed

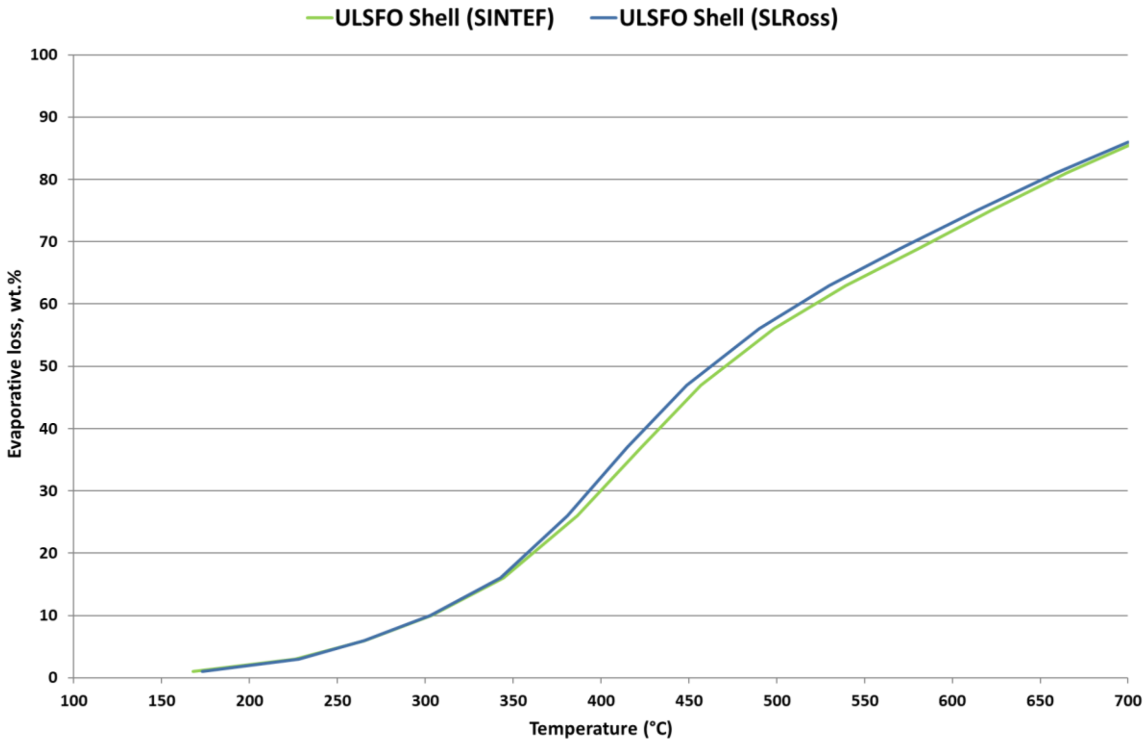


Figure 12-1 Comparison of TBP (True Boiling Point) curve of fresh ULSFO Shell 2019 reported by SINTEF and SL Ross by use of SIMDIS (ASTM 7169)

12.2Emulsification

Emulsification (water uptake) was performed on the ULSFO Shell 2019 at SINTEF and SL Ross. At SINTEF, the emulsification was conducted at 2 and 13 °C, whilst at SL Ross emulsification testing was attempted at 0 and 20 °C. At SL Ross laboratory, the oil had no tendency to form water-in-oil (w/o) emulsions at any degree of evaporation tested when mixed with seawater, neither at 0 nor 20 °C due to solidification and high pour point. At SINTEF laboratory, emulsification was observed for fresh oil and residues at 2 and 13 °C. However, the water uptake was very low at 2 °C, particularly for the residues due to solidifying properties.

Both laboratories operate the rotating cylinder method for emulsion testing as e.g. described in Mackay and Zagorski, 1982, Hokstad et al.1993. One of the reasons for the discrepancy in results can be explained by the preparation of glass cylinders to avoid adhesion of oil to the interior. In general, the cylinders should be washed with alkaline soap and thoroughly rinsed with water. Secondly, there may be different approaches to measure incorporated water in emulsions that do not form measurable meniscus. Thirdly, due to high pour point and tendency to solidify at low temperatures, the pre-handling of the oil prior to emulsion testing may also influence on the results. Nevertheless, ULSFO Shell 2019 was not an optimal for interlaboratory testing on formation of water-in-oil emulsions.

12.3 Dispersibility

Dispersibility study was conducted on ULSFO Shell 2019 at SINTEF and SL Ross. The laboratories apply different bench-scale methods for dispersibility testing of oils:

- SINTEF uses the IFP (low-energy test) and MNS (high-energy) test as described section 6 and in Appendix A.5
- SLRoss uses the Baffled Flask Test (BFT) method that determines dispersant effectiveness at a lab scale. This test is routinely used at SL Ross to evaluate the potential effectiveness of a chemical dispersant on a standard oil, or to study the comparable impacts of chemical dispersants on oils. The BFT procedure is based on Venosa et al. 2002 and Srinivasan et al. 2007. More information about the method and results is given in Appendix E.

The methods of BFT and MNS are comparable in terms of using "high energy" applied to the system that may enhance dispersion of the oil after treatment of dispersant. Corexit 9500A was chosen as dispersant on ULSFO Shell 2019 for comparison. As shown by the results in Table 12-2 and Table 12-3 ULSFO Shell 2019 has a low dispersibility as concluded by SINTEF and SL Ross.

Table 12-2 Summary of dispersibility results on ULFSO Shell 2019 by use of MNS (SINTEF) at 13 °C

	Without Dispersant	**With Corexit 9500A* (DOR 1:25)**
ULSFO Fresh	<1 %**	4 %
ULSFO Fresh 50 % emulsion	< 1%**	2 %
ULSFO Residue	Not tested	Not tested

**Static sampling -: Not quantified due to no efficiency*

Table 12-3 Summary of dispersibility results on ULFSO Shell 2019 by use of the BFT method (SL Ross) at 20 °C

	Without Dispersant	**With Corexit 9500A (DOR1:20)**
ULSFO Fresh (WS0)	< 1%	3 %
ULSFO 2 Day (WS1)	< 1%	7 %
ULSFO 14 Day (WS2)	< 1%	6 %

12.4 Ignitability /ISB

The interlaboratory ignitability / ISB comparison tests on the ULSFO Shell 2019 oil conducted at SINTEF and SL Ross were performed by using their standard ISB-test methods and operating procedures, see details of SINTEF methodology in section 9 and SL Ross in Appendix E. Because of the different bench-scale weathering (evaporative loss and emulsification, see section 12.1-12.2), the three burning tests performed at SL Ross Laboratories included:

- ULSFO fresh (WS0)
- 0.3 vol% evaporated: ULSFO (WS1)
- 1 vol% evaporated: ULSFO (WS2)

As SL ROSS did not obtain any emulsification in the rotating flask method with the ULSFO, they therefore did not prepare any emulsions for the ISB testing. While SINTEF performed the following three ISB tests with the ULSFO oil:

- Fresh (non-weathered) ULSFO water free (0% water)
- Fresh (non-weathered) ULSFO w/o-emulsion (30% water)
- Fresh (non-weathered) ULSFO w/o-emulsion (50% water)

The total six ISB tests was performed at the two laboratories gave therefore a complimentary documentation of the ignitability and burning effectiveness of fresh, weathered, and emulsified ULSFO Shell 2019. Only the burn tests of the fresh, water-free ULFSO at the two laboratories was compared and discussed. The main purpose with interlaboratory ISB testing between SINTEF and SL Ross was to evaluate how the difference in the existing test apparatus and test procedures influence on the test results. The similarities and differences can be sum up by the following bullet points:

- The confinement area / oil volume: SINTEF: 0.36 m^2 (square) / 6 L. SL Ross: 0.13 m^2 (circular ring) / 2.5 L. This give an initial oil layer thickness in the same range: 1.7 cm (SINTEF) and 2.0 cm (SL Ross).
- Ignition: The "step-wise" procedures at the two laboratories to ignite the oil have many similarities, however, the initial propane torch is omitted at SINTEF and the ignition attempt is beginning by applying a plastic bag of 100 mL gelled gasoline/diesel. The starting time (time zero) is defined when the gel is ignited. At SL Ross, the first ignition step is up to three attempts of up to 10 seconds with a propane torch. If unsuccessful, the oil is allowed to cool for approximately 30 minutes before applying and ignition of the gelled gasoline. Starting time (time zero) is defined when the flame starts to spread to the oil.
- Burning time is defined as the intense burn from full ignition of the oil (100 % oil coverage) to burn ramp down to a 50% flame coverage (in both laboratories)
- Burning Effectiveness (% BE): is defined as the mass burn relative to the mass of starting oil (emulsion).
- The main difference in the results between the two test procedures, is the burning time (6 min. at SINTEF versus 17 min. at SL Ross) and the burning effectiveness (BE = 42% at SINTEF versus BE = 93% at SL Ross). The "static" burn conditions in the SINTEF tests approach, is simulating more closely the burn of a "free" drifting oil slick following the upper water layer just beneath the slick. The lower BE obtained in the SINTEF ISB tests, is mainly due to that the upper water layer under the oil will be heated and eventually start to boil at an earlier stage during the burn. The boiling generate turbulence, which will influence on the burn intensity but promote the early termination of the burn. While, in the SL Ross test apparatus having a slow water flow-through (circulation) under the burn containment ring simulates oil being towed in a boom behind a ship. Although it is possible that the slow current creates a deeper slick thickness downstream of the current to support longer burning times, this is likely not a large factor in the increased time period of the SL Ross burns. As the oil burns are reaching completion, the residual burning is not isolated to the downstream portion of the ring.

- Another difference in the ISB test conditions that may contribute to the span in the BE- results, is that the SINTEF testing is an out-door system, with a small "free-board" (approx. 1-2 cm) in order to minimize the heat radiation from the steel-tray. While the heat shields in the SL Ross tank will likely reflect some of the generated heat back to the burn, which helps in maintaining the burn.
- The calculated burning rate during the intense burning period is, however, in the same range for the for the two test systems, i.e.: around 1 mm / min.

12.5 Conclusion of the interlaboratory comparison studies

The ULSFO Shell 2019 was a challenging oil for use as interlaboratory calibration test oil due to its high viscosity, extreme high pour point and solidifying properties and stickiness that influence on the test results. However, there has been a lot of lessons learned for both laboratories from this interlaboratory comparison study that form a good basis for further harmonisation of laboratory test methodologies and standardisation, including harmonized laboratory protocols for:

- Oil weathering (incl. evaporation, emulsification, photooxidation, etc)
- *In-situ* burning testing (both ignitability and burning effectiveness)
- Dispersant effectiveness testing
- WAF / toxicity testing
- Implementation of experimental data into numerical models for oil weathering predictions

It is recommended that this limited interlaboratory comparison study should be followed up with workshops that may also involving other relevant oil spill laboratories for designing a more extensive interlaboratory calibration and harmonization of test methodologies and operational procedure using additional 2-3 different oil qualities (also including mesoscale flume weathering tests). A goal should be to agree upon international standardized test protocols.

13 Conclusion and further recommendations

From January 2020, the International Maritime Organization (IMO) has implemented a new regulation for a 0.5 % Global Sulfur Cap for marine fuel oil used on board ships operating outside designated emission control areas (SECA). This new global limit of 0.5 % m/m (mass by mass) is replacing the former limit of 3.5 % m/m and will significantly reduce the amount of sulfur oxides (SOx) emissions from ships to air. As referred by IMO, this reduction of sulfur in marine fuel oils should have major health and environmental benefits for the world, particularly for populations living close to ports and coasts.

The three sulfur-compliant residual LSFOs tested showed a wide span in the physico-chemical properties that likely reflects the different refineries "recipes" to comply with the new sulfur limits. The oil properties will be dependent on the refinery type, feedstock (e.g. switch to sweeter crude oils) and upgrading of the different conversion processes (e.g. hydro-desulfurization, catalytic cracking, use of visbreaking) to reduce the amount sulfur and residual material.

The project has provided an increased knowledge and documentation of the weathering properties and behaviour of the LSFOs if spilled at sea, both in cold climate (arctic) and moderate (North Sea summer) seawater temperatures. The LSFOs investigated in this project and previous limited studies have showed a wide span in the oil properties with relevance to behaviour when spilled at sea. Moreover, the oils tested indicate a high degree of persistence on the sea surface, and the oil spill response can even be more challenging than the previous traditional intermediately fuel oils (e.g. IFO180 / 380), particularly in cold water spill situations:

- The effectiveness of using dispersants may be limited due to either high viscosities of the emulsions and/or high pour point of the oils
- The potential for use of ISB can be limited as the ignitability may be slow (i.e. extended ignition time) due to low contents of volatiles. Small amount of water uptake (emulsification) may also prevent the oil to be ignited without use of significant amount of primers (e.g. diesel)
- The effectiveness of mechanical recovery is dependent on the choice of skimmer system that force contact between the oil and the recovery unit. Oils with high pour points will e.g. need an "active" high viscosity or belt skimmer designated for solidified oils at sea

From an oil spill response point of view, it is therefore crucial to get a better overview and knowledge of the variability in the weathering processes, fate and behaviour and response capabilities to the new LSFOs. The ongoing change among refineries to comply with the new sulfur regulations require a need for further characterization of the increasing numbers of LSFOs coming on the marked.

Further recommendations:

- Small-volume samples of LSFO marine fuels (both distillate and residual fuels) from a larger number of refineries should be collected for a screening testing of simple oil parameters (e.g. TBP, density viscosities, pour-points, gas-chromatography, emulsifying properties) tested at relevant sea temperatures
- Based on such a preliminary screening, a selection of oils should be followed up with a more extensive oil weathering characterization and meso-scale / basin testing of relevant response techniques (dispersants, ISB, different skimmer concepts etc.), and shoreline adhesion and response techniques
- Further harmonization of test methodologies and test protocols among oil spill laboratories
- Gain a better knowledge of the differences in the chemical composition (e.g. key biomarkers and UCM; unresolved complexed mixture) between "traditional" marine fuels and the new generation of sulfur-compliant marine fuels (both distillates and residuals), by e.g. use of today's high-resolution analytical techniques
- A co-operation with the down-stream refinery industry would facilitate the possibility for refining marine LSFO formulations with improved oil spill response capabilities

14 References

Aurand, D., and G. Coelho. 2005. Cooperative Aquatic Toxicity Testing of Dispersed Oil and the "Chemical Response to Oil Spills: Ecological Research Forum (CROSERF)". Ecosystem Management & Associates, Inc., Lusby, MD. Technical report 07-03, 105 pages + Appendices

Bridié, A.L., Wanders, T. H., Zegweld, W. V. and den Heijde, H. B., 1980. Formation, Prevention and Breaking of Seawater in Crude Oil Emulsions, Chocolate Mousse. Marine Poll. Bull., vol. 11, pp. 343-348.

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.

DiToro, D.M., J.A. McGrath, and W.A. Stubblefield. 2007. Predicting the toxicity of neat and weathered crude oil: Toxic potential and the toxicity of saturated mixtures. Environmental Toxicity and Chemistry. 26: 24-36.

Faksness, L.G. and D. Altin (2017). WAF and toxicity testing of diesel and hybrid oils. SINTEF report OC2017-A122, ISBN 978-82-7174-297-3.

Faksness, L.G., and D. Altin (2019). Chemical characteristics and acute toxicity of field generated in situ burning residues. From Oil-on-eater 2018. SINTFE report 2019:00818, ISBN 978-82-14-06398-1.

Hellstrøm, K.C (2017): Weathering Properties and Toxcicity of Marine Fuel oils. Summary report. SINTEF report OC2017-A124.

Hellstrøm, K.C., Daling. P.S, Brönner U., Sørheim, K.R., Johnsen, M., Leirvik., F. (2017). Memo report. SINTEF OC2017-123.

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

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

IMO International Maritime Organization. http://www.imo.org/en/mediacentre/hottopics/pages/sulphur-2020.aspx

ISO [International Organization for Standardization] 2006a.Water quality - Marine algal growth inhibition test with *Skeletonema costatum* and *Phaeodactylum tricornutum*. ISO 10253:2006.

ISO [International Organization for Standardization] 2006b. Water quality – Guidelines for algal growth inhibition tests with poorly soluble materials, volatile compounds, metals and wastewater. ISO 14442:2006.

ISO [International Organization for Standardization] 1999. Water quality - Determination of acute lethal toxicity to marine copepods (Copepoda, Crustacea). ISO 14669:1999.

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

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

McCarty, L.S., Mackay, D., Smith, A.D., Ozburn, G.W., and Dixon, D.G. (1992). Residue-based interpretation of toxicity and bioconcentration QSARs from aquatic bioassays: Neutral narcotic organics. Environmental Toxicology and Chemistry 11, 917-930.

McCarty, L.S., D. Mackay, A.D. Smith, G.W. Ozburn, and D.G. Dixon. 1993. Residue-based interpretation of toxicity and bioconcentration QSARs from aquatic bioassays: Polar narcotic organics. Ecotoxicology and Environmental Safety. 25, 253-270.

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.

McGrath, J.A., and D.M. DiToro (2009). Validation of the target lipid model for toxicity assessment of residual petroleum constituents: monocyclic and polycyclic aromatic hydrocarbons. Environ. Toxicol. Chem. 28: 1130-1148.

Neff, J.M. 2002. Bioaccumulation in marine organisms. Effects of contaminants from oil well produced water. Elsevier, Amsterdam, Netherlands. 452 p.

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

Rand, G.M., Wells, P.G., and McCarty, L.S. 1995. Introduction to aquatic toxicology. In: Fundamentals of aquatic toxicology 2nd edition (Rand, G.M (ed)), Taylor & Francis Publishers, Washington DC, pp. 3-67.

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

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

Singer, M.M., D. Aurand, G.E. Bragin, J.R. Clark, G.M. Coelho, M.L. Sowby, and R.S. Tjeerdema (2000). Standardization of the Preparation and Quantification of Water-Accommodated Fractions of Petroleum for Toxicity Testing. Marine Pollution Bulletin. 40: 1007-1016.

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

Srinivasan, R., Lu, Q., Sorial, G. A., Venosa, A. D., & Mullin, J. (2007). Dispersant Effectiveness of Heavy Fuel Oils Using Baffled Flask Test. *Environmental Engineering Science*, *24*(9), 1307–1320. https://doi.org/10.1089/ees.2006.0251

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

Sørheim, K.R, Daling, P.S., Pettersen, T-A., Johnsen, M., 2014. Dispergerbarhet av bunkersoljer. Rapport nr. A26179. ISBN:978-821-40-574-09

Sørheim, K.R., and Daling, P.S., 2015. Fysikalsk-kjemiske analyser og emulgeringsegenskaper av ulike dieselkvaliteter. Rapport nr. A27122, ISBN; 987-821-405-844-4

US EPA, Method 8015D. 2003. Non-halogenated organics using GC/FID.http://www.epa.gov/epawaste/hazard/testmethods/sw846/new_meth.htm#8015D

US EPA, Method 8260C, 2006. Volatile organic compounds by gas chromatography/mass spectrometry (GC/MS). http://www.epa.gov/osw/hazard/testmethods/sw846/new_meth.htm#8260C

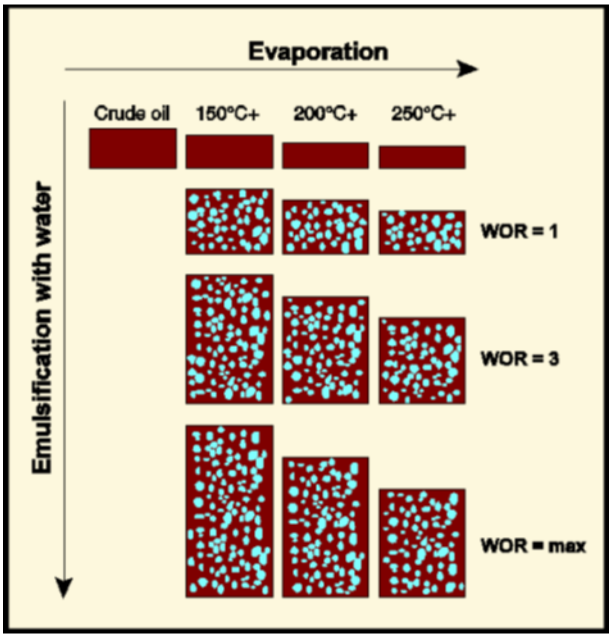
US EPA, Method 8270D, 2007. Semivolatile Organic Compounds by GC/MS. http://www.epa.gov/wastes/hazard/testmethods/sw846/pdfs/8270d.pdf

Venosa, A. D., King, D. W., & Sorial, G. A. (2002). The Baffled Flask Test for Dispersant Effectiveness: A Round Robin Evaluation of Reproducibility and Repeatability. *Spill Science & Technology Bulletin*, *7*(5), 299 308. https://doi.org/10.1016/S1353-2561(02)00072-5

Appendix A Experimental setup

A.1 Bench-scale laboratory methodology

To isolate and map the various weathering processes at sea, the crude oil was exposed to a systematic, stepwise procedure developed at SINTEF (Daling et al. 1990). The general procedure is illustrated in Figure A-1.



WOR: Water to Oil Ratio

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

Figure A-1 ***Bench-scale laboratory weathering flow chart of oil***

A.2 Evaporation

The evaporation procedure used is described in Stiver and Mackay (1984). Evaporation of the lighter compounds from the fresh condensate was carried out as a simple one-step distillation to vapor temperatures of 150°C, 200°C and 250°C, which resulted in 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.

A.3 Physical and chemical analysis

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

Table A-1 ***Analytical methods used to determine the physical properties***

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

Table A-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

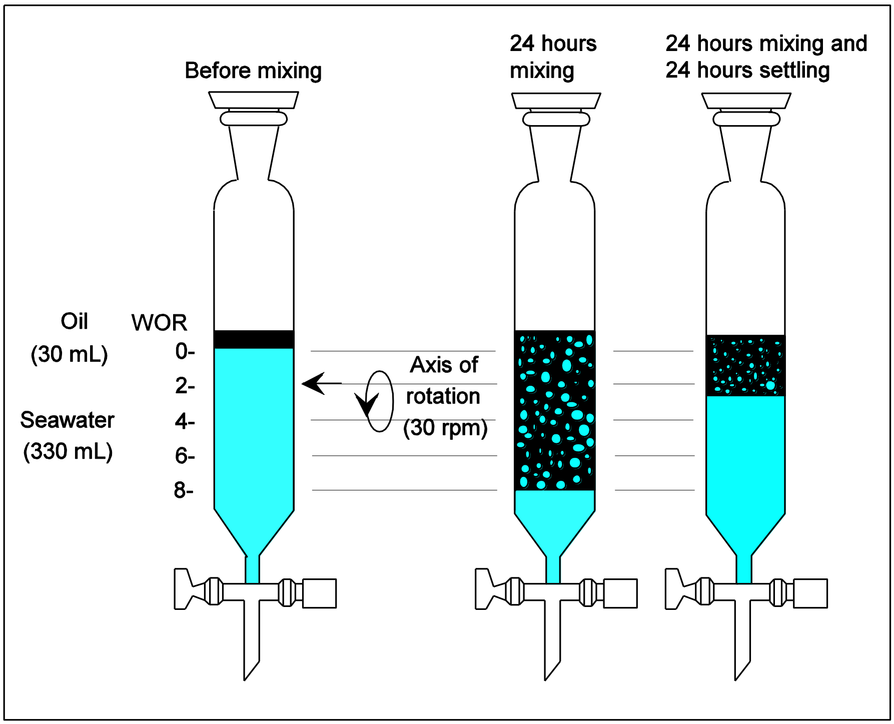
- The distribution of hydrocarbons (nC_5-nC_{40}) was analysed using a Gas Chromatograph coupled with a Flame Ionisation Detector (GC-FID). The Gas Chromatograph used was an Agilent 6890N with a 30m DB1 column.
- The analysis and quantification of PAHs, phenols, and alkylated phenols (C_0-C_4) were completed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

A.4 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 A-2. Oil (30 mL) and seawater (300 mL) are mixed and rotated with a rotation speed of 30 rpm in separating funnels (0.5 L). The emulsification kinetics is mapped by measuring the water content at fixed rotation times. The maximum water content is determined after 24 hours of rotation.



