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Physical and Chemical Analyses of Crude and Refined Oils: Laboratory and Mesoscale Oil Weathering

Final Report

US Department of the Interior
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Physical and Chemical Analyses of Crude and Refined Oils: Laboratory and Mesoscale Oil Weathering

Final Report

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ABOUT THE COVER

Cover photo courtesy of SINTEF Materials and Chemistry.

EXECUTIVE SUMMARY

Spilled oils undergo changes when weathering on the sea surface that affect behavior and oil spill countermeasures in various ways. Oil weathering varies over time and with different environmental conditions. The objectives of this study were to:

(1) To obtain weathering characteristics of crude oils representative of the Alaska OCS (Outer Continental Shelf) and typical refined products transported in offshore waters;

(2) To expand libraries of oil compositions of existing weathering models such as the SINTEF Oil Weathering Model (OWM) and the Automated Data Inquiry for Oil Spills (ADIOS) model from the National Oceanic and Atmospheric Administration (NOAA).

This report covers the physical and chemical analyses of six oils including:

- Three crude oils from Alaska North Slope: Alpine, Kuparuk and Northstar, and
- Three refined products of ADO (Automotive Diesel Oil, also called Ultra-Low-Sulphur Diesel (ULSD)) and MGO (Marine Gas Oil) from the Esso Slagen Refinery Norway, and a WRG (Wide Range Gasoil) from Mongstad Refinery Norway.

The six oils from this study were analyzed for their weathering properties in a standardized bench-scale methodology. In addition, the weathering was studied in the meso-scale flume basin as a supplement to the bench-scale testing for all oils. Dispersant effectiveness testing was beyond this study's scope, however, SINTEF added Corexit 9500 to the emulsified oils at the end of the testing to obtain a visual assessment of potential dispersibility in their weathered state. The resulting laboratory data from this study will be input into oil weathering models, i.e., the OWM and ADIOS, to predict the weathering properties of oils at sea. Including the data in these models will enable evaluation of the experimental data generated both by the bench-scale and meso-scale experiments to consider the most robust oil weathering predictions.

<u>Properties of crude oils from Alaska North Slope:</u>

Alpine is a paraffinic crude oil with a density of 0.832 g/mL (corresponds to API° 38.4). The fresh unweathered oil has a very low pour point (<-36 °C), but increases rapidly with the evaporative loss. The oil has a medium to low wax content of 2.1 wt. %, and has asphaltene content of 0.46 wt. %. The laboratory study showed that the oil forms stable water-in-oil (w/o) emulsions when weathered. However, the emulsion effectively released water when adding the emulsion breaker (Alcopol O 60 %) with a concentration of 2000 ppm. Emulsion breaker may be used during an oil spill operation to remove or reduce water from the emulsion, normally applied after recovery, prior to transfer to storage tank to minimize the storage volume. After three days weathering in the flume basin (meso-scale experiments) Corexit 9500 (*in-situ* application) was added to the emulsion to finalize the testing. The oil/emulsion showed a significant potential for dispersant use as a response option. However, effectiveness testing and determining the specific time-window, or window of opportunity, for dispersant use was not part of this project.

Kuparuk is categorized as a high-density 0.917 g/mL (API° 22.7) asphaltenic (4.7 wt. %) crude oil with a relatively low wax content of 1.3 wt. %. Kuparuk has a low pour point and solidification on the sea surface is not anticipated since solidification typically arises with pour points 10-15 °C above the sea temperature. The crude oil formed stable w/o-emulsions particularly for the 200 and 250°C+ residues with high viscosities. In general, the emulsions require a high dosage of emulsion breaker (Alcopol O 60 % at 2000 ppm) in cases where emulsion breaker might be added as part of a mechanical recovery operation to settle out water and decrease the storage volume needed. After three days of weathering in the meso-scale flume basin Corexit 9500 (*in-situ* application) with a cumulative dosage Dispersant-to-Oil (DOR) ratio of 1:50 was added to the oil/emulsion. The findings indicate that a higher dosage (DOR > 1:50) is recommended to be applied to a slick in an oil spill situation for higher effect, since the efficiency of adding dispersant (DOR 1:50) was not optimal. However, the window of opportunity for use of dispersant as a function of effectiveness and viscosities, and dosage testing for optimal DOR, was not determined in this study.

Northstar is a very light paraffinic crude oil with a density of 0.779 g/ml (API° 50), and exhibits low content of wax (1.7 wt. %) and asphaltenes (0.03 wt. %). The oil is a low-emulsifying crude oil that forms loose emulsions and easily released water with the addition of a concentration of 500 ppm of the emulsion breaker (Alcopol O 60 %). The oil showed high potential for application of dispersant agent (Corexit 9500) based on the results from the meso-scale flume basin. However, no laboratory study was conducted to assess the window of opportunity for using chemical dispersant on this oil.

Properties of refined products:

The ADO (Automotive Diesel Oil) has a density of 0.830 g/mL (corresponds to API° 38.8). The ADO oil has a very low content of wax and asphaltenes; less than 0.05 wt. %. The diesel oil has a very low pour point (<-36 °C) and remained low with evaporative loss. The weathered oil residue did not emulsify during the bench-scale emulsifying testing and showed no water uptake. Based on visual inspection during the meso-scale flume experiment a great majority of the oil was naturally dispersed into the water column, and only a minor amount of the oil was observed on the surface after three days of weathering (~ 3 % of the total released oil into the flume). The remaining oil on the surface became darker with a "slimy" characteristic. The dispersant Corexit 9500 (*in-situ* application) was added and visually showed that the dispersant was effective.

The MGO (Marine Gasoil) has a density of 0.849 g/mL (corresponds to API° 35). The MGO oil has a higher wax content (1.96 wt. %) compared with the ADO. The asphaltene content of the diesel oil is less than 0.05 wt. %. The MGO has a low pour point similar to the ADO. The oil did not emulsify (no significant water uptake) in the bench-scale laboratory testing. During the meso-scale testing, most of the oil was easily naturally dispersed and diluted into the water column during the two days of weathering, and no dispersant agent was therefore applied onto the surface in the flume due to insignificant amount of available surface oil.