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

Figure A-2 Principle of the rotating cylinder method

A.5 Chemical dispersibility testing

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 (Figure A-3).

MNS (Mackay-Nadeau-Szeto test, 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. (Figure A-3).

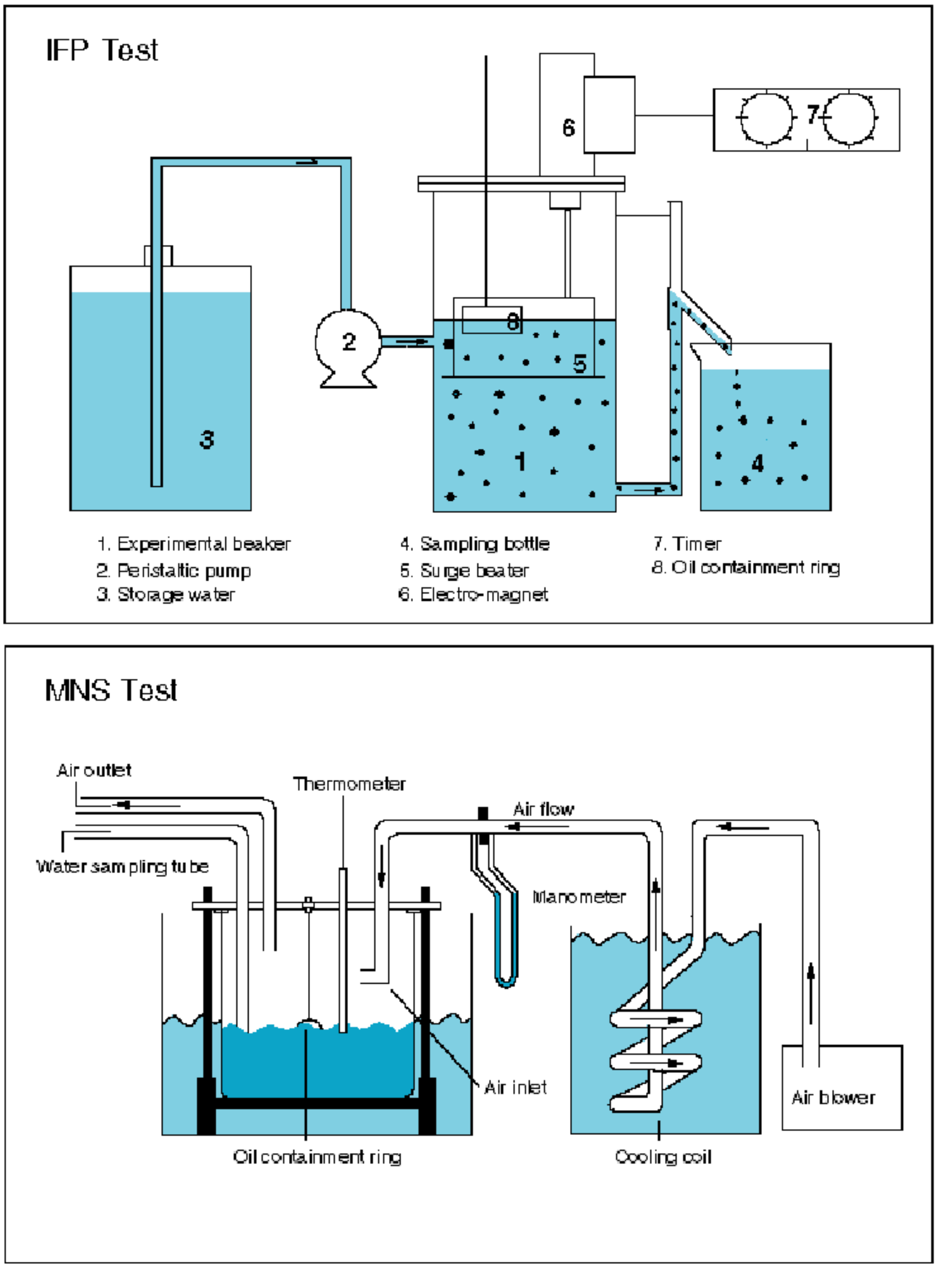


Figure A-3 *IFP and MNS test apparatus*

Appendix B Input data to SINTEF Oil Weathering Model (OWM)

The obtained laboratory data are customized for input to SINTEF OWM (weathering model). The tabulated laboratory oil data for VLSFO Chevron 2019, VLSFO Shell 2019 and ULSFO Shell 2019 tested in this project are given Table B-1 to Table B-8. The input data were based on the weathering data at 13 °C that gave the most reliable predictions at 2 and 15 °C, except from the VLSFO Chevron 2019 where predictions at 2 °C for viscosity and water-uptake harmonized better with the laboratory data at 2 °C.

Table B-1 Physical and chemical properties of the fresh oils for VLSFO Chevron 2019, VLSFO Shell 2019, and ULSFO Shell 2019

Summary properties of fresh oil	VLSFO Chevron 2019 SINTEF ID: 2019-3955	VLSFO Shell 2019 SINTEF ID: 2019-7685	ULSFO Shell 2019 SINTEF ID: 2019-11170
Density (60 F/15.5°C) (g/mL)	0.989	0.9895	0.917
Pour point (°C)	9	3	24
Reference temperature (°C)	2 / 13	13	13
Viscosity at ref. temp. (mPa·s = cP) *	28399 / 3948	16507	5986
Asphaltenes (wt. %)	0.44	4.8	0.14
Wax content (wt. %)	4.5	4.9	20.7
Flash point (°C)	109**	100**	85***
Dispersible for visc. <	4000	20000	-
Not dispersible for visc. >	25000	100000	-

** Measured at shear rate 100 s^{-1} ** From certificate of analysis (COA), ***Data from SLRoss, Canada -:no data*

Table B-2 True boiling point (TBP) curve for VLSFO Chevron 2019 (TBP based on simulated distillation)

Temp. (°C)	VLSFO Chevron 2019 (vol. %)
204	1.4
240	2.6
261	3.8
277	4.9
292	6.1
304	7.3
320	9.6
330	11.8
347	17.5
358	23.1
370	28.8
378	34.3
386	39.9
394	45.5
403	51.0
410	56.5
419	62.0
427	67.5
436	73.0
447	78.0

460	83.8
475	89.2
530	99.9
555	100

Table B-3 True boiling point (TBP) curve for VLSFO Shell 2019 (TBP based on simulated distillation)

Temp. (°C)	**VLSFO Shell 2019 (vol. %)**
186	1.4
207	3.8
221	5.1
247	7.5
271	9.8
292	12.2
320	15.6
336	17.9
357	21.3
368	23.6
393	29.1
415	34.7
455	45.6
476	51.0
496	56.4
515	61.7
536	67.0
557	72.3
576	77.6
595	82.8
616	88.0
640	93.1
656	96.2
685	100

Table B-4 True boiling point (TBP) curve for VLSFO Shell 2019 (TBP based on simulated distillation)

Temp. (°C)	**ULSFO Shell 2019 (vol. %)**
186	1.4
207	3.8
221	5.1
247	7.5
271	9.8
292	12.2
320	15.6
336	17.9
357	21.3

368	23.6
393	29.1

Table B-5 Summary lab weathering and customized data (italic) of VLSFO Chevron 2019, 2 °C

Properties	**Fresh**	**150°C+**	**200°C+**	**250°C+**
Vol. Topped (%)	0	*0.05*	*1.4*	*3.0*
Weight Residue (wt. %)	100	*100*	*99*	*98*
Density (g/mL)	0.989	*0.989*	*0.990*	*0.991*
Pour point (°C)	9	*9*	*10*	*11*
Flash Point (°C)	109	*109*	*110*	*111*
*Viscosity of water-free residue (mPa.s =cP)	28399	*28399*	*30000*	*31000*
**Viscosity of 50% emulsion (mPa.s = cP)	-	-	-	-
**Viscosity of 75% emulsion (mPa.s = cP)	-	-	-	-
**Viscosity of max water (mPa.s = cP)	-	80274	-	-
Max. water cont. (vol. %)	-	27	*27*	*27*
(T1/2) Halftime for water uptake (hrs)	-	3	*3*	*3*
Stability ratio	-	1.0	*1.0*	*1.0*

* Measured at shear rate 100 s^{-1} ** Measured at shear rate 10 s^{-1} - No data

Table B-6 Summary lab weathering and customized data (italic) of VLSFO Chevron 2019, 13 °C

Properties	**Fresh**	**150°C+**	**200°C+**	**250°C+**
Vol. Topped (%)	0	*0.05*	*1.4*	*3.0*
Weight Residue (wt. %)	100	*100*	*99*	*98*
Density (g/mL)	0.989	*0.989*	*0.990*	*0.991*
Pour point (°C)	9	*9*	*10*	*11*
Flash Point (°C)	109	*109*	*110*	*111*
*Viscosity of water-free residue (mPa.s =cP)	3948	*3948*	*4200*	*4300*
**Viscosity of 50% emulsion (mPa.s = cP)	-	-	-	-
**Viscosity of 75% emulsion (mPa.s = cP)	-	-	-	-
**Viscosity of max water (mPa.s = cP)	-	35468	-	-
Max. water cont. (vol. %)	-	54	*54*	*54*
(T1/2) Halftime for water uptake (hrs)	-	4	*4*	*4*
Stability ratio	-	0.82	*0.90*	*1.0*

* Measured at shear rate 100 s^{-1} ** Measured at shear rate 10 s^{-1} - No data

Table B-7 ***Summary lab weathering and customized data (italic) of VLSFO Shell 2019***

Properties	**Fresh**	**150°C+**	**200°C+**	**250°C+**
Vol. Topped (%)	0	*0*	*3.5*	7.9
Weight Residue (wt. %)	100	*100*	*97*	92.7
Density (g/mL)	0.9895	*0.9895*	*0.992*	0.9961
Pour point (°C)	3	*3*	*6*	12
Flash Point (°C)	100	*100*	*105*	110
*Viscosity of water-free residue (mPa.s =cP)	16507	*16507*	*40000*	68041
**Viscosity of 50% emulsion (mPa.s = cP)	-	-	-	-
**Viscosity of 75% emulsion (mPa.s = cP)	-	-	-	-
**Viscosity of max water (mPa.s = cP)	-	76438	*150000*	321340
Max. water cont. (vol. %)	-	57	*55*	52
(T1/2) Halftime for water uptake (hrs)	-	2	*4.4*	6.6
Stability ratio	-	1.0	*0.80*	0.34

** Measured at shear rate 100* s^{-1} *** Measured at shear rate 10* s^{-1} *- No data*

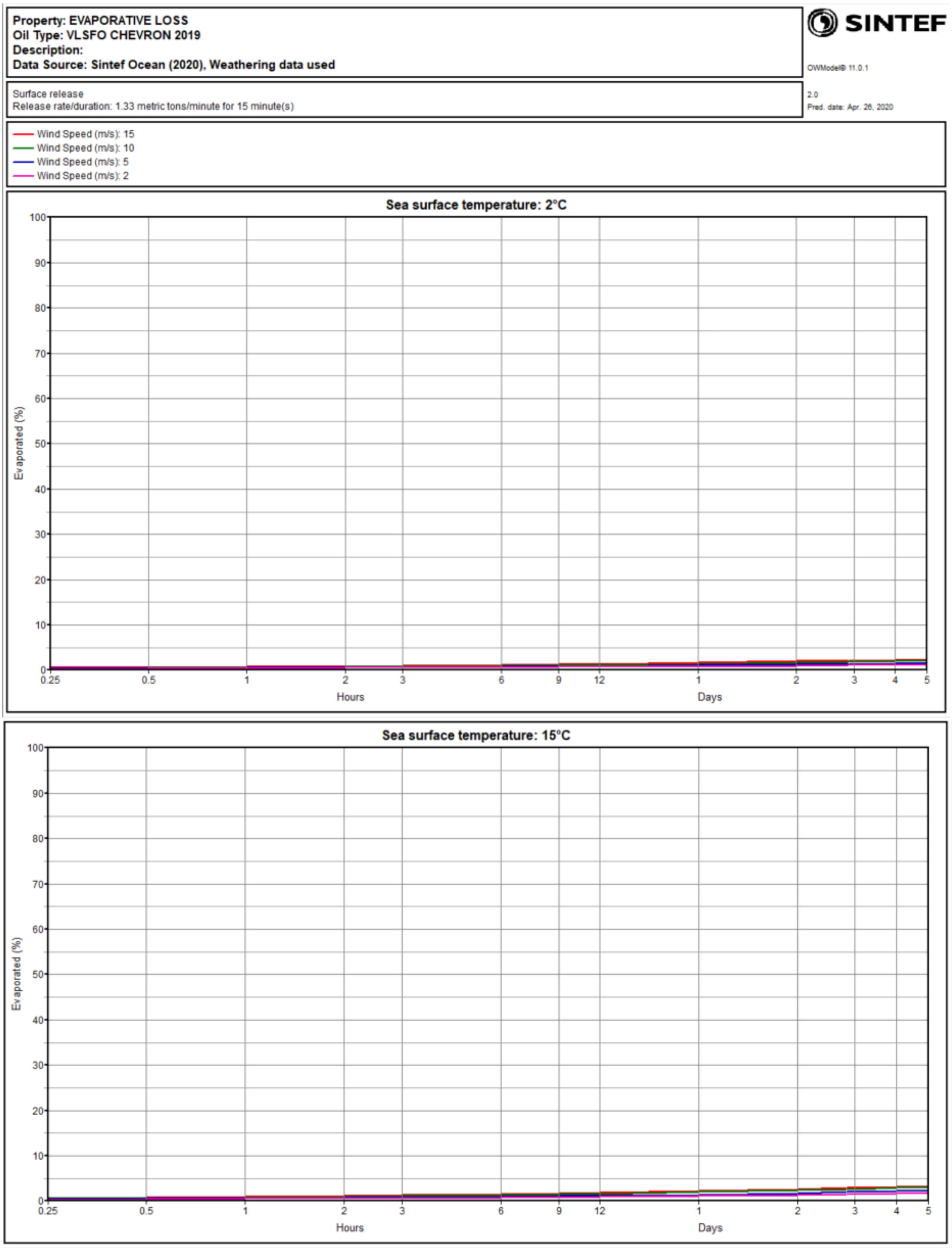
Table B-8 ***Summary lab weathering and customized data (italic) of VLSFO ULSFO***

Properties	**Fresh**	**150°C+**	**200°C+**	**250°C+**
Vol. Topped (%)	0	*0*	3	5
Weight Residue (wt. %)	100	*100*	98	96
Density (g/mL)	0.917	*0.917*	0.920	0.922
Pour point (°C)	24	*24*	27	30
Flash Point (°C)	85	*85*	87	89
*Viscosity of water-free residue (mPa.s =cP)	5986	*5986*	9903	14826
**Viscosity of 50% emulsion (mPa.s = cP)	-	33143	-	-
**Viscosity of 75% emulsion (mPa.s = cP)	-	-	-	-
**Viscosity of max water (mPa.s = cP)	-	38194	36420	60024
Max. water cont. (vol. %)	-	67	38	44
(T1/2) Halftime for water uptake (hrs)	-	67	38	44
Stability ratio	-	1.4	1.5	1.6

** Measured at shear rate 100* s^{-1} *** Measured at shear rate 10* s^{-1} *- No data*

Appendix C OWM predictions

C.1 Predictions of VLSFO Chevron 2019



Property: EVAPORATIVE LOSS
Oil Type: VLSFO CHEVRON 2019
Description:
Data Source: Sintef Ocean (2020), Weathering data used

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

OWModel® 11.0.1
2.0
Pred. date: Apr. 26, 2020

Figure C-1 Evaporative loss VLSFO Chevron 2019 at sea temperatures of 2 and 15 °C

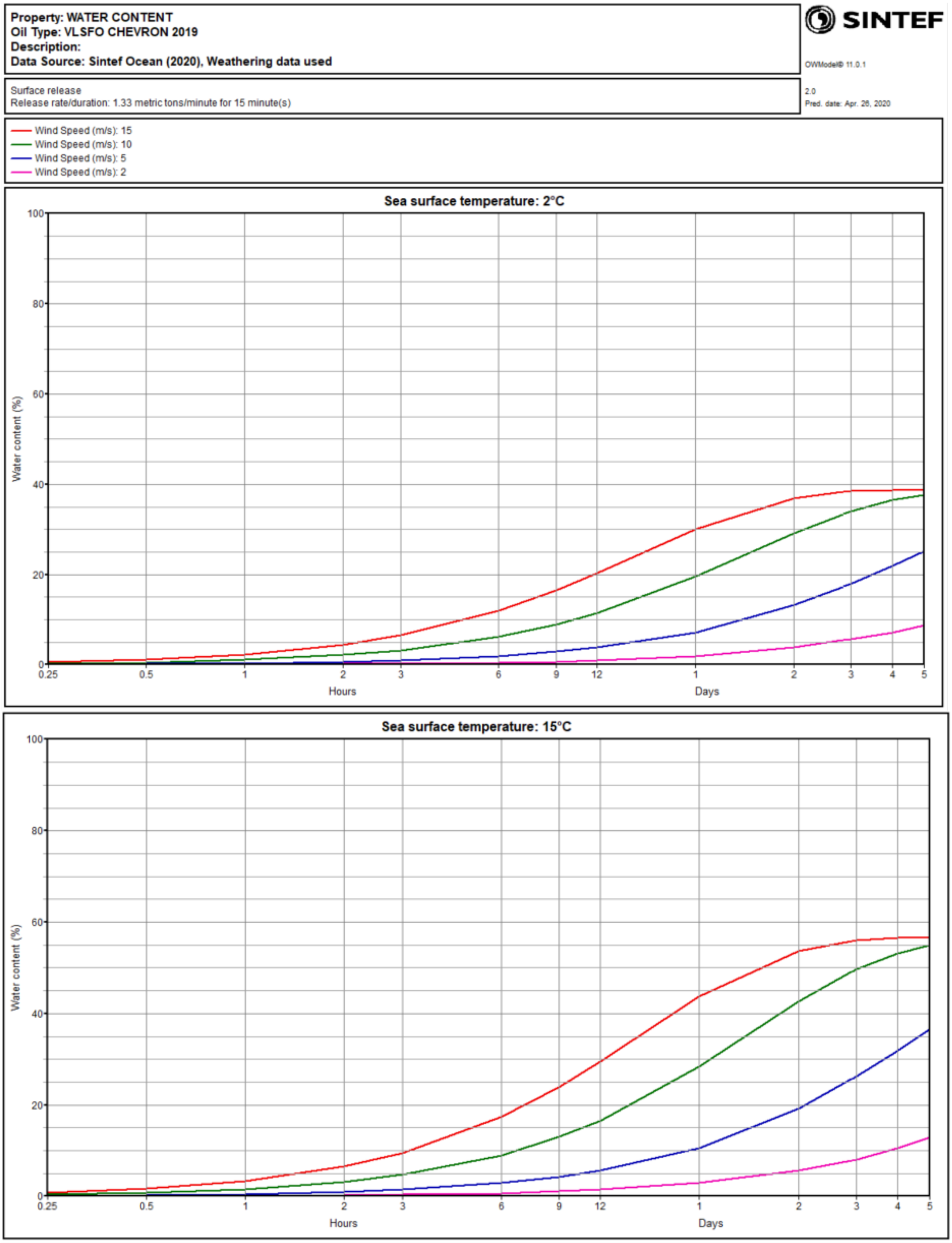
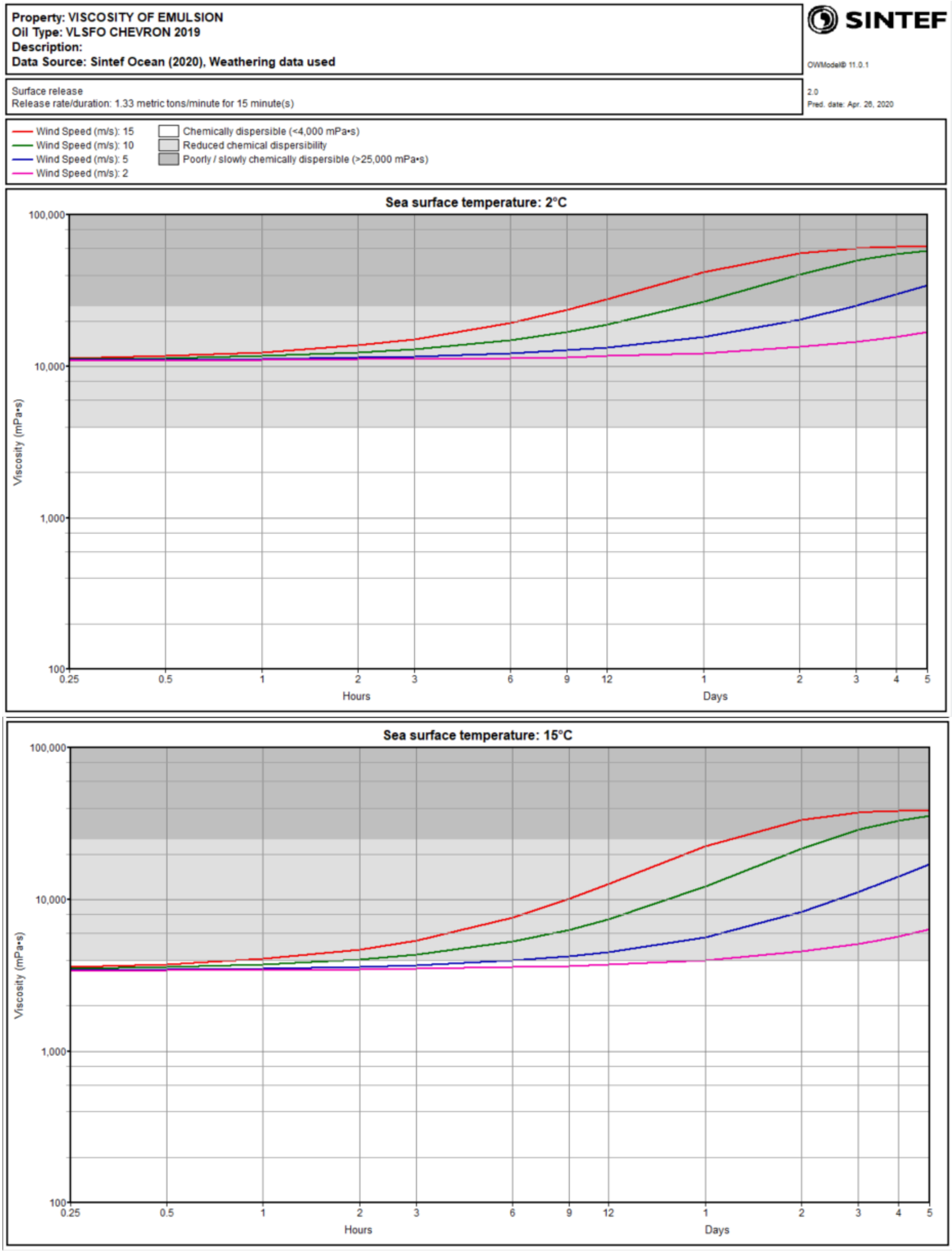


Figure C-2 *Water content of VLSFO Chevron 2019 at sea temperatures of 2 and 15 °C*



Property: VISCOSITY OF EMULSION
Oil Type: VLSFO CHEVRON 2019
Description:
Data Source: Sintef Ocean (2020), Weathering data used

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

OWModel© 11.0.1
2.0
Pred. date: Apr. 26, 2020

Wind Speed (m/s): 15	☐ Chemically dispersible (<4,000 mPa•s)
Wind Speed (m/s): 10	▨ Reduced chemical dispersibility
Wind Speed (m/s): 5	▨ Poorly / slowly chemically dispersible (>25,000 mPa•s)
Wind Speed (m/s): 2	

Figure C-3 Emulsion viscosity of VLSFO Chevron 2019 at sea temperatures of 2 and 15 °C

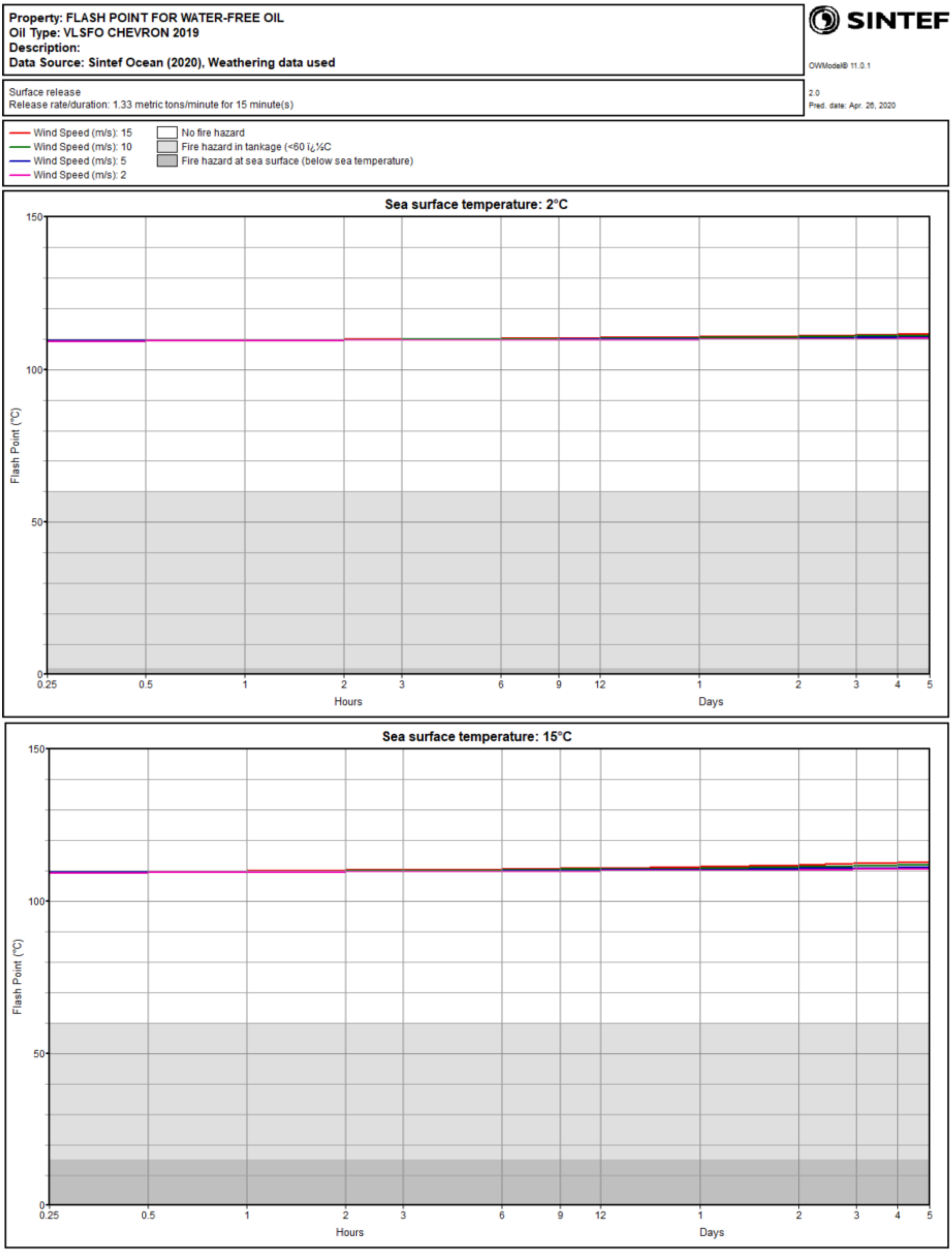
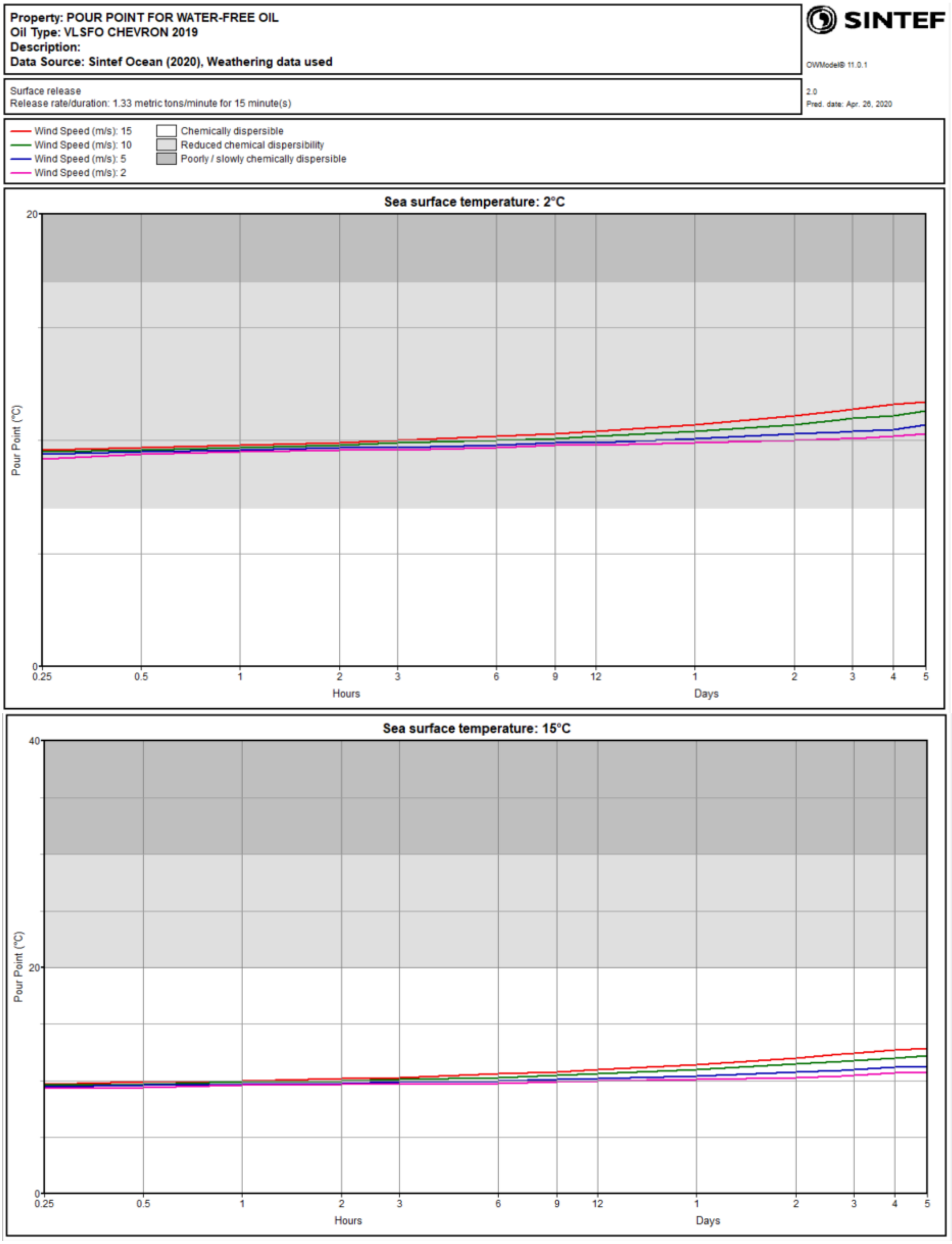


Figure C-4 Flash point of VLSFO Chevron 2019 at sea temperatures of 2 and 15 °C



Property: POUR POINT FOR WATER-FREE OIL
Oil Type: VLSFO CHEVRON 2019
Description:
Data Source: Sintef Ocean (2020), Weathering data used

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

OWModel® 11.0.1
2.0
Pred. date: Apr. 26, 2020

Figure C-5 Pour point of VLSFO Chevron 2019 at sea temperatures of 2 and 15 °C

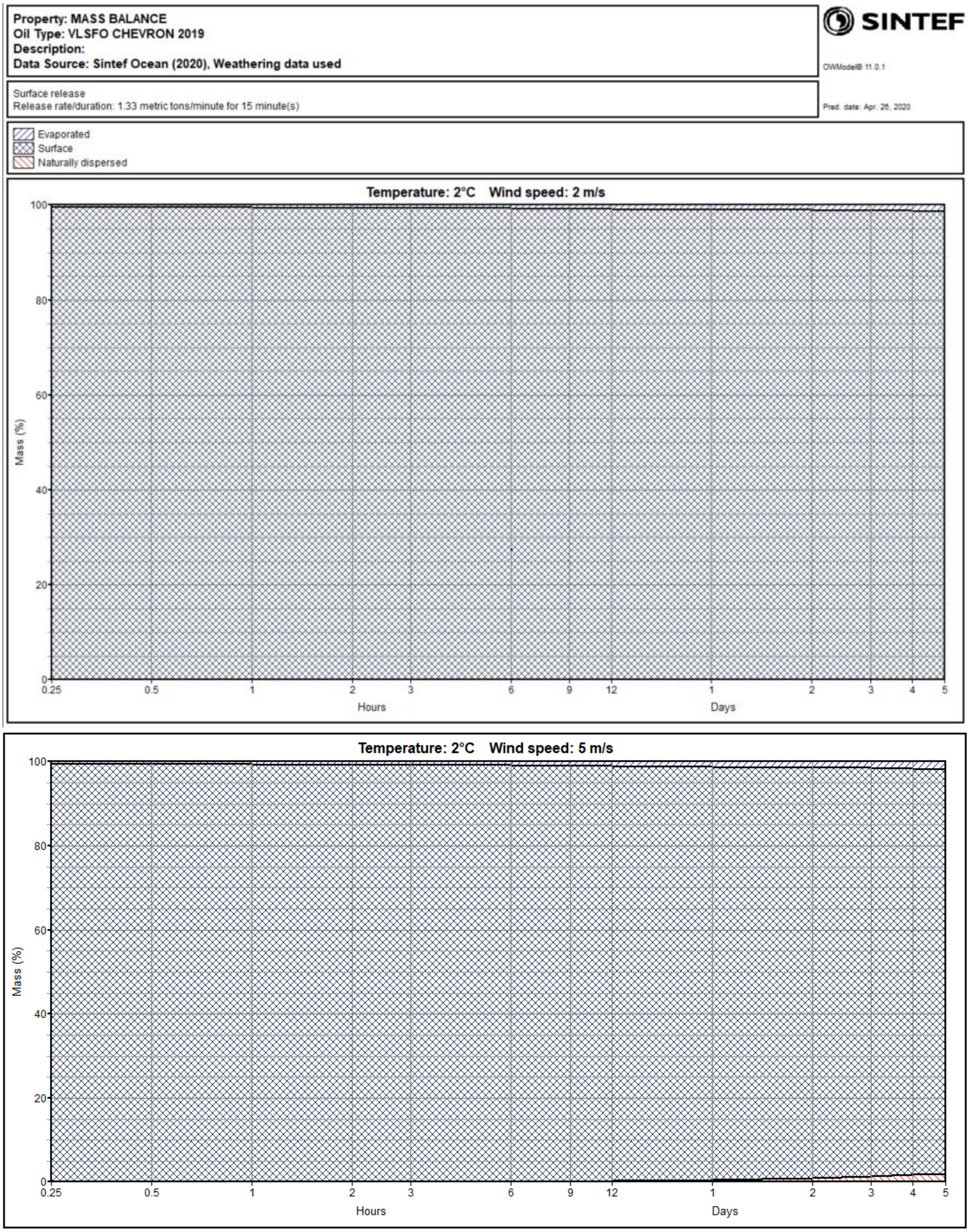


Figure C-6 Mass balance of VLSFO Chevron 2019 at sea temperatures of 2 °C, at 2 and 5 m/s

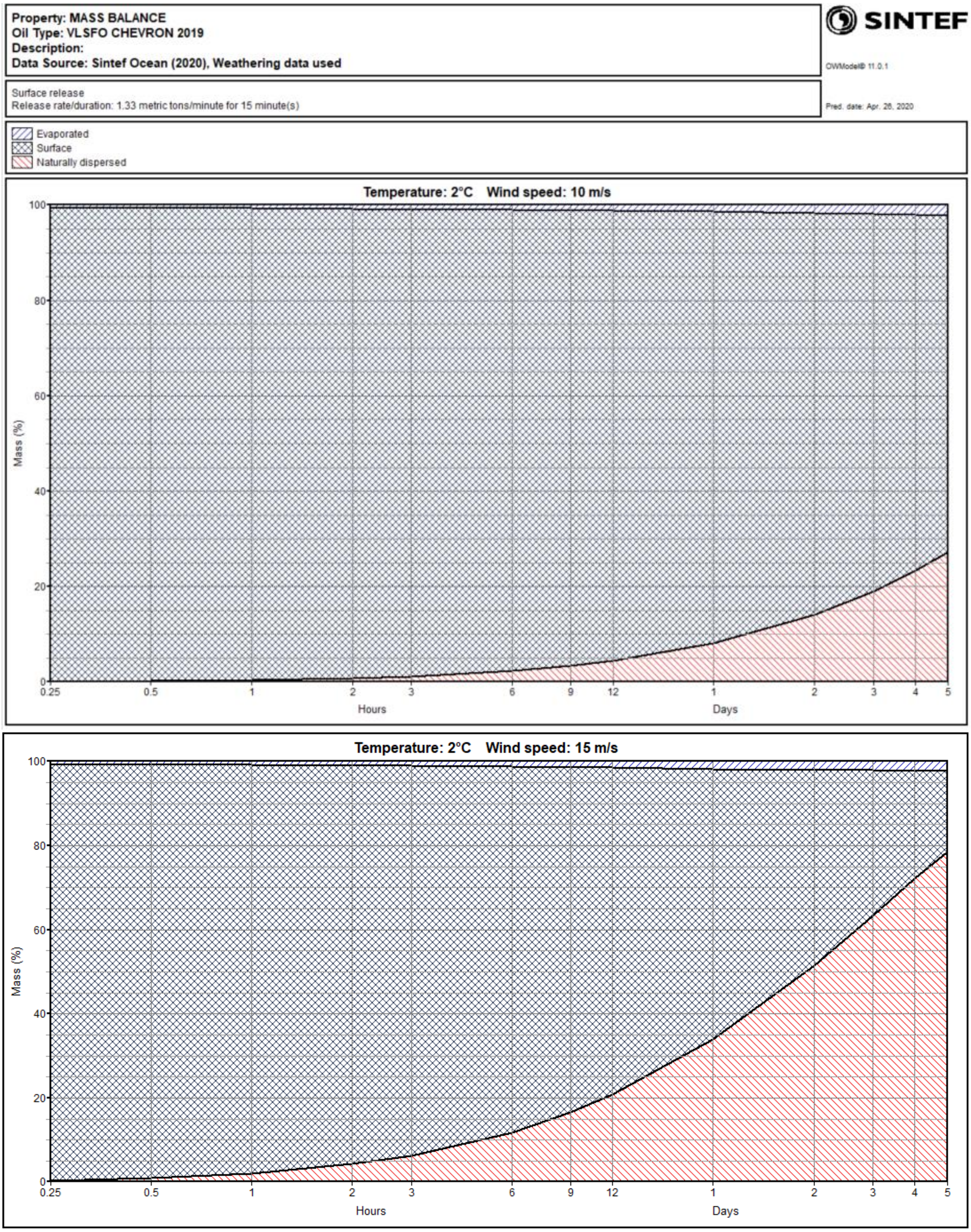


Figure C-7 *Mass balance of VLSFO Chevron 2019 at sea temperatures of 2 °C, at 10 and 15 m/s*

Property: MASS BALANCE
Oil Type: VLSFO CHEVRON 2019
Description:
Data Source: Sintef Ocean (2020), Weathering data used

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

OWModel® 11.0.1
Pred. date: Apr. 28, 2020

Figure C-8 Mass balance of VLSFO Chevron 2019 at sea temperatures of 15 °C, at 2 and 5 m/s

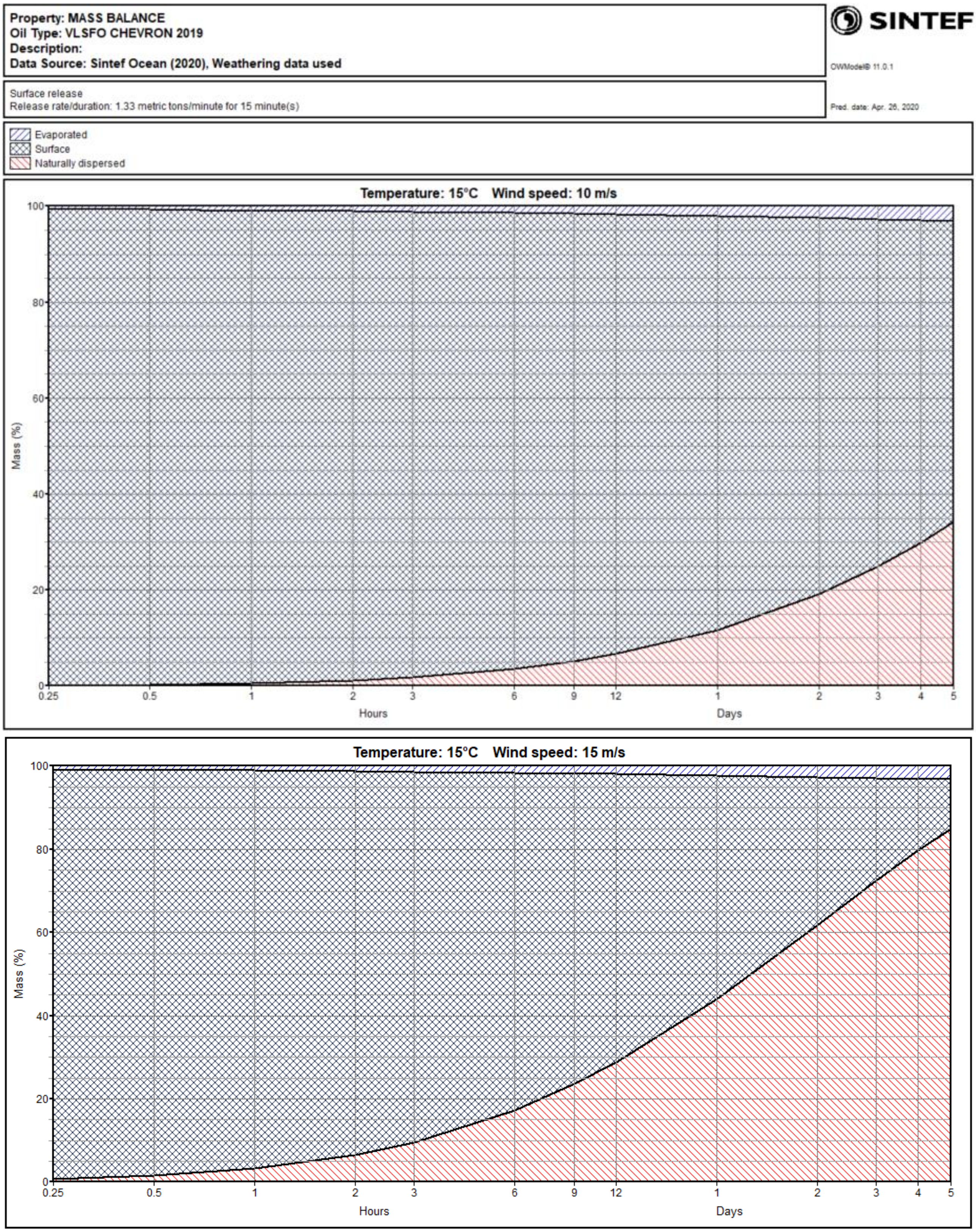
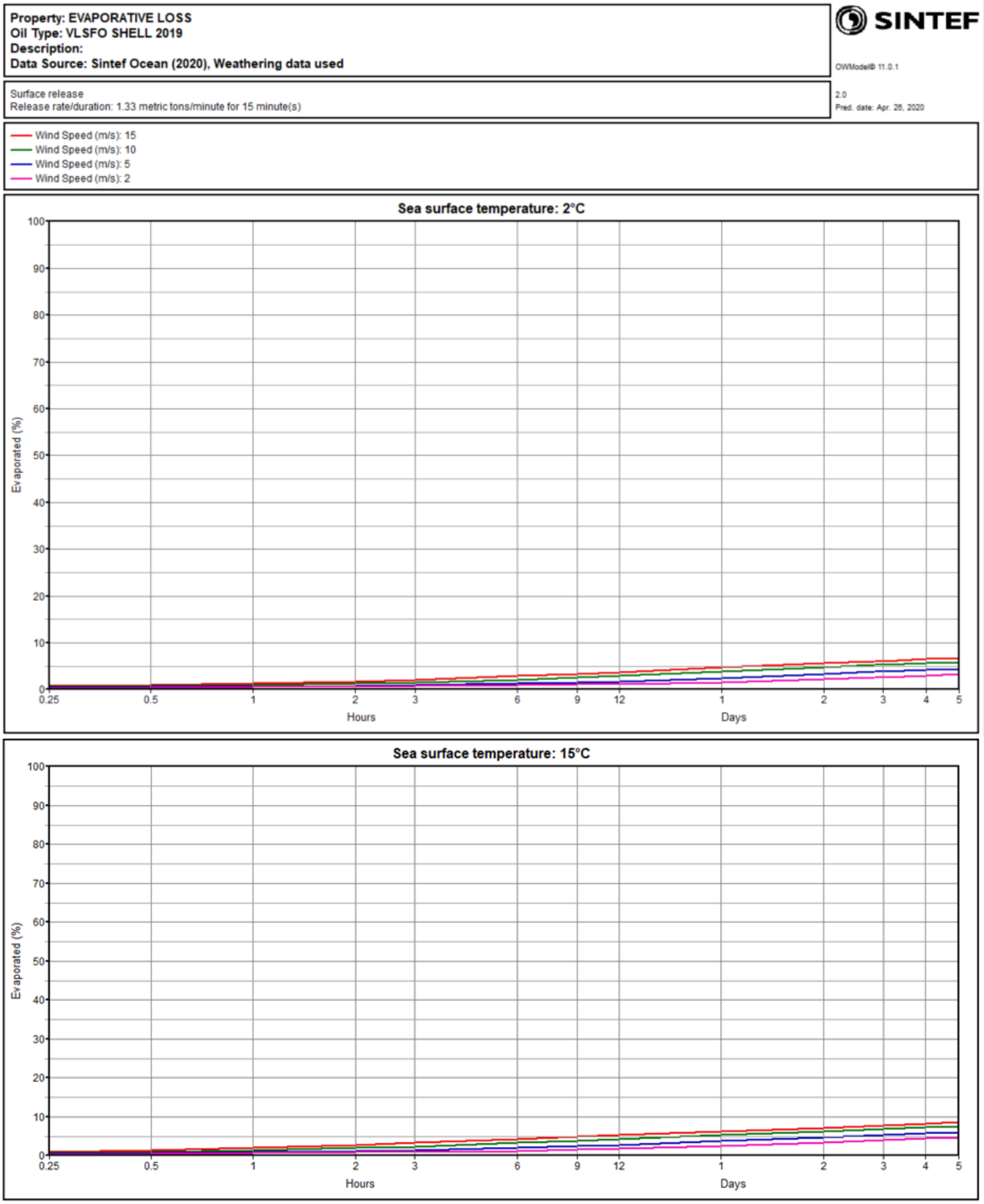


Figure C-9 Mass balance of VLSFO Chevron 2019 at sea temperatures of 15 °C, at 10 and 15 m/s

C.2 Predictions of VLSFO Shell 2019



Property: EVAPORATIVE LOSS
Oil Type: VLSFO SHELL 2019
Description:
Data Source: Sintef Ocean (2020), Weathering data used