The WRG (Wide Range Gasoil) has a density of 0.892 g/mL (corresponds to API° 27) with a medium content of wax (4.8 wt. %) and with low content of asphaltenes (0.05 wt. %). The WRG oil has a low pour point (<-24 °C). Due to lack of lighter compounds, less than 250 °C, the fresh oil was assumed to have similar weathering properties as for the 250°C+ residue. The oil showed emulsifying properties during the bench-scale testing, but the emulsions were very unstable and easily broke up after standing less than an hour. Based on the meso-scale flume experiment a larger amount of the oil was naturally dispersed into the water column, and only a minor amount of the oil was observed on the surface after two days weathering. However, the dispersant agent Corexit 9500 (*in-situ* application) was added on the surface slick and visually showed high efficiency.

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ABBREVIATIONS, ACRONYMS, AND SYMBOLS

~	approximately
C	celsius
cP	centipoise
m^3	cubic meter
°	degree
g	gram
>	greater than
h	hour (s)
<	less than
m	meter
mg	milligram
mL	milliliter
min	minute
mPa.s	millipascal second
n	normal
ppm	parts per million
%	percent
s^{-1}	reciprocal second
rpm	rotation per minute
vol.%	volume percent
w/o	water-in-oil
wt.%	weight percent
ADIOS	Automated Data Inquiry for Oil Spills
ADO	Automotive Diesel oil
ASTM	American Society for Testing and Materials
API	American Petroleum Institute
BSEE	Bureau of Safety and Environment Enforcement
BOEM	Bureau of Ocean Energy Management
DCM	Dichloromethane
DER	Dispersant-to-emulsion Ratio
DM (DMA, DMB, DMC)	Distillate Marine (Marine Fuel ISO 8217)
DOR	Dispersant-to-oil Ratio
DWT	Deadweight tonnage
GC/FID	Gas Chromatography/Flame Ionization Detector
HSE	Health, Safety and Environment
ID	Identification
IFT	Interfacial tension
ISO	International Organization for Standardization
MGO	Marine Gas Oil
MSDS	Material Safety Data Sheet
NCA	Norwegian Coastal Administration
NOAA	National Oceanic and Atmospheric Administration
$T_{1/2}$	(Half) Time
TBP	True Boiling Point
OCS	Outer Continental Shelf
OWM	Oil Weathering Model
UCM	Unresolved Complex Mixture

ULSD	Ultra-Low-Sulphur Diesel
UV	Ultra Violet
WOR	Water-to-oil Ratio
WRG	Wide Range Gasoil

1. INTRODUCTION

SINTEF Materials and Chemistry, Department of Oil Spill Research (hereafter referred as SINTEF) was asked by SEA Consulting Group (hereafter referred as Client) to conduct weathering studies of six oils. A total of three oils were studied in Year One and three additional oils were studied in Year Two. The six oils included:

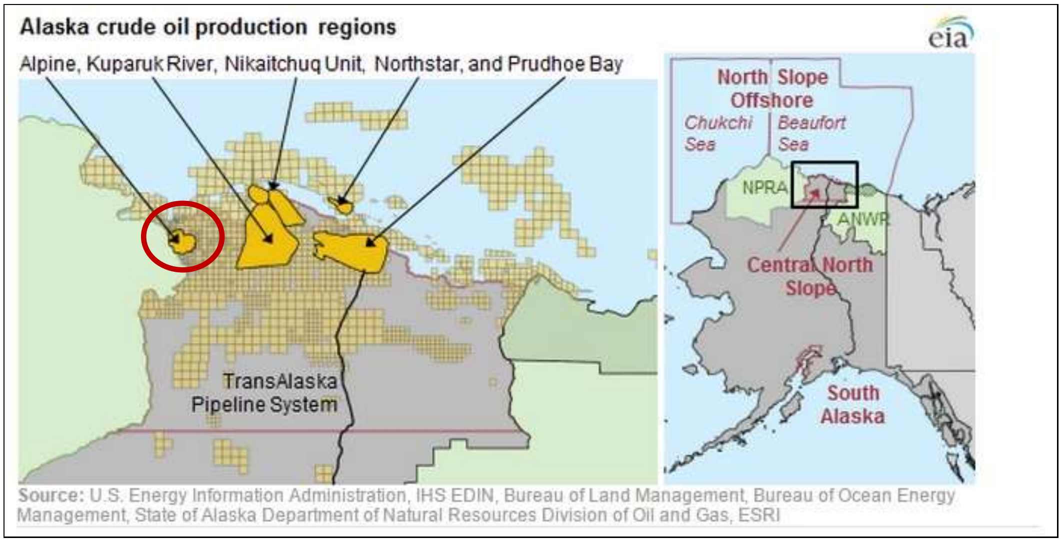
- Year One: One crude oil supplied from Alaska North Slope from ConocoPhillips Alaska, Inc. (Alpine), and two light refined products of ADO (Automotive Diesel Oil, also called Ultra-Low-Sulphur Diesel (ULSD) and MGO (Marine Diesel Oil). The refined products (diesel oils) were supplied from the Esso Slagen refinery in Norway.

- Year Two: The three oils in Year Two included two crude oils supplied from Alaska North Slope from ConocoPhillips Alaska, Inc. (Kuparuk) and Hilcorp Alaska, LLC (Northstar), and one refined product of WRG (Wide Range Gasoil) produced in Norway. The WRG refined product was supplied from Statoil Mongstad refinery in conjunction with another project that SINTEF is conducting (2014-2016) for the Norwegian Coastal Administration (NCA). The NCA project is a weathering and dispersibility study, with screening of dispersant agents for diesel products, including WRG. Findings from a pre-study of weathering properties of another batch of WRG can be found in Sørheim and Daling, 2015 (open report in Norwegian language).