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

OWModel® 11.0.1
2.0
Pred. date: Apr. 26, 2020

Figure C-10 Evaporative loss VLSFO Shell 2019 at sea temperatures of 2 and 15 °C

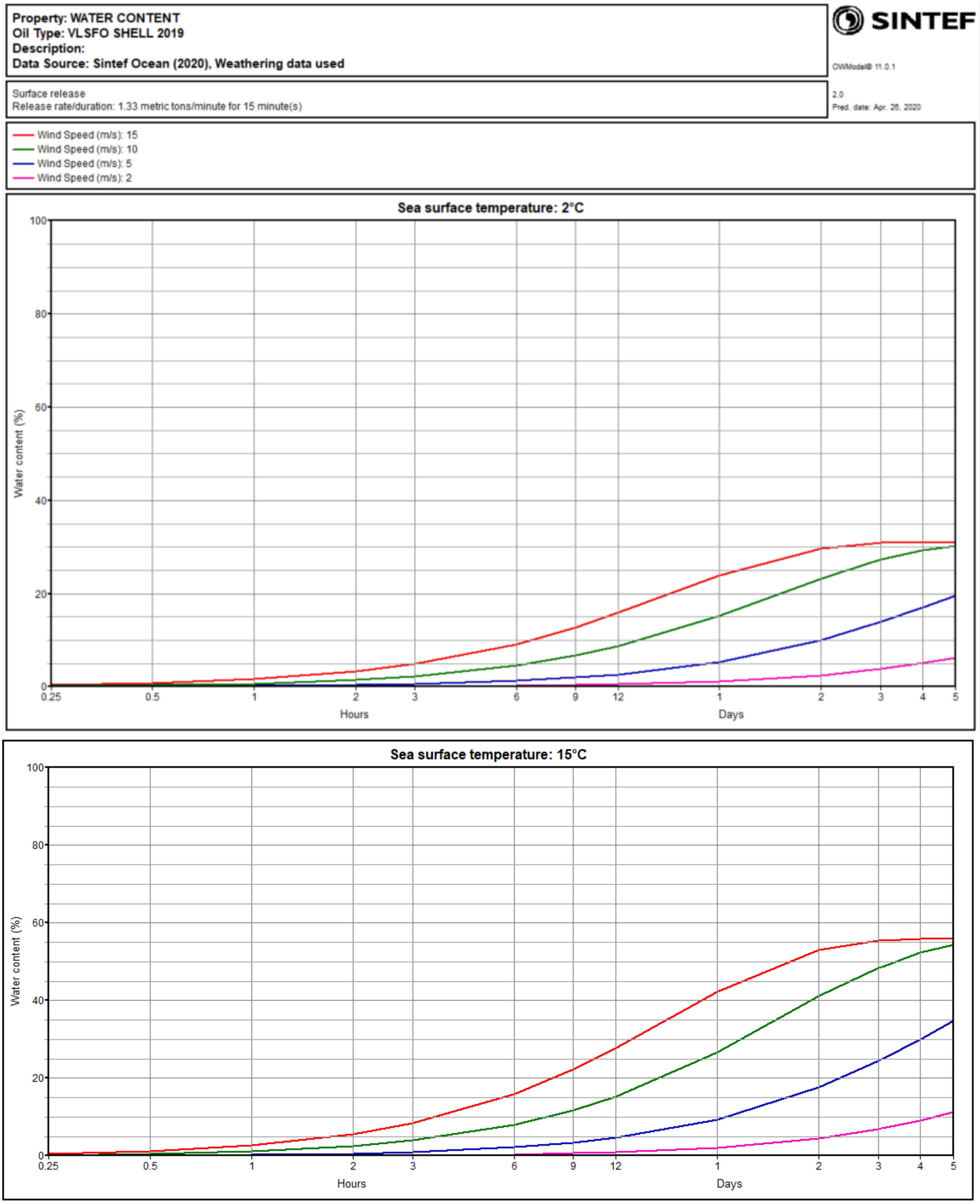


Figure C-11 *Water content VLSFO Shell 2019 at sea temperatures of 2 and 15 °C*

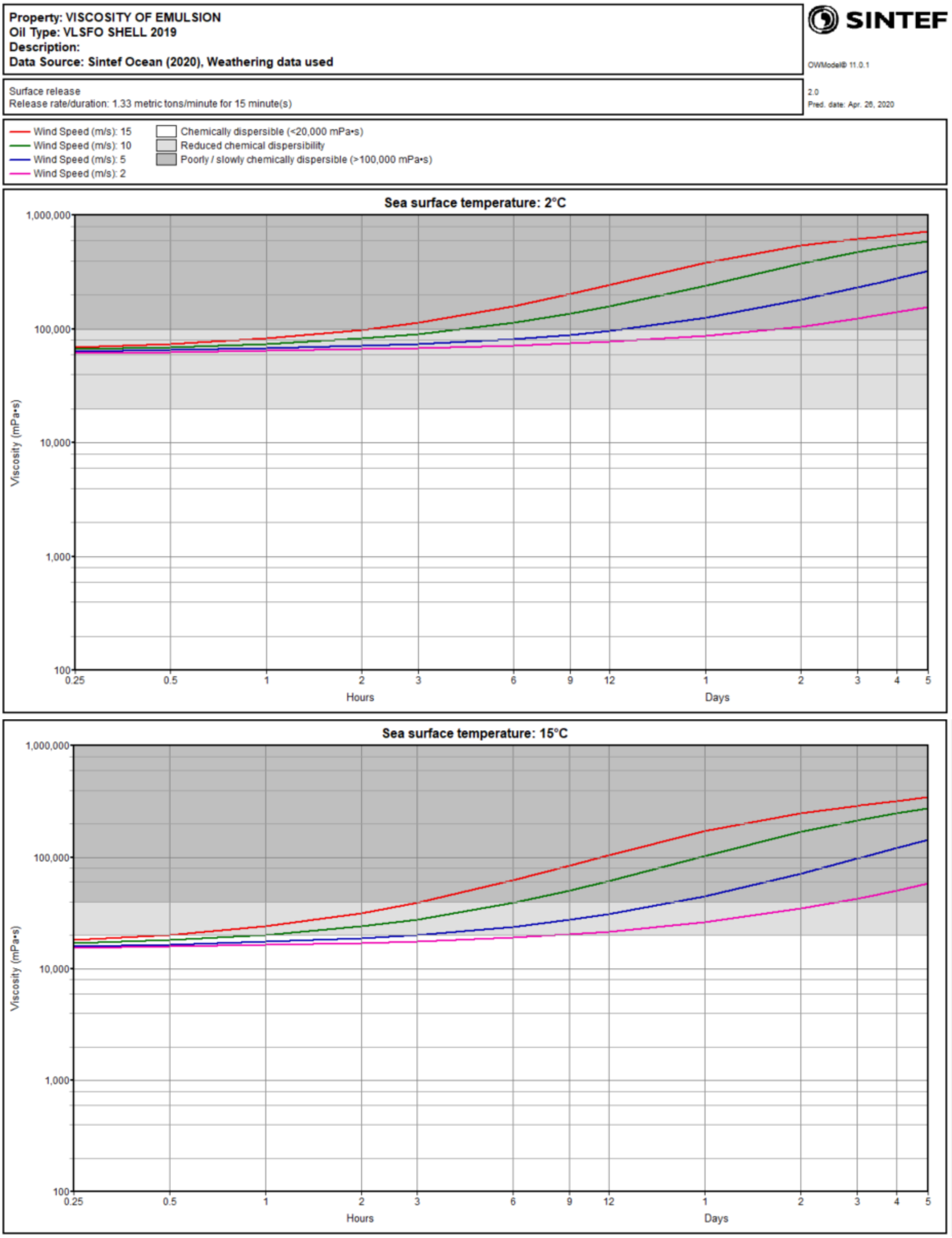


Figure C-12 Emulsion viscosity VLSFO Shell 2019 at sea temperatures of 2 and 15 °C

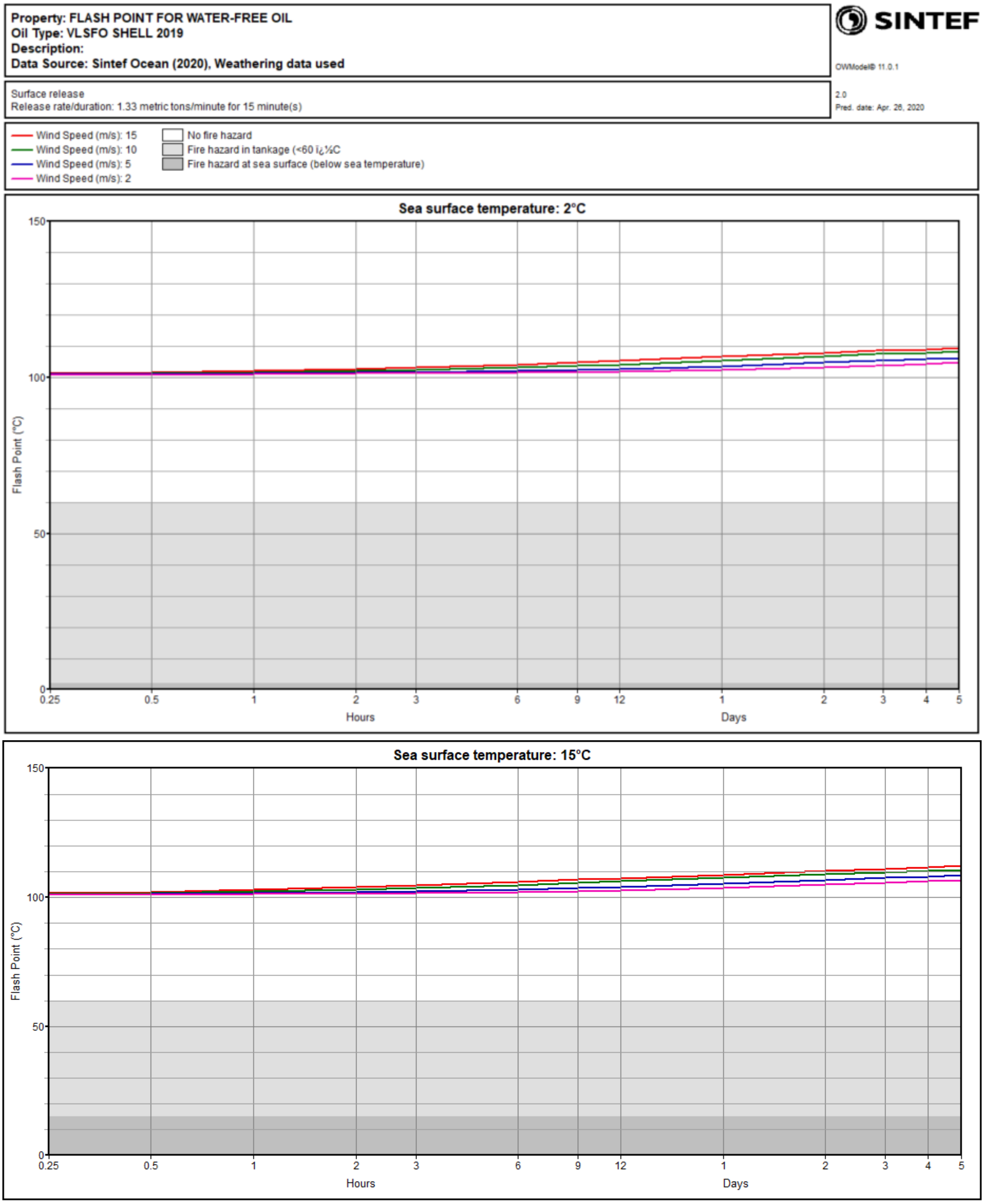
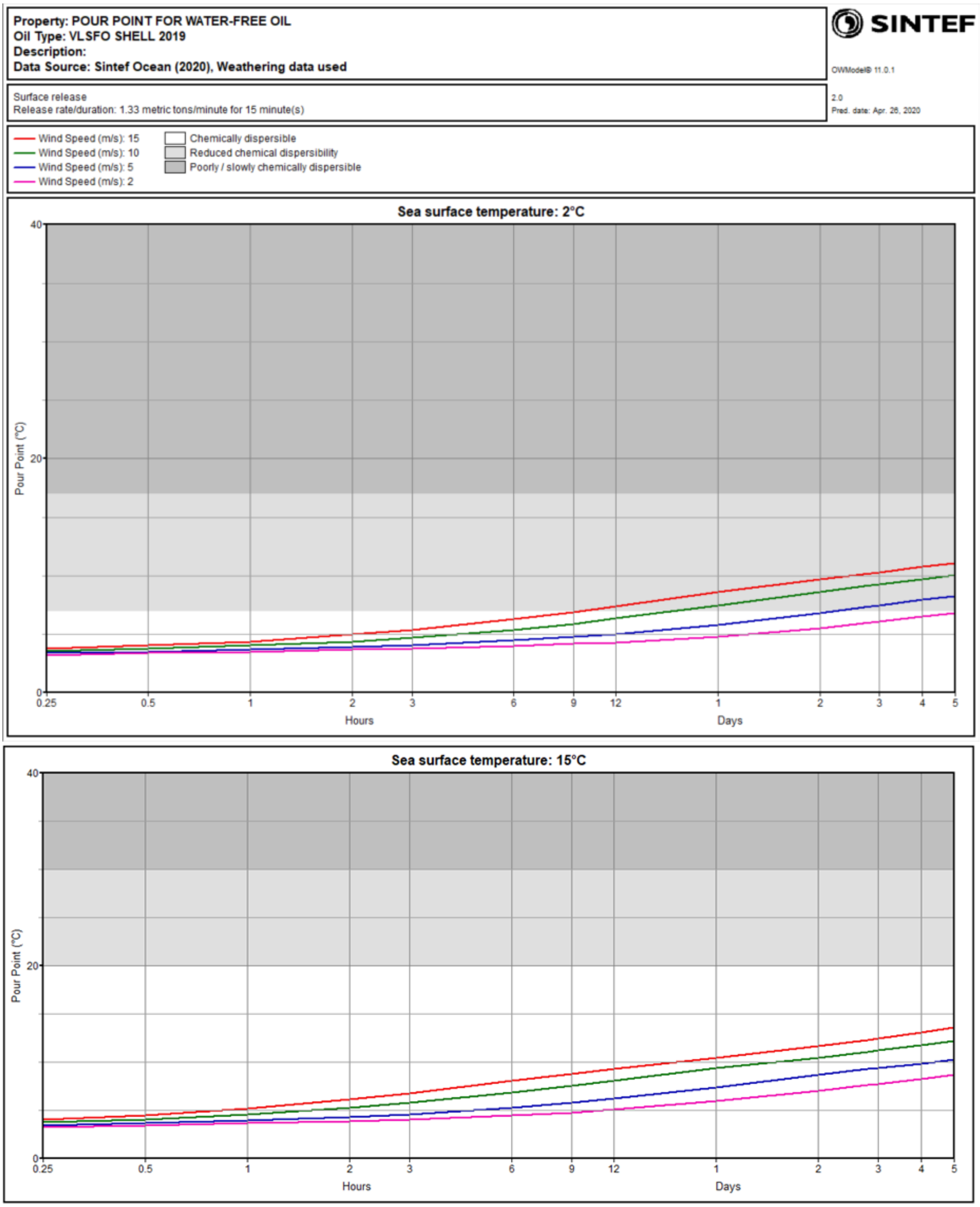


Figure C-13 Emulsion viscosity VLSFO Shell 2019 at sea temperatures of 2 and 15 °C

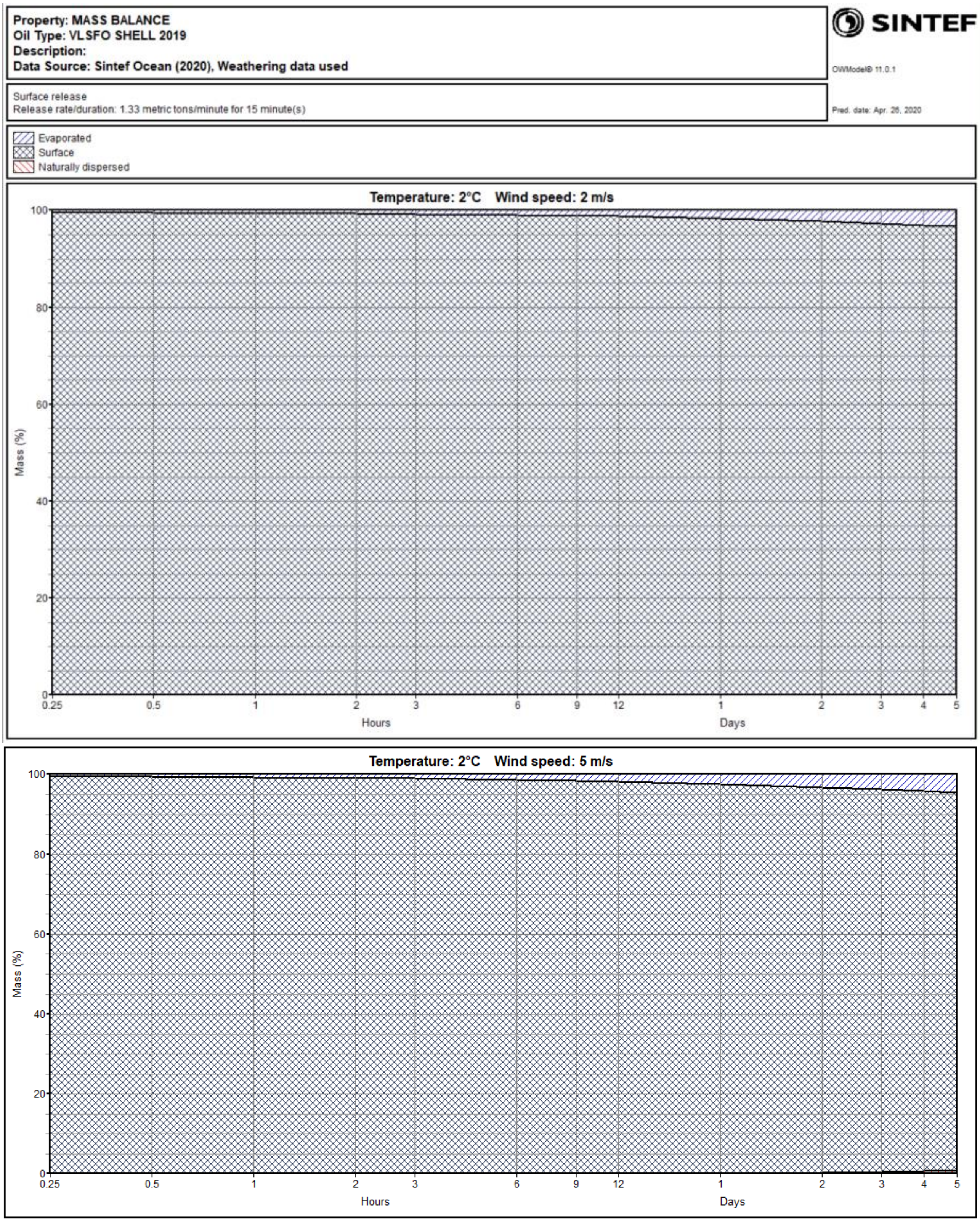


Property: POUR POINT FOR WATER-FREE OIL
Oil Type: VLSFO SHELL 2019
Description:
Data Source: Sintef Ocean (2020), Weathering data used

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

OWModel® 11.0.1
2.0
Pred. date: Apr. 26, 2020

Figure C-14	*Pour point VLSFO Shell 2019 at sea temperatures of 2 and 15 °C*



Property: MASS BALANCE
Oil Type: VLSFO SHELL 2019
Description:
Data Source: Sintef Ocean (2020), Weathering data used

SINTEF
OWModel® 11.0.1

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

Pred. date: Apr. 26, 2020

▨ Evaporated
▩ Surface
▧ Naturally dispersed

Figure C-15 Mass balance VLSFO Shell 2019 at sea temperatures of 2 °C, 2 and 2 and 5 m/s

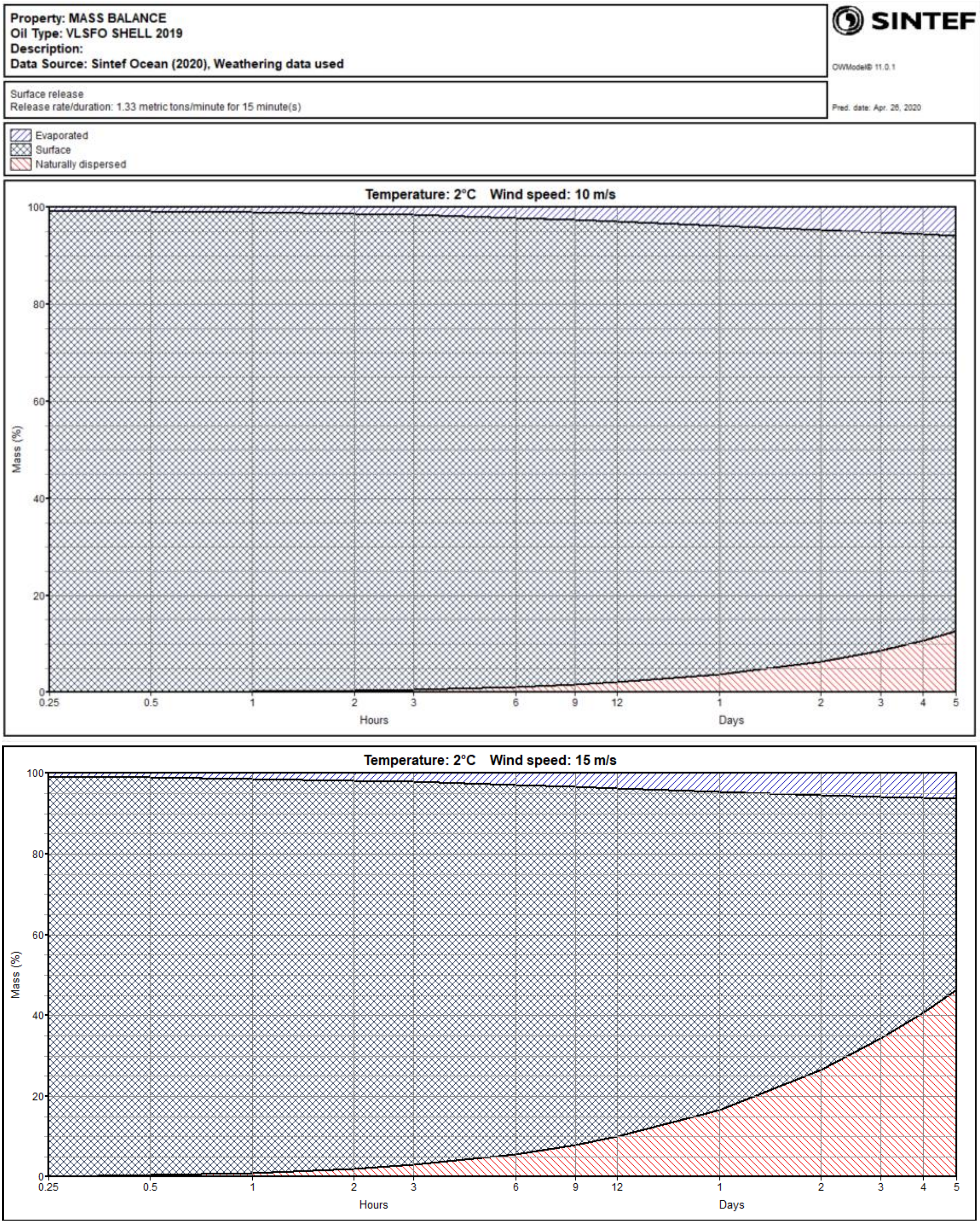
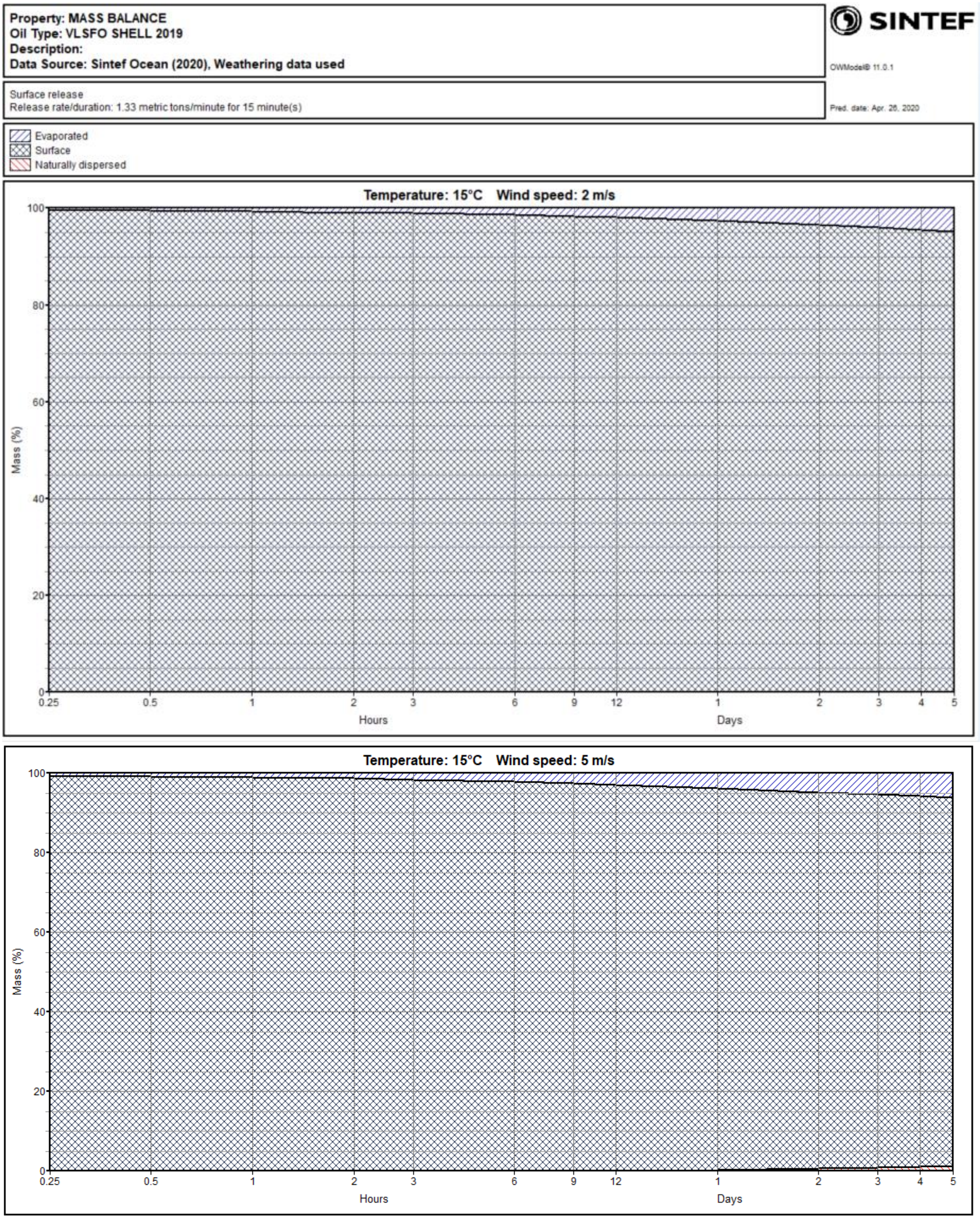


Figure C-16 Mass balance VLSFO Shell 2019 at sea temperatures of 2 °C, 10 and 15 m/s

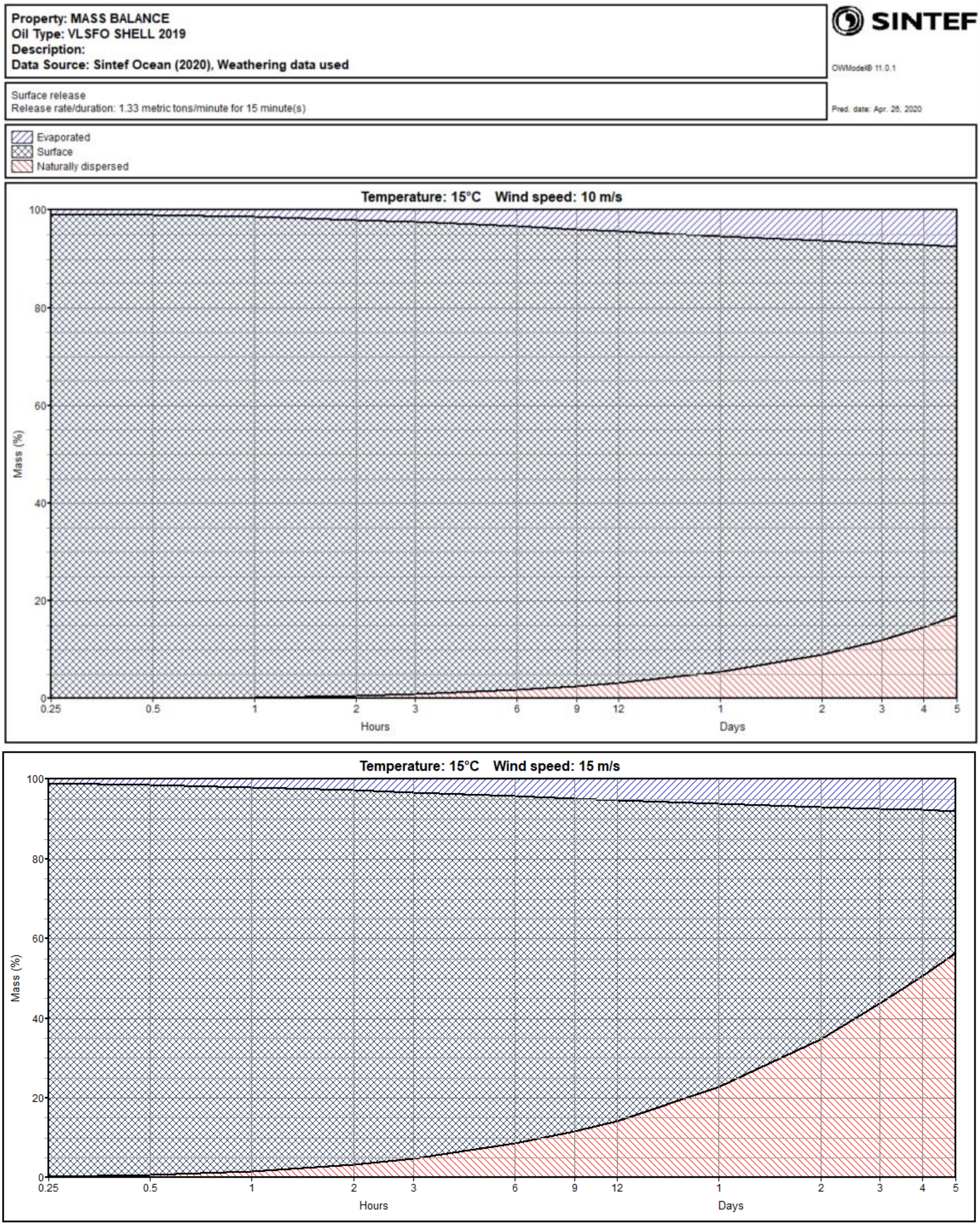


Property: MASS BALANCE
Oil Type: VLSFO SHELL 2019
Description:
Data Source: Sintef Ocean (2020), Weathering data used

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

OWModel® 11.0.1
Pred. date: Apr. 26, 2020

Figure C-17 Mass balance VLSFO Shell 2019 at sea temperatures of 15 °C, 2 and 5 m/s



Property: MASS BALANCE
Oil Type: VLSFO SHELL 2019
Description:
Data Source: Sintef Ocean (2020), Weathering data used

OWModel® 11.0.1

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

Pred. date: Apr. 26, 2020

Figure C-18 Mass balance VLSFO Shell 2019 at sea temperatures of 15 °C, 10 and 15 m/s

C.3 Predictions of ULSFO Shell 2019

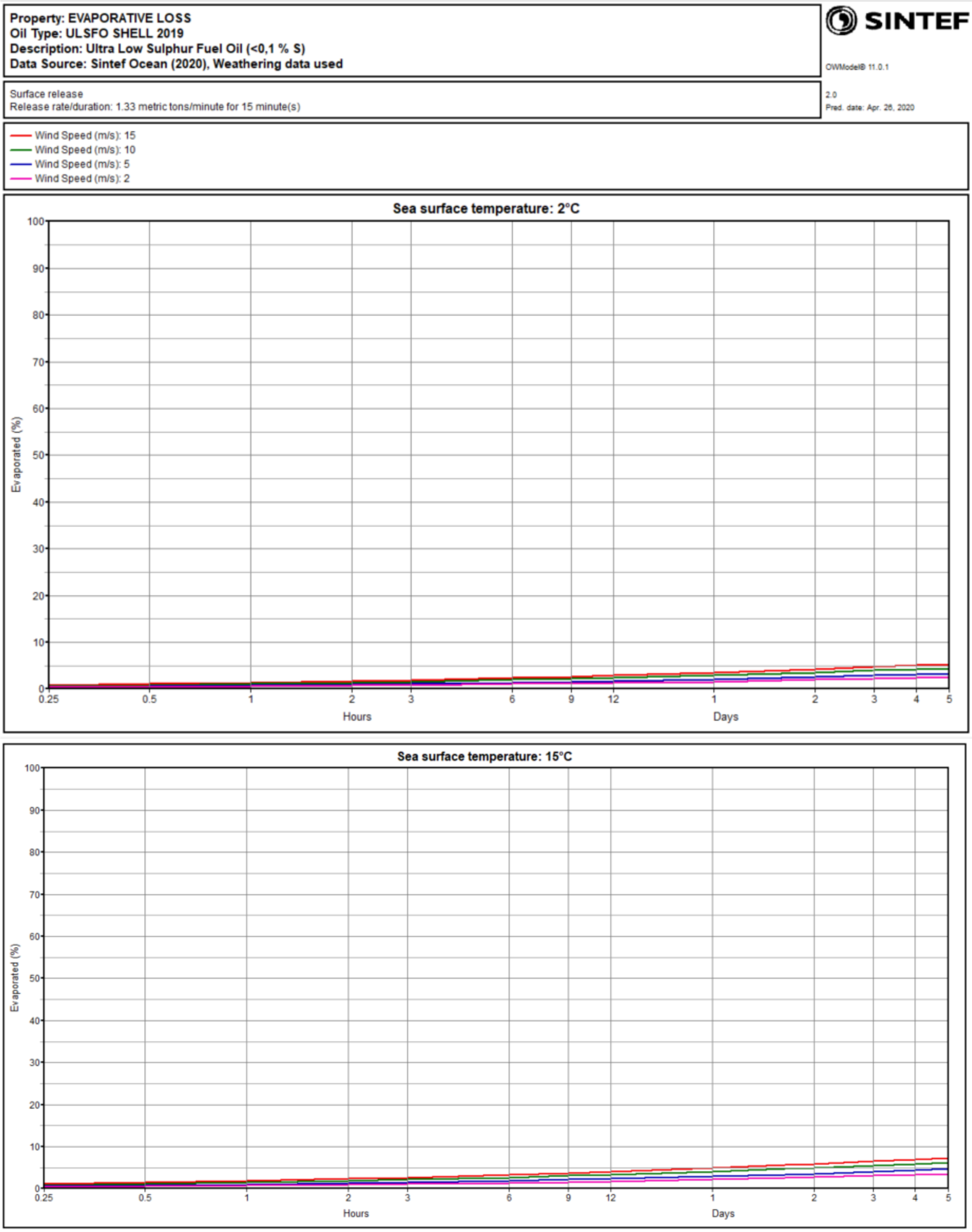
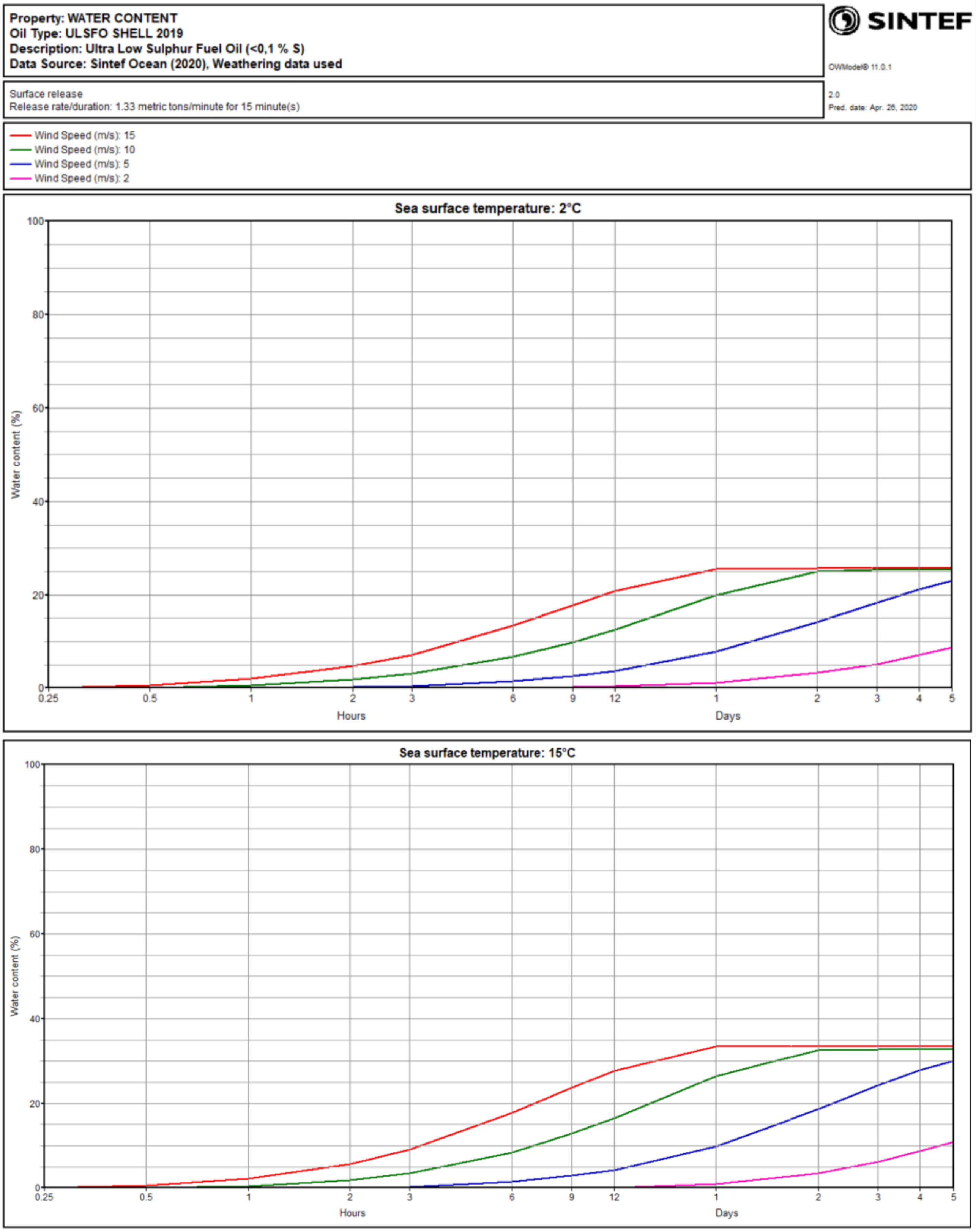


Figure C-19 Evaporative loss ULSFO Shell 2019 at sea temperatures of 2 and 15 °C



Property: WATER CONTENT
Oil Type: ULSFO SHELL 2019
Description: Ultra Low Sulphur Fuel Oil (<0,1 % S)
Data Source: Sintef Ocean (2020), Weathering data used

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

Figure C-20 Water content ULSFO Shell 2019 at sea temperatures of 2 and 15 °C

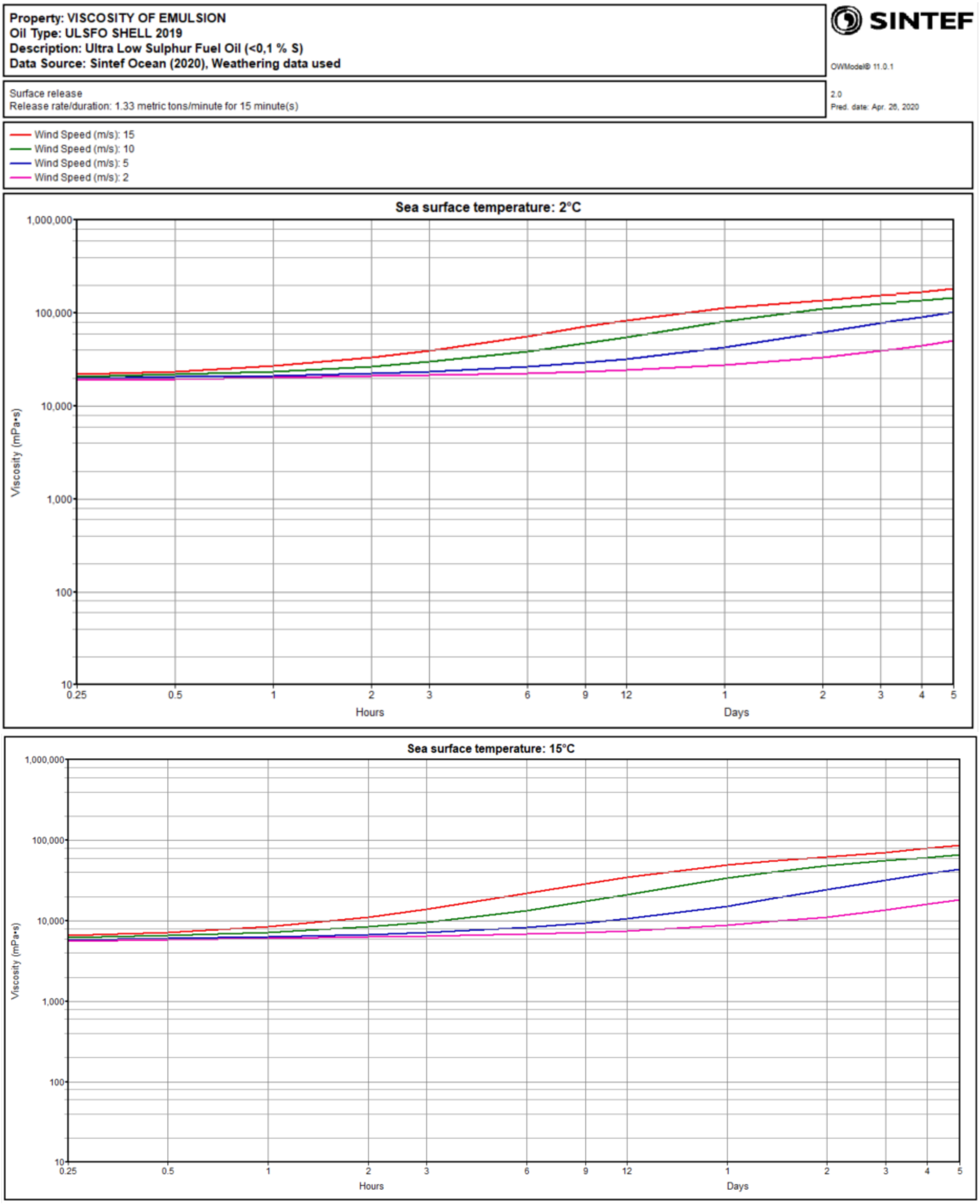


Figure C-21 Emulsion viscosity ULSFO Shell 2019 at sea temperatures of 2 and 15 °C. Viscosity influenced on the high pour point

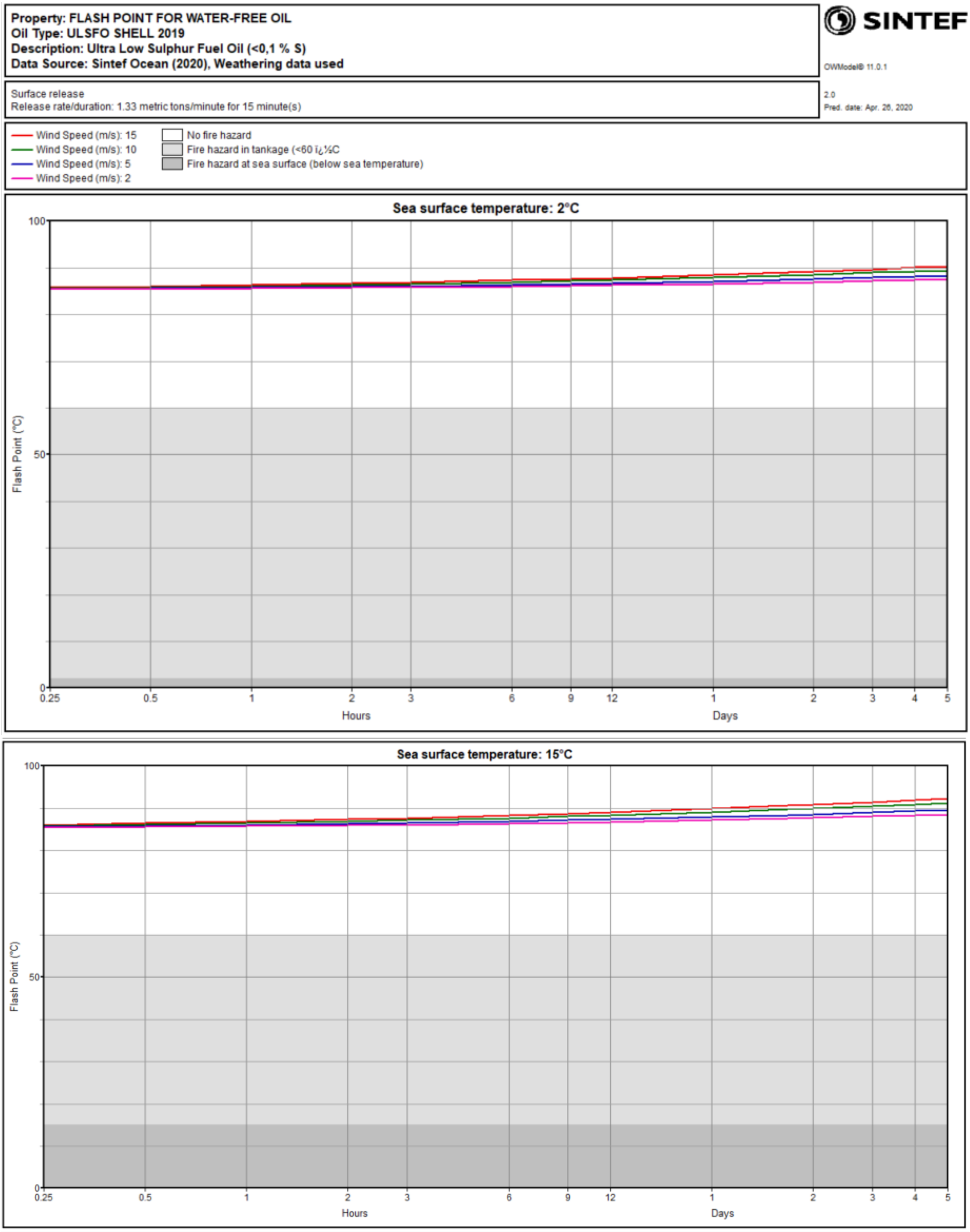
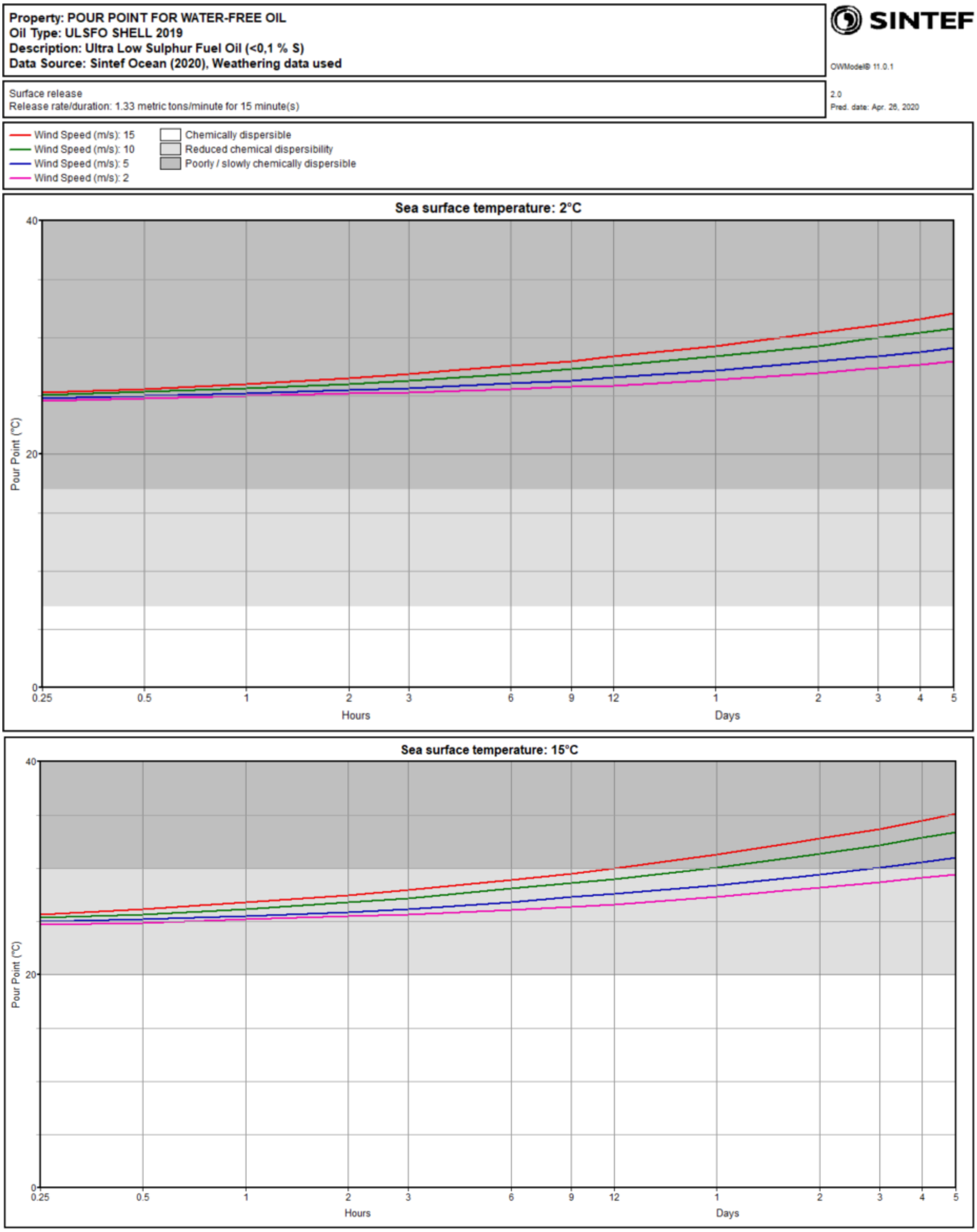