The bench-scale and meso-scale flume laboratory testing of the six oils were conducted at 10 °C, reflecting relevant sea temperature in Alaskan waters, and was defined in agreement with the Client. The experimental data were further customized in tables for use as input to numerical Oil Weathering Models (OWMs), in order to obtain reliable and robust weathering predictions of spill scenarios.

Year One: North Slope Alpine crude oil.

The Alaska oil and gas production is concentrated in three main regions: North Slope Offshore (Nikaitchuq and Northstar), Central North Slope, and Southcentral Alaska, as shown in Figure 1.1. The same figure shows the location of Alpine (CD1) on Alaska's Central North Slope. Figure 1.2 shows the Alpine crude production site (plant) in Alaska.



Alaska crude oil production regions

Source: U.S. Energy Information Administration, IHS EDIN, Bureau of Land Management, Bureau of Ocean Energy Management, State of Alaska Department of Natural Resources Division of Oil and Gas, ESRI

Figure 1.1. Location of Alpine in red circle to the left. Alpine is located on Alaska's Central North Slope, west of the Kuparuk River Field (Kuparuk).
Source: http://www.eia.gov/todayinenergy/detail.cfm?id=21632.

Figure 1.2. Alpine production site in Alaska.
Source: http://alaska.conocophillips.com/PublishingImages/SMID_003_Alpine_BannerHero.jpg

Year One: Refined products from Esso Slagen Refinery.

The two refined oils, ADO (Automotive Diesel Oil, also called Ultra-Low-Sulphur Diesel (ULSD) and MGO (Marine Diesel Oil), from the Esso Slagen Refinery in Norway were chosen as representatives for refined products in Year One. These diesel oils are specified according to the international standard of EN 590 and ISO 8217 Fuel Standard (Distillate Marine fuels /Grade A, or DMA grade). Figure 1.3 shows the refinery situated in the South-East of Norway in the Oslo fjord. The marine terminal consists of a pier about 500 m long with loading/discharging berths on both sides, as shown in Figure 1.3. At present time, the terminal has approximately 800 tanker calls a year with size variation 100 to 250,000 DWT (Deadweight tonnage). The annual import of crude oil and blend stocks is about 6.5 mill. m^3 whereas about 5.7 mill. m^3 petroleum products are shipped out.

Figure 1.3. Location of Esso Slagen Refinery in the South-East of Norway situated on the west bank of the Oslo fjord.
Source: http://www.businesswire.com/multimedia/home/20140903006720/en/

Year Two: North Slope Kuparuk and Northstar crude oils.

As mentioned above in Year One, the Alaska oil and gas production is concentrated in three main regions: North Slope Offshore, Central North Slope, and Southcentral Alaska, as shown in Figure 1.4. The same figure shows the location of Kuparuk and Northstar on Alaska's Central North Slope in red circles.

Figure 1.5 shows the Kuparuk crude production site in Alaska. Northstar is an offshore installation located on an artificial island in the Beaufort Sea, as shown in Figure 1.6.

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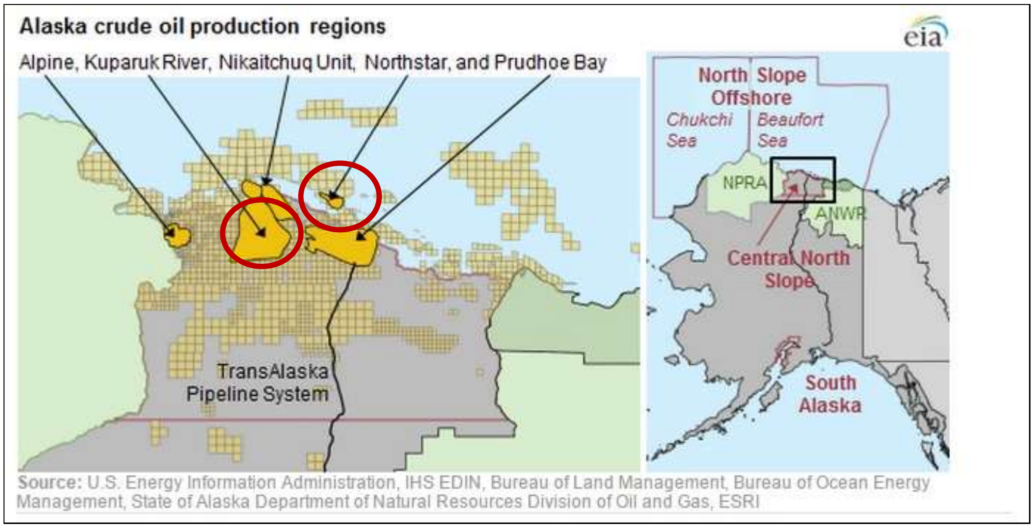


Source: U.S. Energy Information Administration, IHS EDIN, Bureau of Land Management, Bureau of Ocean Energy Management, State of Alaska Department of Natural Resources Division of Oil and Gas, ESRI

Figure 1.4. Location of Kuparuk and Northstar in red circles to the left. Kuparuk and Northstar are located on Alaska's Central North Slope.
Source: http://www.eia.gov/todayinenergy/detail.cfm?id=21632.

Figure 1.5. On Alaska's North Slope, ConocoPhillips Alaska, Inc. operates the Kuparuk River Unit (Kuparuk), North America’s second largest oil field.
Source: http://www.conocophillips.com/newsroom/PublishingImages/Kuparuk.jpg

Figure 1.6. Northstar production site in Alaska operated by Hilcorp Alaska, LLC. Northstar is located on an artificial island. It is located 6 miles offshore in water that experiences significant ice formation. Product flows through a subsea pipeline. Source: http://libertyprojectak.com/

Year Two: Refined product from Statoil Mongstad Refinery.

The refined product of WRG (Wide Range Gasoil) from the Statoil Mongstad Refinery in Norway was chosen as a representative oil type for testing in Year Two. According to the ISO 8217 Fuel standard, the WRG is classified as Distillate Marine, Grade DMB or DMC quality. The Mongstad oil refinery is located in the western part of Norway. The plant has an annual capacity of near 12 million tons of crude. Most of the oil refined comes from the Norwegian continental shelf. Most of the output from the refinery is exported, particularly to continental Europe. The principal outputs are petrol, diesel oil, jet fuel and other light petroleum products. Figure 1.7 shows the refinery area situated in the western part of Norway.