Figure C-22 Flash point ULSFO Shell 2019 at sea temperatures of 2 and 15 °C

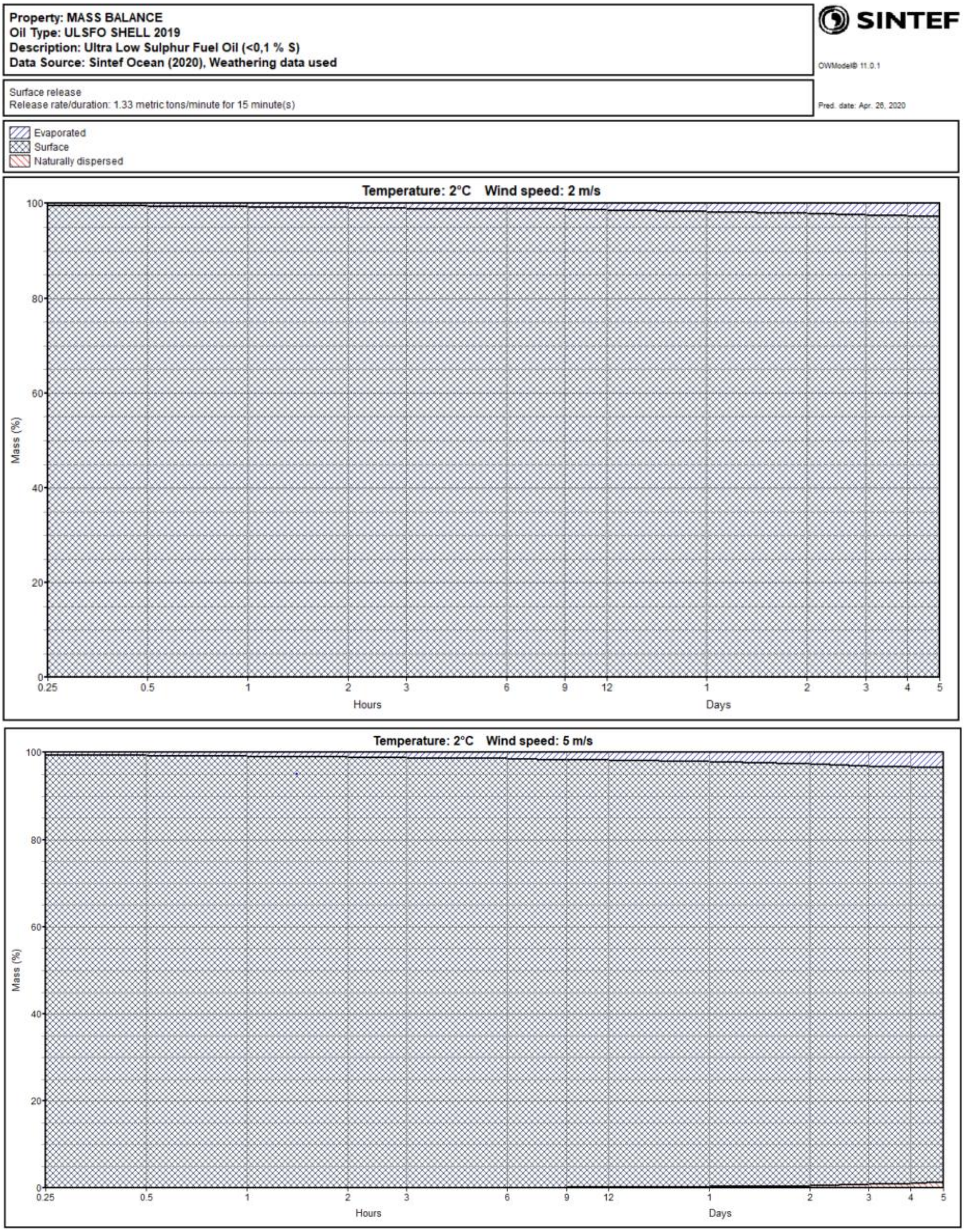


Property: POUR POINT FOR WATER-FREE OIL
Oil Type: ULSFO SHELL 2019
Description: Ultra Low Sulphur Fuel Oil (<0,1 % S)
Data Source: Sintef Ocean (2020), Weathering data used

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

OWModel® 11.0.1
2.0
Pred. date: Apr. 26, 2020

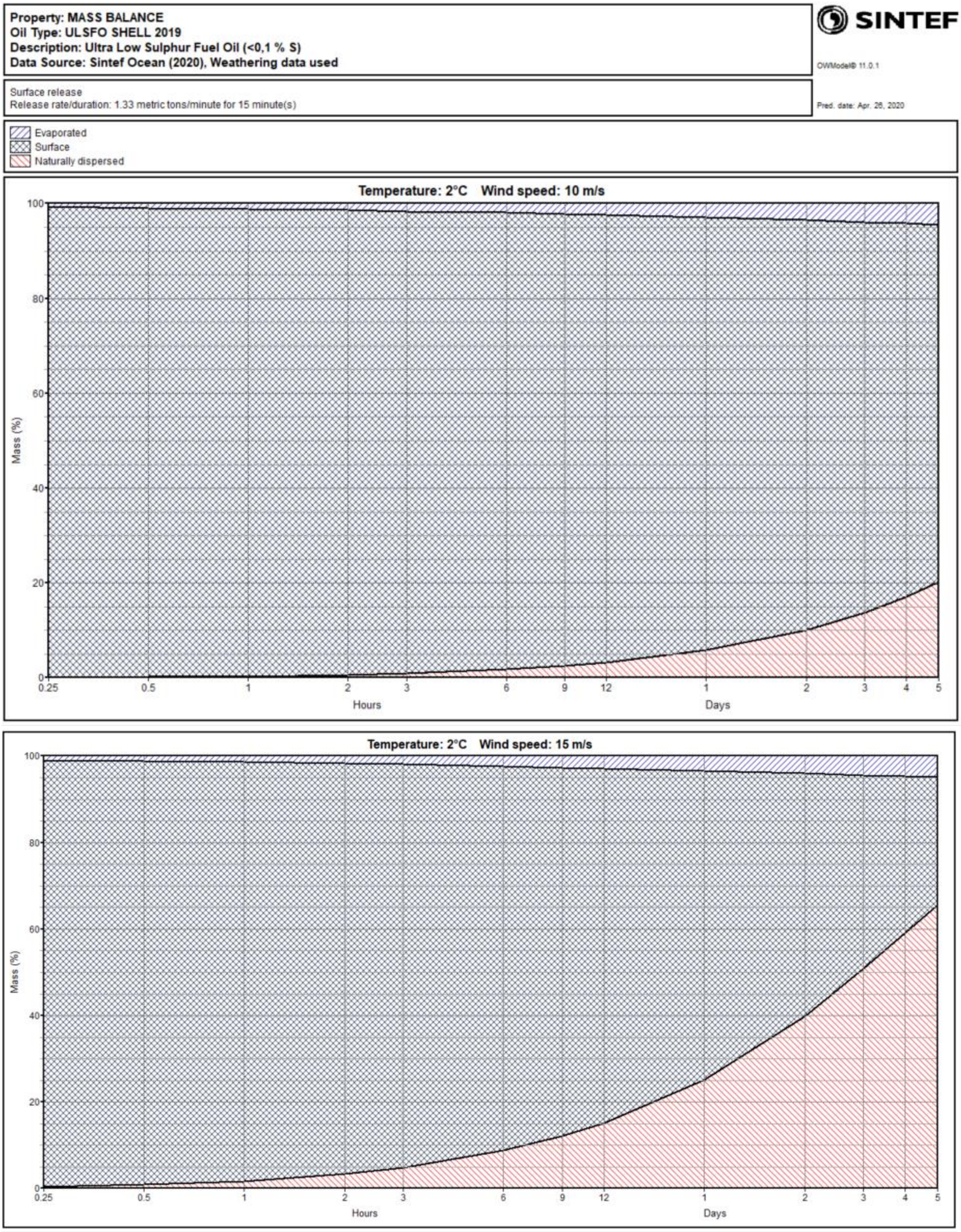
Figure C-23 Pour point ULSFO Shell 2019 at sea temperatures of 2 and 15 °C



Property: MASS BALANCE
Oil Type: ULSFO SHELL 2019
Description: Ultra Low Sulphur Fuel Oil (<0,1 % S)
Data Source: Sintef Ocean (2020), Weathering data used

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

Figure C-24 Mass balance ULSFO Shell 2019 at sea temperatures of 2 °C, 2 and 5 m/s



Property: MASS BALANCE
Oil Type: ULSFO SHELL 2019
Description: Ultra Low Sulphur Fuel Oil (<0,1 % S)
Data Source: Sintef Ocean (2020), Weathering data used

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

OWModel® 11.0.1
Pred. date: Apr. 26, 2020

Figure C-25 Mass balance ULSFO Shell 2019 at sea temperatures of 2 °C, 10 and 15 m/s

Figure C-26 Mass balance ULSFO Shell 2019 at sea temperatures of 15 °C, 2 and 5 m/s

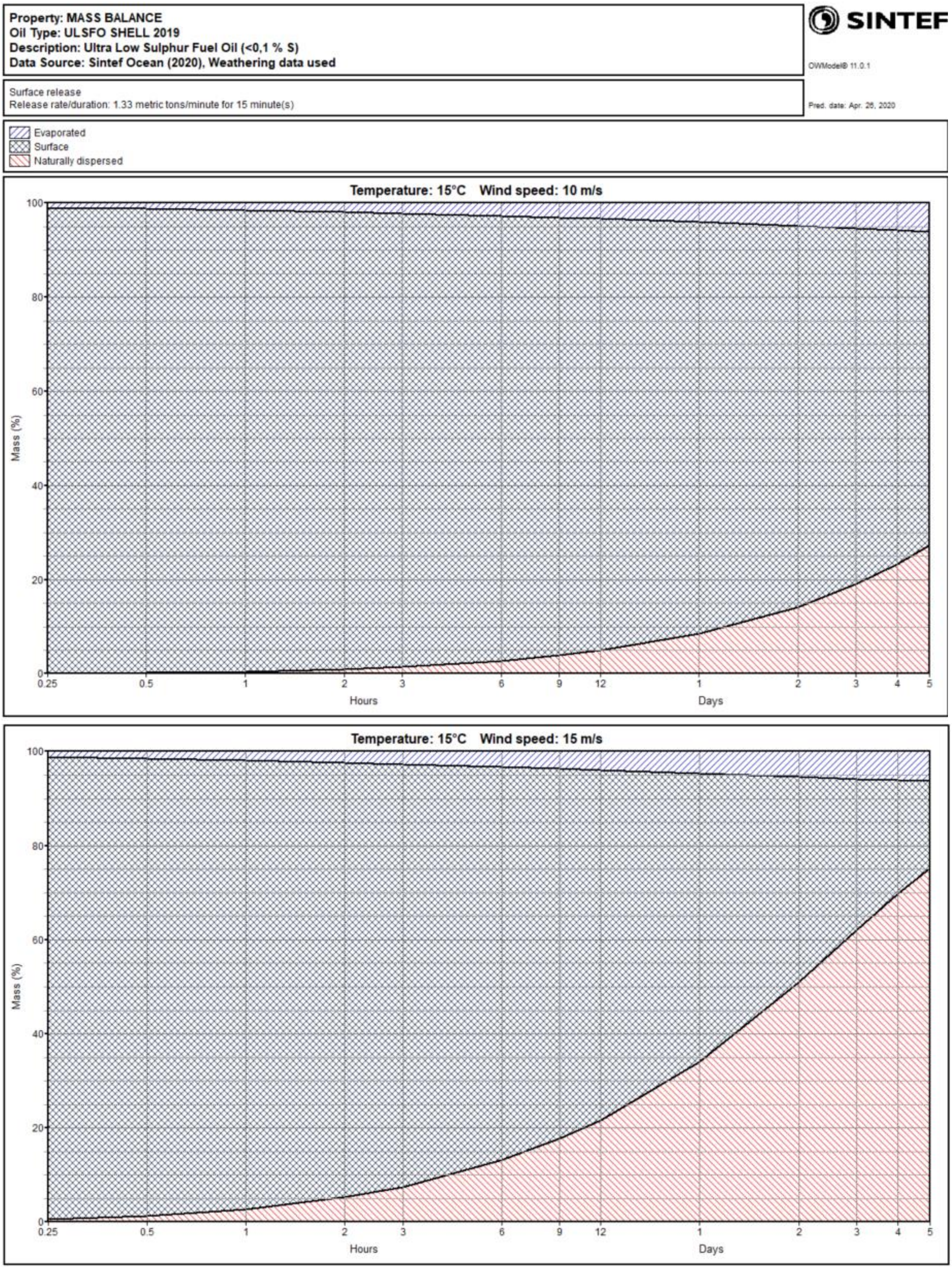


Figure C-27 Mass balance ULSFO Shell 2019 at sea temperatures of 15 °C, 10 and 15 m/s

Appendix D Chemical analysis and toxicity

Growth inhibition to the algae *Skeletonema sp.*

The unicellular marine algae *Skeletonema* sp. (previously known as *S. costatum*, clone NIVA BAC-1) was chosen as a relevant representative of marine producers. The bioassays were performed as a modification of ISO 10253 (2006a) with inhibition of growth rate and biomass production as endpoints (EC_{50}). The original protocol is not designed for testing of solutions containing volatiles, and has been adapted for testing of WAFs by exchanging the recommended semi open Erlenmeyer flasks (250 mL) with closed culture tubes (15 mL) in borosilicate glass following recommendations in ISO 14442 (2006b).

As an experimental design, a fixed dilution scheme with a spacing factor of 1.6 between concentrations (from undiluted 100% WAF to 3% WAF in sea water) was used covering a total of eight different dilutions with six replicate tubes in each dilution. All tubes were inoculated with the same volume of exponentially growing *Skeletonema sp.* (clone NIVA BAC-1) and nutrient mix. All tubes were filled to a headspace of 0.5 mL to ensure mixing in the tube during incubation. As negative control, 12 tubes in each bioassay were filled with autoclaved seawater and inoculated with the algae/nutrient mix in the same manner. *In vivo* fluorescence was measured by a Turner TD700 fluorometer (Turner Systems, Sunnyvale, CA, USA) after preparation. The tubes were then placed horizontally on a rocking shaker in a temperature-controlled room at nominally 20±2°C under a mixture of white (Philips TLD 965 18W) and pale yellow (Philips TL20W/33RS) fluorescent tubes under constant light.

During the test period of 72 hours, *in vivo* fluorescence was measured daily by the Turner TD700 fluorometer. At the end of exposure, pH was measured in a pooled sample from three tubes from the control series as well as from the different dilutions in the exposure series. The calculated values are normalized by setting the response in the control series to 100% for growth rate and then calculating the effect within the span 0 to 100% relative to the control series. The top and bottom of the concentration-effect curve are constrained to 100 and 0, thus eliminating any stimulatory effects.

Acute toxicity to Calanus finmarchicus

Potential effects on primary consumers were assessed with the marine copepod *Calanus finmarchicus*, which is one of the key ecological species in northern boreal to arctic oceans. The acute toxicity testing was performed according to ISO 14669:1999 (ISO, 1999) with lethal immobilization (LC_{50}) as the endpoint. The original ISO protocol is not designed for testing of solutions containing volatiles with *C. finmarchicus*, and was modified by using borosilicate glass bottles (0.5 L) with Teflon lined screw caps to preserve volatiles and to accommodate for the larger body mass of *C. finmarchicus* compared to the listed species in the ISO protocol (ISO, 1999).

To ensure that the observed effects were approaching the incipient toxicity level of LC_{50} for the species, the exposure time was increased to 96 hours at a set temperature of 10±2°C. The WAF samples were diluted in a series of seven concentrations with a spacing factor of 1.7 between dilutions with each exposure concentration made in triplicate. Six bottles were used as negative controls containing seawater only and three bottles with 0.8 mg L^{-1} of 3,5-dichlorophenol were used as positive control. The exposure vessels were filled close to the rim to keep potential evaporative loss to a minimum during exposure, and each vessel was stocked with seven copepodites V of *C. finmarchicus* at onset exposure. Mortality was monitored at 24, 48, 72 and 96 hours. The test animals were not fed during exposure. The calculated values are not corrected for any mortality in the control series and the effect is calculated within the span 0-100% effect by constraining the top and bottom of the concentration-effect curve to 100 and 0.

Predicted toxicity using toxic units

In the WAFs from petrogenic products, the compounds of concern for toxicity assessment are typically limited to the VOCs and SVOCs, which are structurally classified as Type I narcotics. The target lipid model of narcotic toxicity demonstrates that the acute toxicities of these chemicals vary and are correlated with the octanol-water partition coefficient (K_{ow}) such that LC_{50} decreases with increasing K_{ow} (DiToro et al. 2007). A toxic unit (TU) for the individual compounds is computed by dividing the measured concentration in the WAF by the compound's water effect concentration using regression models. It appears to be a linear negative relation between log LC_{50} of the marine organisms and log Kow of the components that may cause toxic effects (McCarty et al. (1992; 1993) and Di Toro et al. (2007)):

$$\log LC_{50} = m \log (K_{ow}) + b \qquad (1)$$

The slope (m), log K_{ow}, and the intercept (b) for different component groups (e.g MAH, PAH and phenols) are given in McCarty (1993) and Neff et al. (2002). The LC_{50} (mg/L) is calculated for each component by use of equation (1). Different regression coefficients can be used to calculate TU relative to different species (McGrath and DiToro, 2009), resulting in other values of the TU than these calculated here. However, all oils used for comparison in this report are calculated using the same equation.

In the WAFs, the TUs of the individual components are summed up to compute the total TUs of the WAF. If the sum of the TUs is less than 1 (TU<1), observed effects should be lower than as defined by the water effect concentration (e.g. 50% lethality if using the LC_{50}). If the sum of the TUs in the WAF is greater than 1 (TU>1), adverse effects could potentially be observed.

Table D-1 *Summary of the chemical composition of the oils (in g analyte/kg oil) and their WAFs (in µg analyte/L water). Total WAF concentration, TPH and UCM are not quantified in the oils (ND: Not detected). Total WAF concentration is the sum of TPH and total VOC, total SVOC is the sum of decalins, naphthalenes, 2-6 ring PAHs, and phenols, total VOC concentration is the sum of BTEX, C3-benzenes, and other volatiles from C5 to C9. All WAFs were generated at 13 °C. (ND: Not detected).*

	2019-3955	2019-7685	2019-11170	2019-3955	2019-7685	2019-11170
	VLSFO	VLSFO Shell 2019	ULSFO	VLSFO	VLSFO Shell 2019	ULSFO
	Oil	Oil	Oil	WAF 1:40	WAF 1:40	WAF 1:40
	g/kg	g/kg	g/kg	µg/L	µg/L	µg/L
Tot WAF				1067	1595	609
TPH				531	1322	243
UCM				377	744	210
Sum SVOC	75,5	34,2	19,7	194	578	32,7
Sum VOC	0,35	0,25	2,22	536	273	366
Decalins	0,35	0,25	2,22	0,12	0,08	0,10
Naphthalenes	9,20	9,81	2,53	147	475	24,3
2-3 ring PAH	33,5	11,8	6,01	19,5	26,4	5,07
4-6 ring PAH	32,2	12,3	8,88	1,71	0,88	1,18
C0-C5 phenols	0,12	0,01	0,02	26,3	76,0	2,03
BTEX	0,30	0,16	0,23	378	189	193
C3-benzenes	0,31	0,24	0,29	95,3	73,0	65,1
Other VOC	0,47	0,11	2,59	62,7	11,0	108

Table D-2 *Semi volatiles in the oils (in g analyte/kg oil) and their WAFs (in µg analyte/L water). (ND: Not detected).*

SINTEF ID	2019-3955	2019-7685	2019-11170	2019-3955	2019-7685	2019-11170
Sample ID	VLSFO	VLSFO Shell 2019	ULSFO	VLSFO	VLSFO Shell 2019	ULSFO
	Oil	Oil	Oil	WAF	WAF	WAF
	g/kg	g/kg	g/kg	µg/L	µg/L	µg/L
Decalin	0,03	0,01	0,15	0,02	0,01	0,06
C1-decalins	0,07	0,03	0,38	0,03	0,07	0,04
C2-decalins	0,09	0,06	0,51	0,02	ND	ND
C3-decalins	0,09	0,06	0,56	0,02	ND	ND
C4-decalins	0,08	0,10	0,62	0,03	ND	ND
Benzo(b)thiophene	0,01	0,01	ND	1,67	2,26	0,04
Naphthalene	0,49	1,55	0,07	69,3	345	8,56
C1-naphthalenes	1,37	2,26	0,22	52,2	104	6,81
C2-naphthalenes	2,66	2,62	0,64	17,5	18,6	5,48
C3-naphthalenes	2,85	2,17	0,95	6,21	5,45	2,78
C4-naphthalenes	1,83	1,23	0,65	1,63	1,43	0,66
Biphenyl	0,04	0,43	0,02	0,59	7,63	0,19
Acenaphthylene	0,02	0,22	ND	0,17	0,52	0,05
Acenaphthene	0,06	0,18	0,01	0,81	2,38	0,17
Dibenzofuran	0,02	0,04	0,01	0,22	0,38	0,07
Fluorene	0,12	0,29	0,03	1,11	2,70	0,43
C1-fluorenes	0,42	0,74	0,11	0,91	1,91	0,48
C2-fluorenes	1,09	0,64	0,33	0,68	0,58	0,44
C3-fluorenes	1,77	0,56	0,39	0,40	0,14	0,19
Phenanthrene	0,72	0,82	0,12	3,12	3,26	0,70
Anthracene	0,14	0,13	0,01	0,31	0,25	0,05
C1-phenanthrenes/anthracenes	3,53	1,60	0,57	4,01	1,57	0,95
C2-phenanthrenes/anthracenes	8,25	2,22	1,71	3,12	0,71	0,74
C3-phenanthrenes/anthracenes	8,84	1,82	2,29	0,91	0,18	0,29
C4-phenanthrenes/anthracenes	6,10	1,03	0,04	0,30	0,05	0,04
Dibenzothiophene	0,06	0,05	0,02	0,26	0,25	0,04
C1-dibenzothiophenes	0,28	0,20	0,06	0,52	0,72	0,11
C2-dibenzothiophenes	0,63	0,34	0,09	0,29	0,60	0,08
C3-dibenzothiophenes	0,88	0,33	0,12	0,12	0,22	ND
C4-dibenzothiophenes	0,53	0,19	0,08	0,03	0,07	ND
Fluoranthene	0,12	0,07	0,05	0,07	0,06	0,06
Pyrene	0,66	0,34	0,30	0,51	0,22	0,32
C1-fluoranthenes/pyrenes	3,35	1,55	1,25	0,60	0,28	0,41
C2-fluoranthenes/pyrenes	1,24	2,51	1,69	0,06	0,16	0,21
C3-fluoranthenes/pyrenes	6,04	2,11	1,44	0,09	0,05	ND
Benz(a)anthracene	0,70	0,20	0,17	0,06	0,02	0,03
Chrysene	0,79	0,31	0,20	0,08	0,03	0,04

SINTEF ID	2019-3955	2019-7685	2019-11170	2019-3955	2019-7685	2019-11170
Sample ID	VLSFO	VLSFO Shell 2019	ULSFO	VLSFO	VLSFO Shell 2019	ULSFO
	Oil	Oil	Oil	WAF	WAF	WAF
	g/kg	g/kg	g/kg	µg/L	µg/L	µg/L
C1-chrysenes	4,12	1,46	1,08	0,14	0,04	0,07
C2-chrysenes	6,13	1,72	1,28	0,06	0,02	0,03
C3-chrysenes	4,84	0,98	0,76	0,01	ND	ND
C4-chrysenes	2,91	0,35	0,35	0,02	ND	ND
Benzo(b)fluoranthene	0,18	0,07	0,04	ND	ND	ND
Benzo(k)fluoranthene	0,03	ND	0,01	ND	ND	ND
Benzo(e)pyrene	0,39	0,20	0,11	0,01	0,01	ND
Benzo(a)pyrene	0,34	0,14	0,06	ND	ND	ND
Perylene	0,11	0,09	0,03	ND	ND	ND
Indeno(1,2,3-c,d)pyrene	0,04	0,02	0,01	ND	ND	ND
Dibenz(a,h)anthracene	0,10	ND	0,02	ND	ND	ND
Benzo(g,h,i)perylene	0,15	0,17	0,05	ND	ND	ND
Phenol	ND	ND	ND	0,64	3,78	0,49
C1-Phenols (o- og p-cresol)	ND	0,01	ND	3,95	11,8	0,09
C2-Phenols	0,01	ND	0,01	10,4	15,4	0,26
C3-Phenols	0,02	ND	ND	7,24	23,4	0,59
C4-Phenols	0,04	ND	ND	3,08	15,3	0,26
C5-Phenols	0,05	ND	ND	0,99	6,36	0,33
30 ab hopane	0,06	0,16	0,41	ND	ND	ND
Sum all compounds	75,5	34,2	19,7	194	578	32,7
Sum decalins	0,35	0,25	2,22	0,12	0,08	0,10
Naphthalenes	9,20	9,81	2,53	147	475	24,3
2-3 ring PAHs	33,5	11,8	6,01	19,5	26,4	5,07
4-6 ring PAHs	32,2	12,3	8,88	1,71	0,88	1,18
C0-C5 Phenols	0,12	0,01	0,02	26,3	76,0	2,03

Table D-3 *Composition of volatiles in the oils (in g analyte/kg oil) and their WAFs (in µg analyte/L water). (ND: Not detected).*

SINTEF ID	2019-3955	2019-7685	2019-11170	2019-3955	2019-7685	2019-11170
Sample ID	VLSFO	VLSFO Shell 2019	ULSFO	VLSFO	VLSFO Shell 2019	ULSFO
	Oil	Oil	Oil	WAF	WAF	WAF
	g/kg	g/kg	g/kg	µg/L	µg/L	µg/L
Isopentane	0,06	ND	0,02	27,3	ND	13,1
n-C5 (Pentane)	0,02	ND	0,08	7,41	ND	11,2
Cyclopentane	ND	ND	0,02	2,92	ND	22,1
2-methylpentane	0,03	ND	0,05	3,38	0,60	3,56
3-Methylpentane	0,02	ND	0,03	2,58	0,36	2,42
n-C6 (Hexane)	0,01	ND	0,13	0,80	0,54	3,10
Methylcyclopentane	0,02	ND	0,08	6,92	2,02	16,6

Benzene	0,01	ND	0,01	54,2	20,4	42,4
Cyclohexane	ND	ND	0,06	1,82	1,19	21,1
2,3-Dimethylpentane	ND	ND	ND	ND	ND	0,37
3-methylhexane	0,02	ND	0,06	0,54	ND	0,58
n-C7 (Heptane)	0,01	ND	0,20	ND	ND	0,15
Methylcyclohexane	0,02	ND	0,22	2,59	ND	9,83
Toluene	0,07	0,03	0,05	151	60,5	63,7
2,4 diethylhexane	ND	ND	ND	ND	ND	ND
2-Methylheptane	0,02	ND	0,11	0,08	ND	ND
n-C8 (Octane)	0,03	ND	0,32	0,05	ND	ND
Ethylbenzene	0,03	0,02	0,02	23,6	17,1	8,82
m-Xylene	0,10	0,06	0,09	75,1	46,5	44,9
p-Xylene	0,04	0,02	0,03	28,6	13,9	12,5
o-Xylene	0,05	0,03	0,03	44,9	31,1	20,7
n-C9 (Nonane)	0,06	0,02	0,47	ND	ND	ND
Propylbenzene	0,01	0,01	0,01	3,19	2,94	0,98
1-Methyl-3-ethylbenzene	0,06	0,05	0,03	17,7	14,5	5,67
1-Methyl-4-ethylbenzene	0,03	0,02	0,02	7,03	5,32	3,33
1,3,5-trimethylbenzene	0,03	0,02	0,04	8,37	5,45	6,20
1-Methyl-2-ethylbenzene	0,02	0,02	0,01	7,87	6,87	2,80
1,2,4-Trimethylbenzene	0,13	0,09	0,11	37,2	25,3	24,4
n-C10 (Decane)	0,08	0,03	0,72	ND	ND	ND
1,2,3-Trimethylbenzene	0,03	0,03	0,07	14,0	12,6	21,8
n-Butylbenzene	0,01	0,01	ND	0,44	0,51	0,18
1,2,4,5-Tetramethylbenzene	0,05	0,03	0,03	5,78	2,93	2,34
n-Pentylbenzene	0,01	0,02	ND	0,14	2,87	1,37
C4-Benzenes	0,31	0,36	0,11	36,9	36,6	9,02
C5-Benzenes	0,25	0,46	0,25	9,52	12,2	7,17
Sum all VOC	1,08	0,52	3,10	536	273	366
Sum BTEX	0,30	0,16	0,23	378	189	193
Sum C3-benzenes	0,31	0,24	0,29	95,3	73,0	65,1
Sum other VOC	0,47	0,11	2,59	62,7	11,0	108

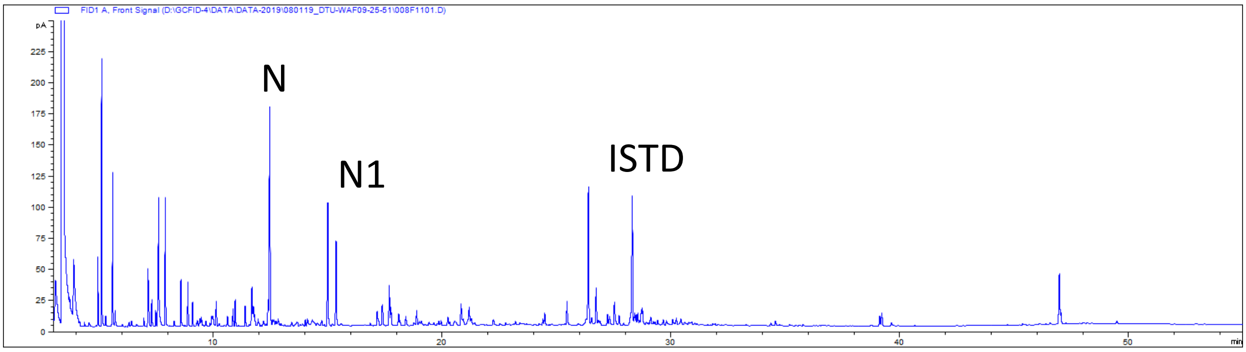


Figure D-2 *GC chromatogram of WAF of VLSFO Chevron 2019 (SINTEF ID 2019-3955). The peaks for naphthalene (N) and C1-napthalenes (N1) are indicated on the chromatogram. Peaks between 26 and 30 min are added internal standards (ISTD).*

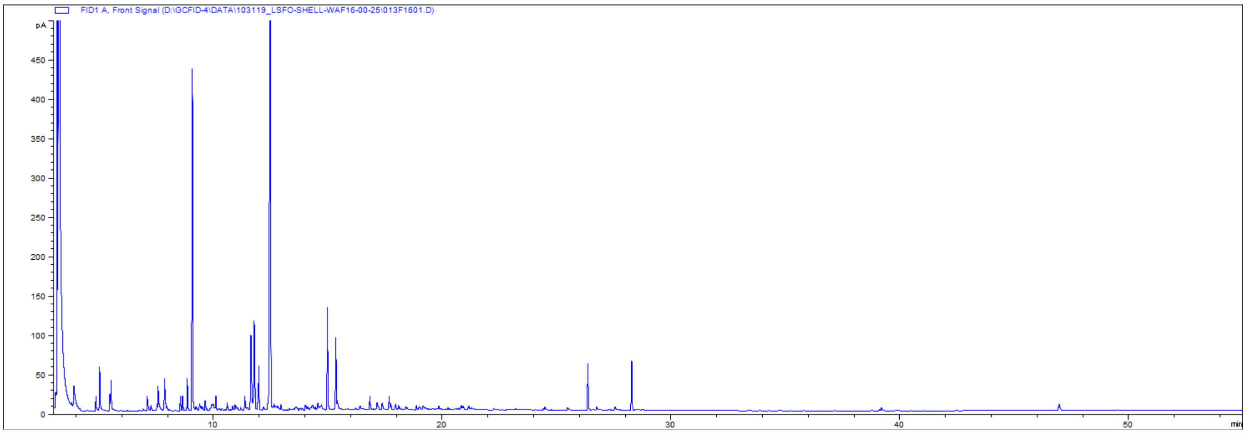


Figure D-3 GC chromatogram of WAF of VLSFO Shell 2019 (SINTEF ID 2019-7685).

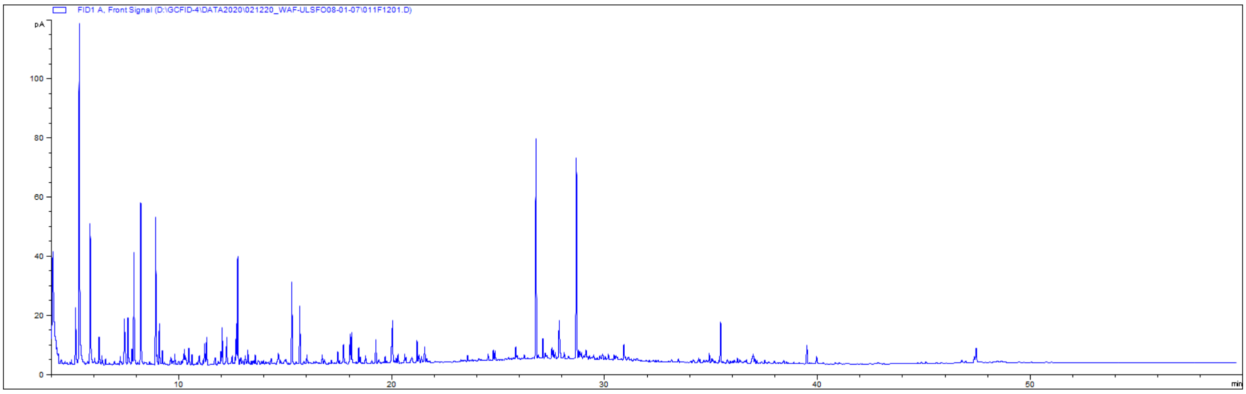


Figure D-4 GC chromatogram of WAF of ULSFO Shell 2019 (SINTEF ID 2019-11170).

Table D-4 Summary of the toxicity results. All WAFs are prepared at 13 ^{o}C. Acute specific toxicities are normalized to total WAF concentration, and are given as both LC$_{50}$ and EC$_{50}$, and LC$_{10}$ and EC$_{10}$. In addition, percentage effect in 100% WAF (non-diluted) at test endpoint, meaning % reduction in growth rate and biomass for the algae, and % mortality for the copepod.

	2019-3955	2019-7685	2019-11170
	VLSFO	VLSFO Shell 2019	ULSFO
	1:40	1:40	1:40
Total WAF concentration (ppm)	1067	1595	609
Skeletonema sp. EC$_{50}$ (%) (growth rate)	23,1	40,4	57,8
Skeletonema sp. EC$_{50}$ (%) (biomass prod)	19,4	36,5	40,5
C. finmarchicus LC$_{50}$ (%)	54,3	39,4	>100
Skeletonema sp. EC$_{10}$ (%) (growth rate)	21,2	36,2	38,7
Skeletonema sp. EC$_{10}$ (%) (biomass prod)	14,6	27,8	28,7
C. finmarchicus LC$_{10}$ (%)	27,9	19,9	98,1
Skeletonema sp. EC$_{50}$ (ppm) (growth rate)	0,244	0,644	0,352
Skeletonema sp. EC$_{50}$ (ppm) (biomass prod)	0,206	0,583	0,247
C. finmarchicus LC$_{50}$ (ppm)	0,575	0,628	NC
Skeletonema sp. EC$_{10}$ (ppm) (growth rate)	0,224	0,577	0,214
Skeletonema sp. EC$_{10}$ (ppm) (biomass prod)	0,155	0,444	0,150
C. finmarchicus LC$_{10}$ (ppm)	0,296	0,317	0,597
Toxic unit	1,14	0,51	0,24

*NC: Not calculated; * Ambiguous data.*

Table D-5 Predicted acute toxicity expressed as toxic unit for the WAFs.

	BTEX	C3-benzenes	Decalins	Naphthalenes	2-3 ring PAH	4-6 ring PAH	C0-C5 phenols	**Total TU**
VLSFO	0,023	0,037	0,177	0,1412	0,4129	0,22467	0,0049	1,01
VLSFO Shell 2019	0,013	0,028	0,005	0,211	0,177	0,06202	0,0167	0,51
ULSFO	0,011	0,025	0,004	0,045	0,095	0,06204	0,0004	0,24

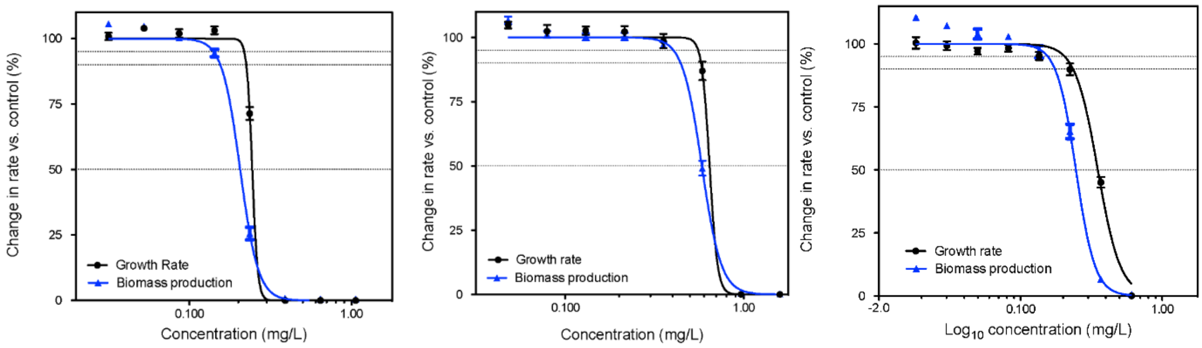


Figure C-5 Reduction in growth rate ad biomass production for S. costatum *as a function on WAF concentration: VSLFO (left graph); VLSFO Shell 2019 (middle graph); ULSFO (right graph).*

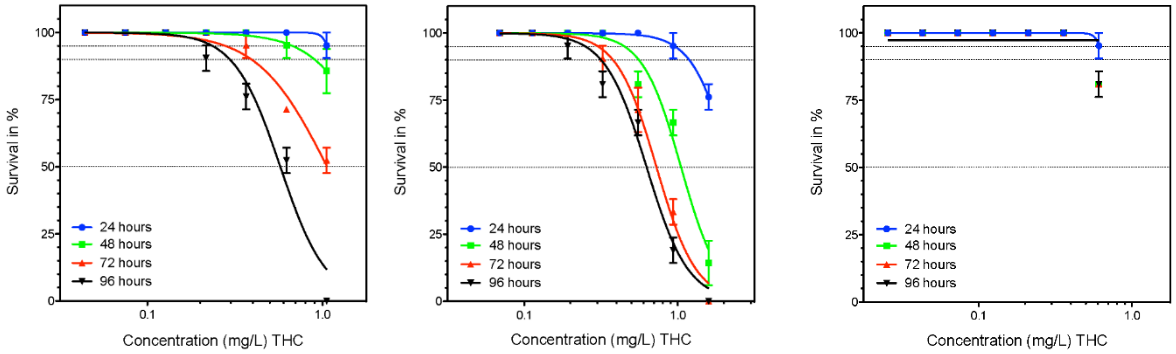


Figure D-6 Survival (y-axis) for Calanus finmarchicus *exposed for 24, 28, 72 and 96 hours to different concentrations of WAFs prepared from VSLFO (left graph), VLSFO Shell 2019, and ULSFO.*

Table D-6 Target organic analytes (SVOC: Semi volatile organic compounds, VOC: Volatile organic compounds, TPH: Total petroleum hydrocarbons, UCM. Unresolved organic materials).

	Compound	Abb	Group	Compound	Abb
SVOC	Decalin	DE	C0-C5 phenols	Phenol	PH
	C1-decalins	DE1		C1-phenols	PH1
	C2-decalins	DE2		C2-phenols	PH2
	C3-decalins	DE3		C3-phenols	PH3
	C4-decalins	DE4		C4-phenols	PH4
Naphthalenes	Naphthalene	N		C5-phenols	PH5
	C1-naphthalenes	N1	Other VOC	Isopentane	
	C2-naphthalenes	N2		n-C5 (Pentane)	
	C3-naphthalenes	N3		Cyclopentane	
	C4-naphthalenes	N4		2-methylpentane	
2-3 ring PAHs	Benzo(b)thiophene	BT		3-methylpentane	
	Biphenyl	B		n-C6 (Hexane)	
	Acenaphthylene	ANY		Methylcyclopentane	
	Acenaphthene	ANA		Cyclohexane	

	Dibenzofuran	DBF		2,3-dimethylpentane	
	Fluorene	F		3-methylhexane	
	C1-fluorenes	F1		n-C7 (Heptane)	
	C2-fluorenes	F2		Methylcyclohexane	
	C3-fluorenes	F3		2,4-dimethylhexane	
	Phenanthrene	P		2-methylheptane	
	Anthracene	A		n-C8 (Octane)	
	C1-phenanthrenes/anthracenes	P1		n-C9 (Nonane)	
	C2-phenanthrenes/anthracenes	P2		n-C10 (Decane)	
	C3-phenanthrenes/anthracenes	P3		n-Butylbenzene	
	C4-phenanthrenes/anthracenes	P4		1,2,4,5-tetramethylbenzene	
	Dibenzothiophene	D		n-pentylbenzene	
	C1-dibenzothiophenes	D1	BTEX	Benzene	
	C2-dibenzothiophenes	D2		Toluene	
	C3-dibenzothiophenes	D3		Ethylbenzene	
	C4-dibenzothiophenes	D4		*m*-xylene	
4-6 ring PAHs	Fluoranthene	FL		*p*-xylene	
	Pyrene	PY		*o*-xylene	
	C1-fluoranthrenes/pyrenes	FL1	C3-benzenes	Propylbenzene	
	C2-fluoranthenes/pyrenes	FL2		1-methyl-3-ethylbenzene	
	C3-fluoranthenes/pyrenes	FL3		1-methyl-4-ethylbenzene	
	Benz[*a*]anthracene	BA		1,3,5-Trimethylbenzene	
	Chrysene	C		1-methyl-2-ethylbenzene	
	C1-chrysenes	C1		1,2,4-trimethylbenzene	
	C2-chrysenes	C2		1,2,3-trimethylbenzene	
	C3-chrysenes	C3			
	C4-chrysenes	C4			
	Benzo[*b*]fluoranthene	BBF			
	Benzo[*k*]fluoranthene	BKF	TPH	C10-C36	
	Benzo[*e*]pyrene	BEP	WAF	Sum of VOC and TPH	
	Benzo[*a*]pyrene	BAP	UCM	TPH - SVOC	
	Perylene	PE			
	Indeno[*1,2,3-c,d*]pyrene	IN			
	Dibenz[*a,h*]anthracene	DBA			
	Benzo(g,h,i)perylene	BPE			

Appendix E Lab scale ULSFO Alternative Countermeasures Study Summary Report (SLRoss)

Lab Scale ULSFO Alternative Countermeasures Study Summary Report

For:

SINTEF, Norway

By:

SL Ross Environmental Research Ltd.
1140 Morrison Drive, Suite #200, Ottawa, ON K2H 8S9

DISCLAIMER

SINTEF does not endorse, nor reject, the contents of this report, nor does the report necessarily represent the views or opinions of SINTEF and/or its management. The conclusions and recommendations contained within this report are those of SL Ross Environmental Research Ltd.

TABLE OF CONTENTS

1 INTRODUCTION

A series of experiments were performed to determine the performance of a range of alternative countermeasures when evaluated with an Ultra Low Sulphur Fuel Oil (ULSFO) supplied by SINTEF, sampled in 2019. Countermeasures used in this series of evaluations include Dispersant Effectiveness Testing – Baffled Flask Test (Exxon Mobil), and In-situ Burning experiments at the 40 cm diameter ring scale. In addition, an initial series of tests were performed to determine physical properties of the oils that would be of interest from a spill response and modeling perspective. Summary results of the physical properties are presented below, complete data of the physical properties is available in a dedicated Properties Analysis Report.

2 OIL WEATHERING PROPERTIES

A Each of the oils was weathered to two weathered states for this initial series of testing. The weathered states correlate to time spent in the SL Ross wind tunnel, as shown below in Table 2–1. Depending on the conditions at a spill site, the Weathered States (WS) would typically correlate to periods from a few hours to a few days for a spill on water. Physical properties (density, viscosity) are measured at multiple temperatures to provide additional property information about the oil sample, and are shown below in *Table 2–2*.

Table 2–1 Weathered States

Weathered State	**Time in Wind Tunnel**
Fresh	0 days, as received
WS-1	2 days
WS-2	2 weeks

Table 2–2: Physical Properties of ULSFO

PROPERTY	**FRESH ULSFO**	**ULSFO WS-1 (0.3% loss)**	**ULSFO WS-2 (1.0% loss)**
Density g/mL @0°C	0.919	0.919	0.919
Density g/mL @15°C	0.911	0.913	0.913
Density g/mL @20°C	0.909	0.911	0.911
Density g/mL @30°C	0.904	0.907	0.907
Viscosity cP @0°C, SR 100 s^{-1}	42,607	58,307	59,636
Viscosity cP @15°C, SR 100 s^{-1}	4,663	5,292	5,725
Viscosity cP @20°C, SR 100 s^{-1}	2,103	2,391	2,562
Viscosity cP @30°C, SR 100 s^{-1}	419	482	549

Data from the physical parameters testing are used to generate parameters that can be fed into modeling software, which are then capable of predicting behaviour based upon a wide range of environmental conditions. Examples of these outputs (direct measurements and predicted outputs) are show below in Figure 2-1 through Figure 2-3.