Figure 1.7. Location of Statoil Mongstad Refinery at the west coast of Norway.
Source:
http://www.statoil.com/en/ouroperations/terminalsrefining/prodfacilitiesmongstad/pages/energiverkmongstad.aspx

2. OIL SAMPLES/MATERIALS

2.1 ALPINE CRUDE OIL

The Central North Slope Alpine crude oil arrived at the SINTEF laboratory on the 19th of March, 2015 via air cargo from DHL. The oil sample was registered in the SINTEF laboratory database system, and given a unique identification number: SINTEF ID: 2015-0258. SINTEF received the Material Safety Data Sheet (MSDS) and a crude assay of the boiling point curve of Alpine. Figure 2.1 shows the barrels upon arrival and a sample description.

Sample description:

4 x 20 liter barrels

Alpine sales crude

Sampled December 20, 2014 at 12:59

Figure 2.1. Oil samples of Alpine crude oil upon arrival at SINTEF laboratory, 19th of March 2015.

2.2 REFINED DIESEL PRODUCTS (ADO, MGO)

The two refined diesel products of ADO (Auto diesel base = Ultra-Low-Sulfur Diesel (ULSD)) and MGO (Marine Gas Oil) arrived at the SINTEF laboratory on the 23rd of October, 2014 from the Esso Slagen refinery in Norway. The samples were registered in the SINTEF laboratory database system, and were given the following identification numbers: SINTEF ID: 2014-0491 (ADO) and 2014-0492 (MGO). The material safety data sheet (MSDS) and certificate of quality were given from the refinery. Figure 2.2 and Figure 2.3 show the barrels upon arrival and sample descriptions.

Sample description:

2 x 25 liter barrels

Sent from Esso Norge AS, Slagen

Type: ADO

Shore tank no: 801

Unit: OMS

Date: 20/10-14

Time: 13:45

Sample no: 141015108

Figure 2.2. Oil samples of ADO upon arrival at SINTEF laboratory, 23rd October 2014.

Sample description:

2 x 25 liter barrels

Sent from Esso Norge AS, Slagen

Type: MGO

Shore tank no: 803

Unit: OMS

Date: 20/10-14

Time: 15:35 and 15:55

Sample no: 141019027

Figure 2.3. Oil samples of MGO upon arrival at SINTEF laboratory, 23rd of October, 2014.

2.3 KUPARUK CRUDE OIL

A total of 80 liters of Central North Slope Kuparuk crude oil arrived at the SINTEF laboratory on the 19th of March, 2015 via air cargo from DHL. The oil sample was registered in the SINTEF laboratory database system, and given a unique identification number: SINTEF ID: 2015-0259. SINTEF received the Material Safety Data Sheet (MSDS) and a crude assay of the boiling point curve of Kuparuk from the Client. Figure 2.4 shows the barrels upon arrival and sample description.

Sample description:
4 x 20 liter barrels
Kuparuk sales crude
From CPF-1
Sampled January 16, 2015 at 3:52 PM

Figure 2.4. Oil samples of Kuparuk crude oil upon arrival at SINTEF laboratory, 19th of March 2015.

2.4 NORTHSTAR CRUDE OIL

A total of 80 liters of Central North Slope Northstar crude oil arrived at the SINTEF laboratory on 2nd of June, 2015 via air cargo from DHL. The oil sample was registered in the SINTEF laboratory database system, and given a unique identification number: SINTEF ID: 2015-0469. SINTEF received the Material Safety Data Sheet (MSDS) and a crude assay of the boiling point curve of Northstar from the Client. Figure 2.5 shows the barrels upon arrival and sample description.

Sample description:
4 x 20 liter barrels
Chemical Name: Northstar crude oil (from shipping pumps)

Sampled: 3-15-15

Figure 2.5. Oil samples of Northstar upon arrival at SINTEF laboratory, 2nd June 2015.

2.5 WIDE RANGE GASOIL (WRG)

SINTEF received in mid-November 2015 a container of 1000 Liters of a batch of WRG produced at the Statoil Mongstad refinery in Norway. The sampling and shipment was arranged through the Norwegian Coastal Administration (NCA). A total of 200 Liters from the container was transferred to a separate barrel, and an aliquot of 25 Liters was further sampled to a separate can. The 25 Liters sample of WRG was used in this study. The sample was registered in the SINTEF laboratory database system, and was given the following identification number: SINTEF ID: 2016-0106. A certificate of quality of WRG including the boiling point curve was customized by the refinery. Figure 2.6 shows the 1000 Liters container of WRG upon arrival and the aliquots of 25 Liters for analysis.

Figure 2.6. 1000 liters container of WRG (right). 25 liters aliquot of WRG ready for analysis (left)

3. BENCH-SCALE LABORATORY TESTING RESULTS

The bench-scale methodology is thoroughly described in Appendix A. As some of the tested oils exhibit similar properties and characteristics, this section is organized by the various composition and property testing conducted and combines and summarizes results.

3.1 PRE-HANDLING AND ANALYSIS

Pre-handling and analysis of oils from Year One

The samples of Alpine crude oil and the two refined diesel oils were measured for water content and densities upon arrival, and were further homogenized prior to the testing of the chemical composition and physical properties related to the weathering study. An overview of the results and comments are given in Table 3.1, Table 3.2, and Table 3.3.

Neither Alpine nor the two refined products showed high level of water content, therefore no extra distillation /topping was required. The original barrels containing the Alpine crude were dented upon arrival at the laboratory; however, the damage did not influence on the quality of the crude oil for the physical and chemical properties and conducting the weathering study.