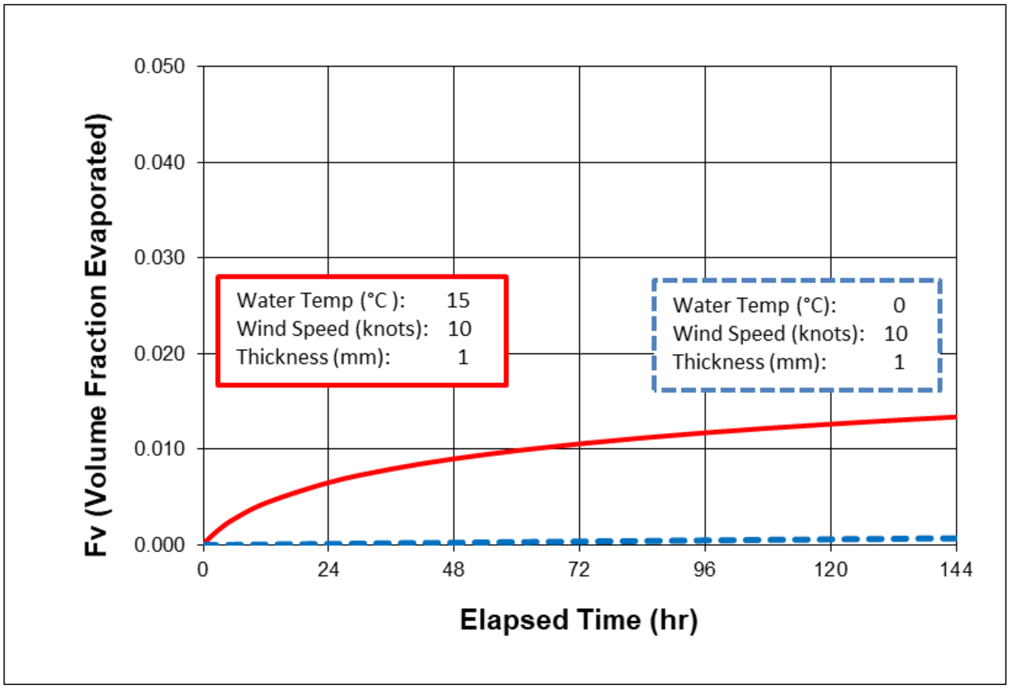


Figure 2-1: Evaporation of ULSFO 2019

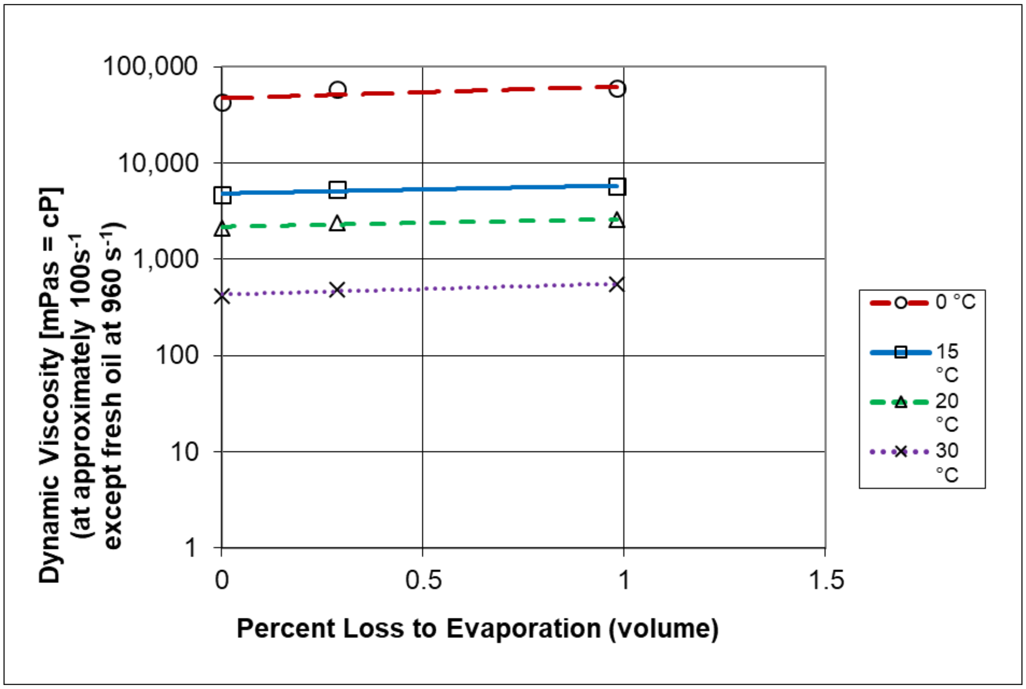


Figure 2-2 Effect of Evaporation on Oil Viscosity

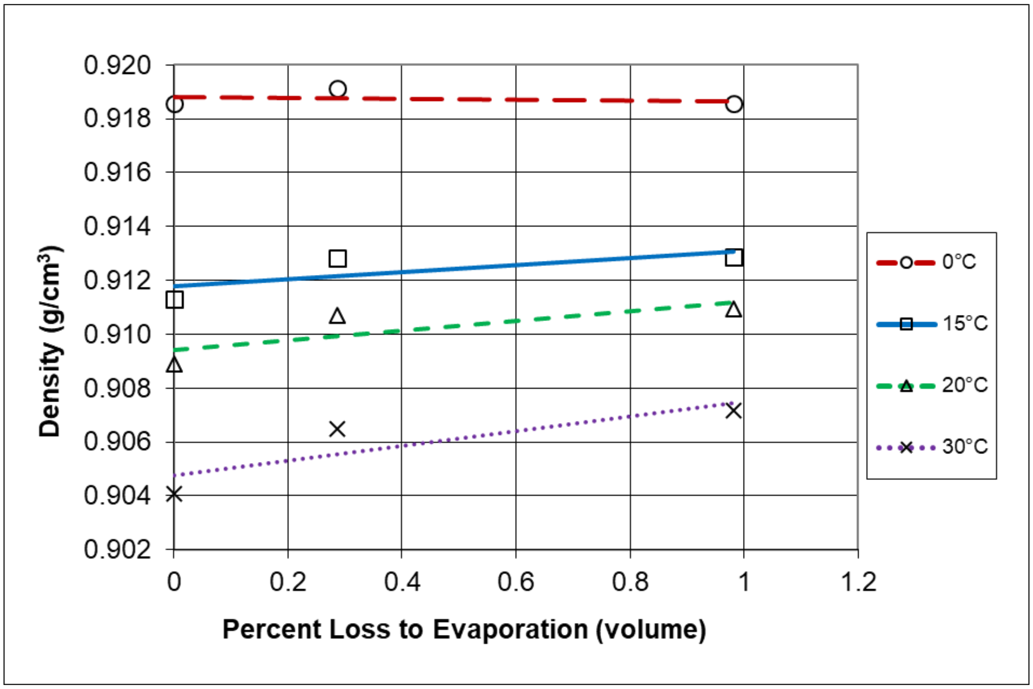


Figure 2-3 Effect of Evaporation on Oil Density

Additional physical parameters including surface tension, flash point, pour point, emulsification tendency, a simulated distillation, and calculated parameters for modeling inputs can be found in the ULSFO 2019 Property Analysis Report.

3 DISPERSANT EFFECTIVENESS TESTING – BAFFLED FLASK TEST (EXXON MOBIL)

The Baffled Flask Test (BFT) is a test that determines dispersant effectiveness at a lab scale. This test is routinely used to evaluate the potential effectiveness of a chemical dispersant on a standard oil, or to study the comparable impacts of chemical dispersants on oils. The baffled flask test has been identified as a replacement for a previous protocol, the swirling flask test, due to the improved energy impacting the oil/dispersant during testing which is more closely relatable to energies measured during larger scale testing.

DET-BFT TEST PROCEDURE

This procedure is based on Venosa et al., 2002 and Srinivasan et al., 2007. For each set of tests, three replicates are run with dispersant and three replicates are run without dispersant. If the relative standard deviation exceeds 15% between the four replicates, then the test is repeated. The samples are analysed using UV/Vis spectrometry.

PROTOCOL

1. Measure out 120ml of salt (3.4%) water at 20° C in six 250mL Baffled Trypsinizing Flasks.
2. Place the flasks on an orbital shaker.
3. Add 100 µL of the test oil to the surface of the water.
4. Add 5 µL of dispersant (Corexit 9500) onto the oil surface (giving a ratio of 1:20) on three of the flasks. The other three flasks do not receive dispersant and are considered controls.
5. Mix for 10 minutes at 200 RPM on an orbital shaker with a 2cm orbital diameter.
6. After 10 minutes stop the shaker and remove the flask(s).
7. Let stand for 10 minutes.
8. Drain 2 mL using stopcock and discard.
9. Transfer 70 mL from the bottom using the stopcock into a 100 mL graduated cylinder.
10. Transfer quantitatively to a 250 mL separatory funnel.
11. Extract with 3 x 5 mL dichloromethane and transfer extracts to a 25 mL graduated cylinder.
12. Make up to 20 mL.
13. Analyse by UV/Vis using the calibration curve for the oil being tested. Each oil (and weathered state) requires its own calibration curve.

UV/VIS ANALYSIS OF OIL:

Preparation of calibration curve:

1. Weight out approximately 2mL of oil in a 100 mL volumetric flask. Record the exact mass by the difference between the syringe before and after dispensing on the 4-place balance.
2. Prepare dilutions as follows:

Dilution	1:1000	1:500	1:250	1:100	1:50	1:25
Volume (mL) in 25 mL toluene	100µL in 100mL	100 µL in 50mL	100 µL in 25 mL	1000 µL in 100 mL	1000 µL in 50mL	1000 µL in 25 mL

3. Scan the solutions, including DCM as a blank, between 325 nm and 400 nm on the Novaspec III spectrometer while acquiring the data using the Grafico software.
4. Create a calibration curve using the absorbance vs concentration for the average absorbance between 325nm and 400 nm.
5. If the absorbance for the dilutions is above 2, do not use that data in the generation of the standard curve. With heavier oils, the 1:25 dilution would not be included in the generation of the calibration curve, since it is too concentrated.
6. Generate a tend line (solving for the concentration) and display the *linear* equation and r^2. The r^2 should be close to 1. If not redo. Use this equation to determine the concentration of the extracts.

Analysis:

1. Measure the extract on the Novaspec III by scanning between 325nm and 400 nm. If the absorbance is greater than the linear portion of the calibration curve, dilute the extract.
2. Export the data as a .csv file into the SINTEF ULFO.xls file. This will automatically solve for the dispersion efficiency. Dispersion efficiency is calculated as:

$$\text{Dipersant efficiency} = \frac{\text{mass of oil dispered}}{\text{mass of oil applied}} * 100\%$$

Results:

Table 3–1: Dispersant Efficiency Results

	Without Dispersant				**With Corexit 9500**			
ULSFO	Rep 1	Rep 2	Rep 3	Ave	Rep 1	Rep 2	Rep 3	Ave
Fresh	0.6%	0.4%	0.6%	0.5%	2.8%	3.1%	2.8%	2.9%
2 Day	0.5%	0.4%	0.6%	0.5%	7.2%	6.4%	6.1%	6.6%
14 Day	0.7%	0.5%	0.6%	0.6%	6.1%	4.9%	4.3%	5.1%

Table 3–2: Summary of Results

	Without Dispersant	**With Corexit 9500**
ULSFO Fresh	< 1%	3 %
ULSFO 2 Day	< 1%	7 %
ULSFO 14 Day	< 1%	5 %

Conclusions:

As shown by the results in the above tables, this oil has a low dispersibility when tested with Corexit 9500. The physical and chemical properties of the oil including high starting viscosity, high pour point, and low evaporation rate (low volatile compounds concentrations) support these results. Dispersibility is affected by the prominence, or lack thereof, of low molecular weight – higher volatile compounds which disperse and dissolve more easily into the water column.

REFERENCES:

Srinivasan, R., Lu, Q., Sorial, G. A., Venosa, A. D., & Mullin, J. (2007). Dispersant Effectiveness of Heavy Fuel Oils Using Baffled Flask Test. *Environmental Engineering Science*, *24*(9), 1307–1320. https://doi.org/10.1089/ees.2006.0251

Venosa, A. D., King, D. W., & Sorial, G. A. (2002). The Baffled Flask Test for Dispersant Effectiveness: A Round Robin Evaluation of Reproducibility and Repeatability. *Spill Science & Technology Bulletin*, *7*(5), 299–308. https://doi.org/10.1016/S1353-2561(02)00072-5

4 SMALL SCALE IN-SITU BURNING

The burns were performed in the SL Ross wind/wave tank. The tank is constructed of marine-grade aluminum, measuring 11 meters long by 1.2 meters wide by 1.2 meters deep (Figure 4-1). A fume hood is positioned over one section of the tank to exhaust smoke and combustion gases from the burns. All burns were conducted within a floating 40-cm diameter circular ring to contain the oil (Figure 4-2). A small electric trolling motor was used to create a current underneath the oil containment ring, to simulate the oil being towed in a fire boom on the ocean. It is important to simulate the resultant cooling action of the water movement to reduce or eliminate the vigorous burn phase that is sometimes seen in laboratory experiments but not in the field. The tank was filled with fresh water and brought to a salinity of 35 ‰ at ambient temperature of approximately 15°C (±1°C). All burns were done in calm conditions (i.e., some water movement but no waves).

Figure 4-1: SL Ross wind/wave tank

Figure 4-2: 40-cm diameter containment/burn ring

SMALL SCALE BURN PROTOCOL

The burns were conducted targeting 2.5 litres of fresh or evaporated oil resulting in an initial slick thickness of 20 mm. This should theoretically burn down to between 1 and 1.5 mm and result in a maximum target burn efficiency of approximately 95%. The burn time and burn efficiency were recorded as well as any observations. The burns were video recorded.

Set up:

1. Fill tank with fresh water and add NaCl to a 35 ‰ (3.5%) solution.
2. Set test tank temperature control unit to 15°C.
3. Ensure heat shields are installed and prepare power source for trolling motor.
4. Place 40 cm fire containment ring in the test tank centered beneath the vent hood.
5. Synchronize the clocks on all still and video cameras.

Experimental:

1. Record temperature of water,
2. Take sample of oil for all analysis.

3. Tare clean sorbents and clean, empty sample containers.
4. Add 2.5L of oil to be tested (record mass). This results in a starting slick layer of +/-20mm.
5. Start trolling motor to cool the bottom of the slick.
6. Start the video cameras and stopwatch. Take still photos as required.
7. Attempt to ignite the oil as follows:
    a. Use propane torch impinging on slick for up to 10 seconds. If ignition is not sustained after 1 attempt;
    b. add approximately 50 mL of **gelled gasoline** in a blob as an igniter (allow to spread), along with 3 seconds of a propane torch impingement. If unsuccessful;
    c. add 50 mL of **gelled gasoline** *and* 70 mL of **diesel fuel** as a primer (equivalent to a slick of 1 mm on the top of the oil layer) (picture), along with 3 seconds of a propane torch flame impingement.
    d. add 50 mL of **gelled gasoline** *and* an additional 140 mL of **diesel fuel** as a primer (equivalent to a slick of 2 mm on the top of the oil layer) (It is assumed that the previous 70m of diesel has been burnt off), along with 3 seconds of a propane torch flame impingement.
    e. If this fails, the slick will be designated as 'unignitable'.
8. If oil ignites, allow to burn to completion. Record observations
9. Stop recording.
10. Collect residue in a tared sample container and clean up residue with tared sorbents. Record masses.
11. Mix collected sample and distribute to appropriate sample vials. Heat to get sample flowing if necessary.

Preparation of gelled gasoline:

To produce 50 mL of gelled gasoline, add **0.4** grams of 'SureFire' gelling agent. Mix and used within 30 minutes of preparation.

Burn ring set-up:

The test ring was floated in the wave tank, positioned under the exhaust shroud, and retained by chains to maintain its relative position within the tank. The 40 cm ring had a 7 cm draft (below the waterline) and a 9 cm freeboard (above the waterline). As it sat under the exhaust shroud, there was approximately 40 cm from the outside edge of the ring to either side of the tank, as shown below in Figure 4-3.

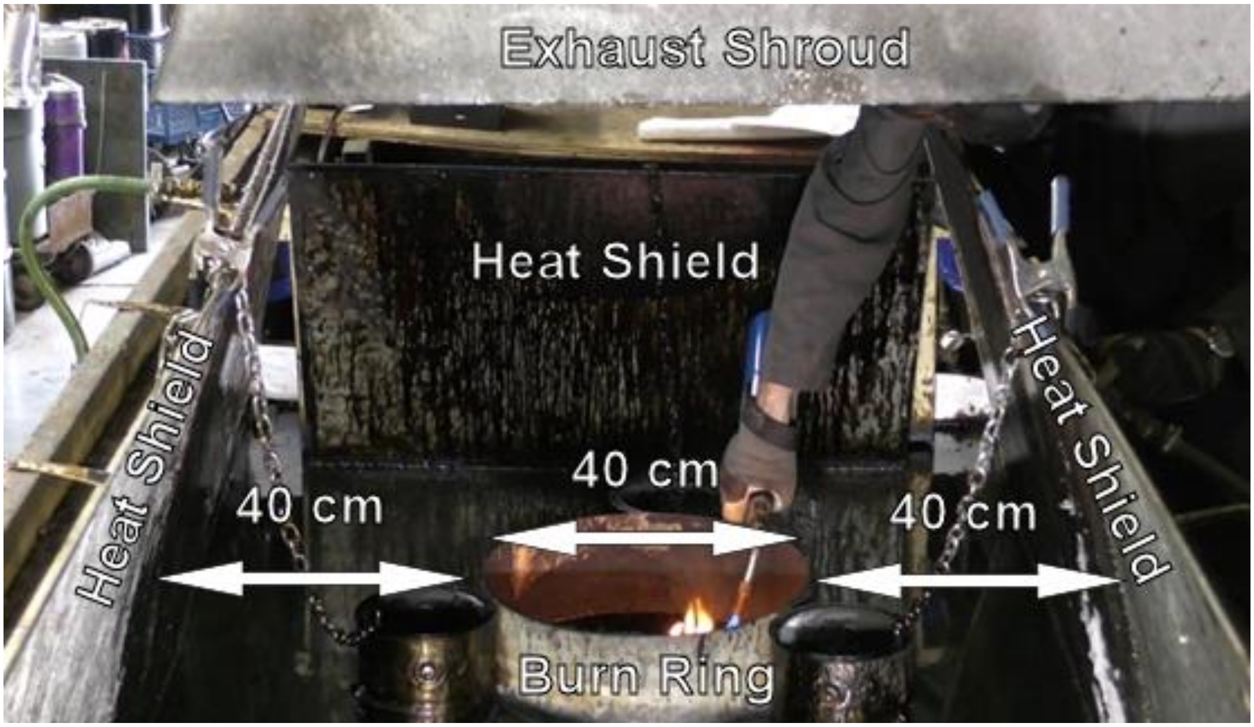


Figure 4-3: Burn Ring Set-up

RESULTS:

A total of three tests were performed, one on each weathered state of the oil (fresh (WS-0), WS-1, WS-2). Each of the burns failed to ignite with the short-term impingement from the propane torch and had to be initiated with the application of the gelled gasoline igniter. The first test, consisting of the fresh sample, resulted in a burn time of close to 17 minutes, with no evidence of the "boil over" phenomenon other than some minor crackling occurring early in the burn at the 1:42 mark. The burn resulted in an ending average residue thickness of 1.3 mm and an efficiency of approximately 93%. The second burn was with the WS-2 sample (weathered for 2 days in wind tunnel). This burn lasted slightly longer at 17:38, and resulted in a mild short boil-over occurring between 13:13 and 15:23 of the burn. The calculated efficiency of this burn was close to 84%. The final burn lasted for 18:43 and did not sustain a boil-over period. The efficiency of this last bun was near 85%. It is important to note that the efficiencies are useful in making comparisons between burns conducted under similar conditions, and they should not be taken out of context. Because these burns are conducted in a batch format, a larger starting volume of oil should generate better calculated efficiencies if the oil burns terminate at similar final residue slick thickness. Detailed measurements and timings are shown below in Table 4–1, photos taken during burns are shown below in Figure 4-4 through Figure 4-7.

Table 4–1: Burn Measurements and Timings

ULSFO SINTEF 2019 ISB– Data Sheet			
Run #:	1	2	3
Date:	12-Mar-20	12-Mar-20	12-Mar-20
Test Parameters:			
Oil:	ULSFO	ULSFO	ULSFO
Weathered state equivalent	WS-0 Fresh	WS-1 (2day in fh)	WS-2 (14day in fh)
Air Temp (C):	18.1	17.7	16.7
Water Temp (C):	15.7	15.9	16.3
Salt (%)	3.5	3.5	3.5
Density @ 20C (g/mL)	0.91313	0.91324	0.91345
Pre Burn:			
Weight of oil and container (g):	2760.7	2845.7	2789.7
Weight of empty container (g):	479.6	475.4	463.7
Mass of Clean Sorbent (g):	225.96	149.9	187.21
Mass of empty oil collection vessels (g):	297.31	296.36	296.76
Mass of Clean Spatula (g)	169.83	169.88	169.88
Mass of Clean funnel (g)			
Parameters to Record During Burn:			
Ignition (time to nearest second)	0:00:00	0:00:00	0:00:00
Stabilized Flame (50% flame coverage)	0:00:00	0:22:00	0:02:00
Full Ignition	0:00:00	1:01:00	0:05:00
Intense burn start (boil over)	13:08:00	15:23:00	14:41:00
Intense burn end	16:43:00	17:49:00	18:35:00
Burn ramp down (50% flame coverage)	16:54:00	18:39:00	18:48:00
Burn end (no flame)	16:55:00	18:56:00	19:02:00
Ignitability (Propane/Gelled fuel/Diesel)	Gelled fuel	Gelled fuel	Gelled fuel
Burn time (Full ignition to 50%):	16:54:00	17:38:00	18:43:00
Observations / Comments / Remarks	1:42 cracking heard	13:13 to 15:23 mild "boil over"	No evidence of "boil over"
Post Burn:			
Mass of sorbents after test (g):	286.61	214.49	255.36
Mass of full collection vessel (g):	394.69	591.66	580.06
Mass of spatula (g)	174.05	198.31	176.44
Calculations:			
Mass of oil applied (g):	2281.1	2370.3	2326
Mass of oil recovered (g):	162.25	388.32	358.01

% Mass Burned	93	84	85
Density of residue (g/mL)	0.96898	0.96017	0.96474
Initial Volume (mL)	2498	2595	2546
Final Volume (mL)	167	404	371
Burn efficiency volume removed (%)	93.1%	83.8%	84.9%
Starting thickness (mm)	19.9	20.7	20.3
Ending thicknesss (mm)	1.3	3.2	3.0

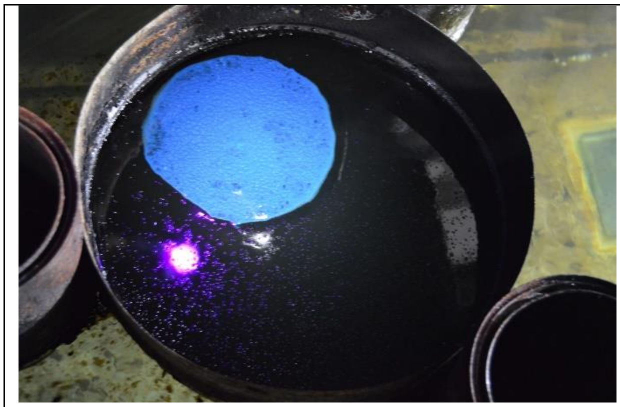


Figure 4-4: Gelled gasoline on oil layer under UV detection light

Figure 4-5: Burn conducted between heat shields, under exhaust shroud

Figure 4-6: Test burn in 40cm burn ring

Figure 4-7: Test burn residue recovery from burn ring

CONCLUSIONS

Burns were successfully performed on three weathered states of ULSFO 2019 oil. This refined product was ignited with gelled gasoline for all three burns. The burning process for each of the burns resulted in burn efficiencies in excess of 80%, which makes this product a candidate for in-situ burning as a countermeasure in the event of a spill.