Pre-handling and analysis of oils from Year Two

Samples of the two crude oils (Kuparuk and Northstar) and the refined WRG were measured for water content and densities upon arrival, and further homogenized prior to the testing of chemical composition and physical properties related to the weathering study. An overview of the results and comments are given in Table 3.4, Table 3.5, and, Table 3.6.

Some free-water was observed in the bottom of all the barrels of Kuparuk as described in the table below. It was decided to remove water/oil from the bottom of each barrel prior to homogenization to avoid any free-water from being incorporated into the whole sample. High water content is not beneficial for topping/distillation due to a HSE (Health, Safety and Environmental) aspect.

Neither Northstar crude oil nor the WRG showed any significant level of water content upon arrival, and no extra precaution prior to topping/ distillation were required. The original barrels containing the Kuparuk crude were dented upon arrival; however, the damage did not influence the quality of the crude oil for the physical and chemical properties and conducting the weathering study. The color appearance of Northstar was light brown and translucent, and the visual inspection indicated a low content of asphaltene. In addition, no visual precipitation of wax in a sample of Northstar crude oil, stored at a lower temperature (5 °C), was observed.

Table 3.1

Pre-handling and analysis of water content and density of Alpine crude oil.

Barrel	Water content (vol. %) * Bottom sample	Density (g/mL)	Comments Alpine crude oil (SINTEF ID: 2015-0258)
1 of 4	<0.01	0.835	The original barrel was highly dented upon arrival, but no leakage. The sample was transferred to a separate jerry can.
2 of 4	< 0.01	0.831	The original barrel was highly dented upon arrival, but no leakage. The sample was transferred to a separate jerry can.
3 of 4	< 0.01	0.831	The original barrel was highly dented upon arrival, but no leakage. The sample was transferred to a separate jerry can.
4 of 4	< 0.01	0.832	The original barrel was highly dented upon arrival, but no leakage. The sample was transferred to a separate jerry can.

**Measured with KF: Karl Fisher titration methodology*

Table 3.2

Pre-handling and analysis of water content and density of ADO diesel oil

Barrel	Water content (vol. %) * Bottom sample	Density (g/mL)	Comments ADO (Auto diesel) (SINTEF ID: 2015-0491)
1 of 2	< 0.01	0.830	None
2 of 2	< 0.01	0.830	None

**Measured with KF: Karl Fisher titration methodology*

Table 3.3

Pre-handling and analysis of water content and density of MGO diesel oil

Barrel	Water content (vol. %) * Bottom sample	Density (g/mL)	Comments MGO (Marine Gas Oil) (SINTEF ID: 2015-0492)
1 of 2	< 0.01	0.849	None
2 of 2	< 0.01	0.849	None

**Measured with KF: Karl Fisher titration methodology*

Table 3.4

Pre-handling and analysis of water content and density of Kuparuk crude oil

Barrel	Water content (vol. %) * Homogenized sample	Density (g/mL)	Comments Kuparuk crude oil (SINTEF ID: 2015-0259)
1 of 4	0.1	0.918	The original barrel was dented upon arrival, but had no leakage. Some free-water was observed. Approx.400 mL was removed from the bottom of the barrel. The barrel was further homogenized and the water content was quantified
2 of 4	0.1	0.917	The original barrel was dented upon arrival, but had no leakage. Some free-water was observed. Approx.400 mL was removed from the bottom of the barrel. The barrel was further homogenized and the water content was quantified
3 of 4	0.1	0.917	The original barrel was dented upon arrival, but had no leakage. Some free-water was observed. Approx.400 mL was removed from the bottom of the barrel. The barrel was further homogenized and the water content was quantified
4 of 4	0.1	0.917	The original barrel was dented upon arrival, but had no leakage. Some free-water was observed. Approx.400 mL was removed from the bottom of the barrel. The barrel was further homogenized and the water content was quantified

**Measured with KF: Karl Fisher titration methodology*

Table 3.5

Pre-handling and analysis of water content and density of Northstar crude oil

Barrel	Water content (vol. %) * Bottom sample	Density (g/mL)	Comments Northstar crude oil (SINTEF ID: 2015-0469)
1 of 4	0.14	0.779	The barrel was filled up with oil, and the homogenization was performed carefully and pre-heating at 50 °C was not considered necessary.
2 of 4	0.23	0.778	The barrel was filled up with oil, and the homogenization was performed carefully and pre-heating at 50 °C was not considered necessary.
3 of 4	0.31	0.778	The barrel was filled up with oil, and the homogenization was performed carefully and pre-heating at 50 °C was not considered necessary.
4 of 4	0.1	0.779	The barrel was filled up with oil, and the homogenization was performed carefully and pre-heating at 50 °C was not considered necessary.

**Measured with KF: Karl Fisher titration methodology*

Table 3.6

Pre-handling and analysis of water content and density of WRG

Barrel	Water content (vol. %) * Bottom sample	Density (g/mL)	Comments WRG (Wide Range Gasoil) (SINTEF ID: 2016-0106)
1 of 1	0.07	0.892	The 1000 litres container of WRG was stored upon arrival in room temperature for some weeks before an aliquot of 200 Liters was transferred to a separate barrel. The barrel was stored in room temperature prior sampling of 25 Liters.

**Measured with KF: Karl Fisher titration methodology*

3.2 CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES

3.2.1 Gas chromatographic (GC/FID) characterization

The gas chromatograms show the *n*-alkanes as systematic narrow peaks. The first peaks in the chromatogram represent components with the lowest boiling points. Some of the more complex components, such as resins and naphthenes, 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 (> nC_{40}) are not possible to analyze with this technique. The gas chromatographic characterization of the hydrocarbon distributing of the fresh oil and its corresponding residues (150, 200 and 200°C+) verifies the artificial evaporation of the oil by use of distillation (topping) in the laboratory.

GC/FID characterization of oils from Year One

The chemical composition of Alpine crude oil and the two refined products of ADO and MGO diesel oil, as characterized by gas chromatography (GC/FID), are shown in Figure 3.1, Figure 3.2, and Figure 3.3. No evaporation loss lower than 150 °C was observed. The GC/FID characterization indicates that Alpine crude oil is categorized as a paraffinic crude oil reflecting a medium to low amount of wax /paraffinic components in the range of nC_{20}-nC_{30} and a minor content of UCM.

GC/FID characterization of oil from Year Two

The chemical composition of Kuparuk and Northstar crude oil and the refined product of WRG, as characterized by gas chromatography (GC/FID), are shown in Figure 3.4, Figure 3.5 and Figure 3.6, respectively. The fresh sample of WRG showed insignificant evaporation loss lower than 250 °C.

The GC/FID characterization indicates that Kuparuk contains a relatively high amount of UCM that has possibly been caused by biodegradation in the reservoir. The oil reflects a medium to low amount of wax /paraffinic components in the range of nC_{20}-nC_{30}. However, since the oil contains high amount of asphaltenes as shown in Table 3.7, the Kuparuk crude oil classifies as an asphaltenic crude oil.

The Northstar crude oil is categorized as light paraffinic crude with low content of UCM, reflecting a medium to low amount of wax /paraffinic components in the range of nC_{20}-nC_{30}. In comparison, Kuparuk contains fewer lower molecular weight components and has a larger UCM envelope than Northstar and is also the heaviest crude oil (high density).

The fresh samples of ADO and MGO correspond to their 150°C+ residues due to no observed evaporation loss lower than 150 °C during distillation, and the corresponding GC-chromatograms (Figure 3.2 and Figure 3.3) verify that the distillates have minor content of the lightest component. However, MGO has a higher amount of *n*-alkanes in area from nC_{20} compared with the ADO reflecting wax-components.

WRG (Wide Range Gasoil) is a distillate with minor content of the lightest components and exhibits a high amount of *n*-alkanes of nC_{20}-nC_{26} reflecting wax-components with a well-defined UCM in this area.

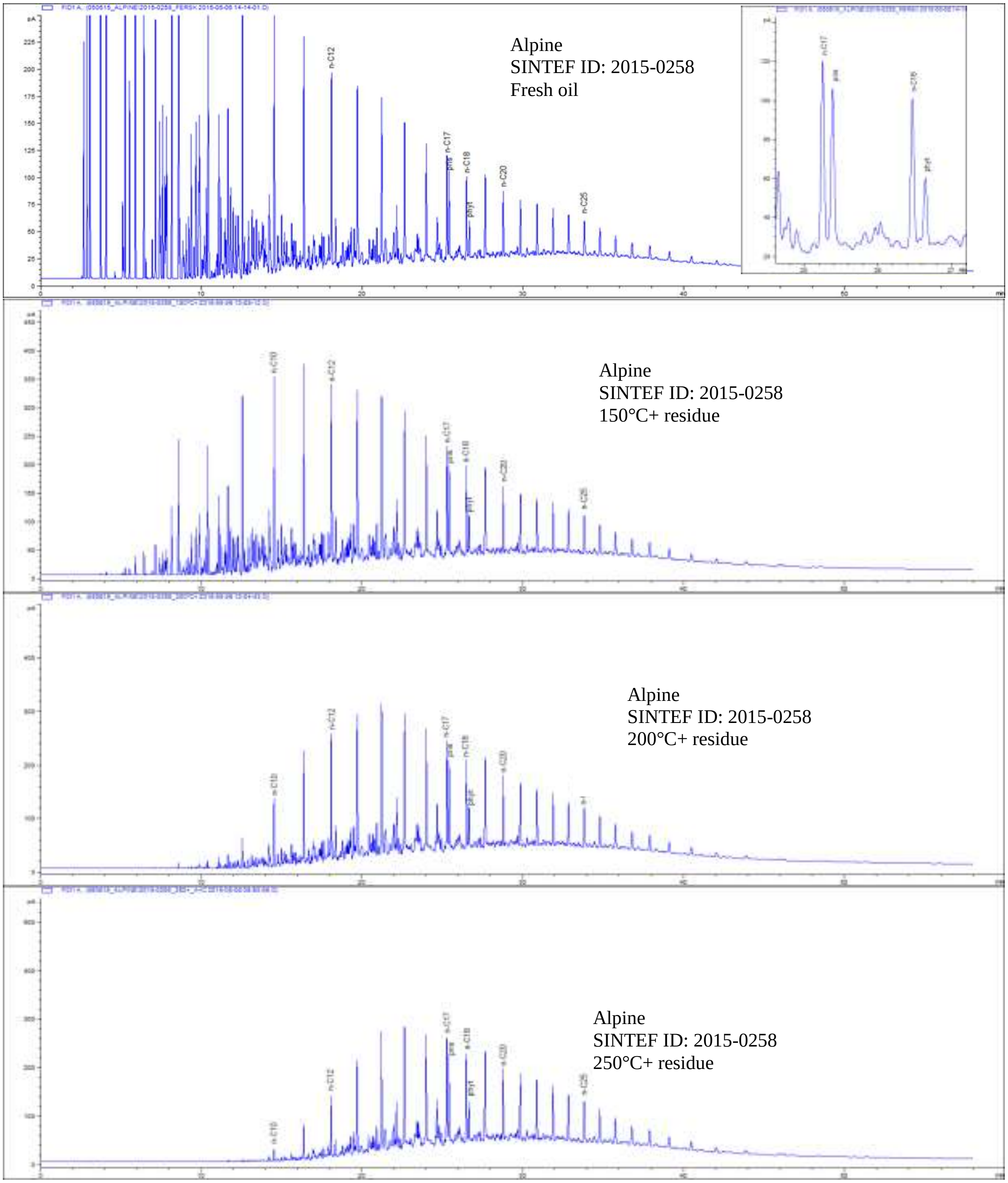
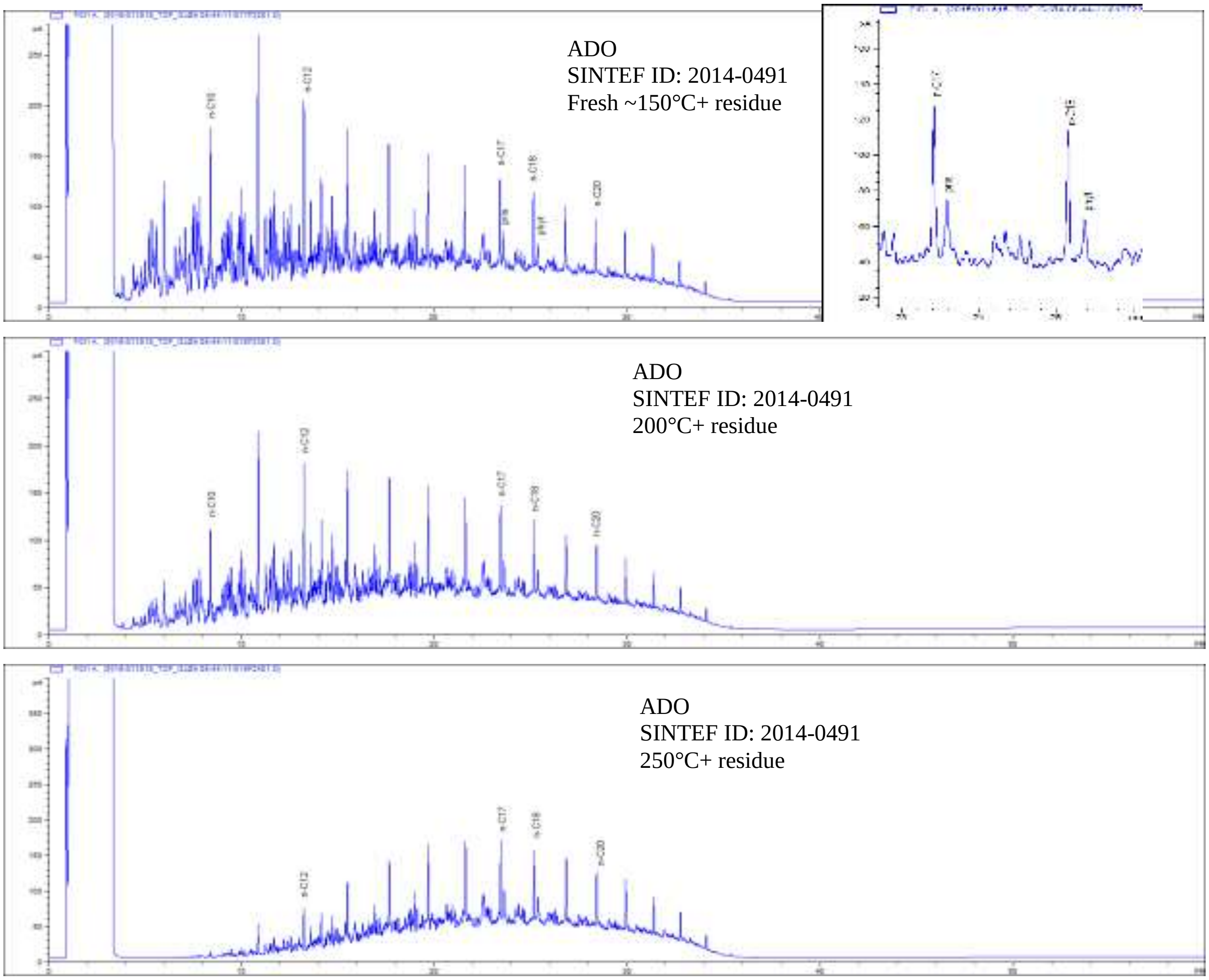


Figure 3.1. GC/FID chromatograms of the fresh and its evaporated residues of Alpine crude oil (SINTEF ID: 2015-0258)



ADO
SINTEF ID: 2014-0491
Fresh ~150°C+ residue

ADO
SINTEF ID: 2014-0491
200°C+ residue

ADO
SINTEF ID: 2014-0491
250°C+ residue

Figure 3.2. GC/FID chromatograms of the fresh and its evaporated residues of ADO (SINTEF ID: 2014-0491)

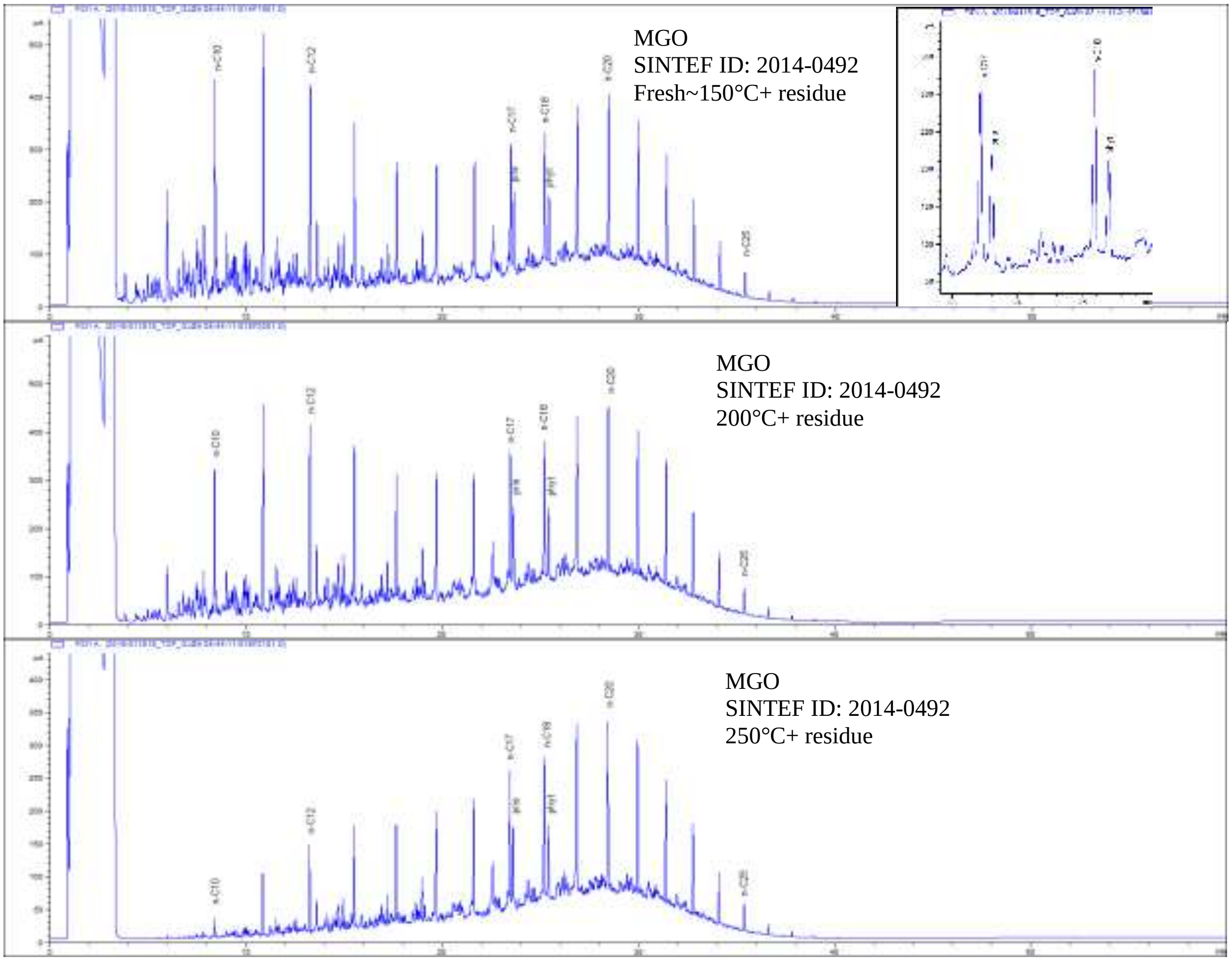


Figure 3.3. GC/FID chromatograms of the fresh and its evaporated residues of MGO (SINTEF ID: 2014-0492).

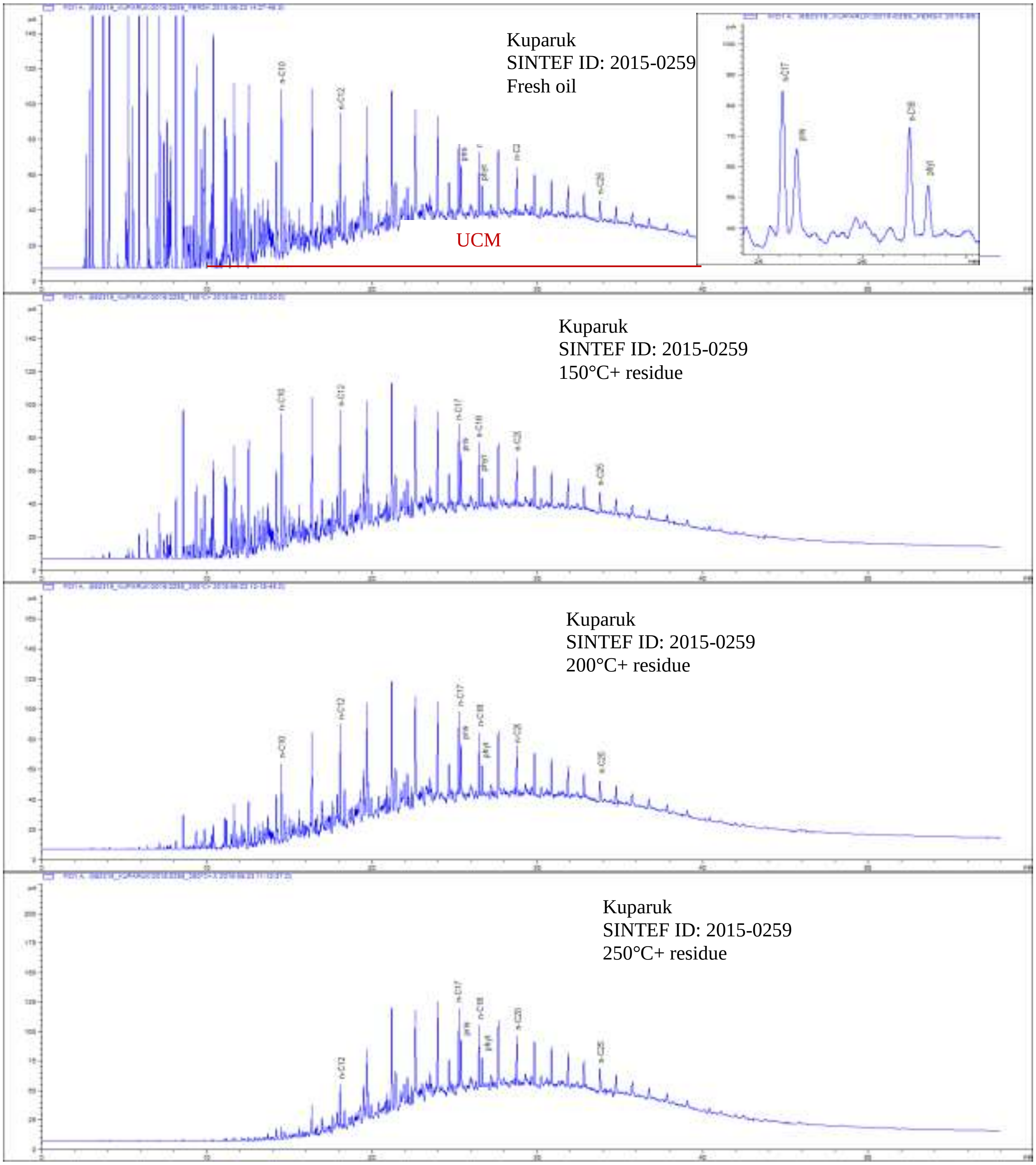


Figure 3.4. GC/FID chromatograms of the fresh and its evaporated residues of Kuparuk crude oil (SINTEF ID: 2015-0258)

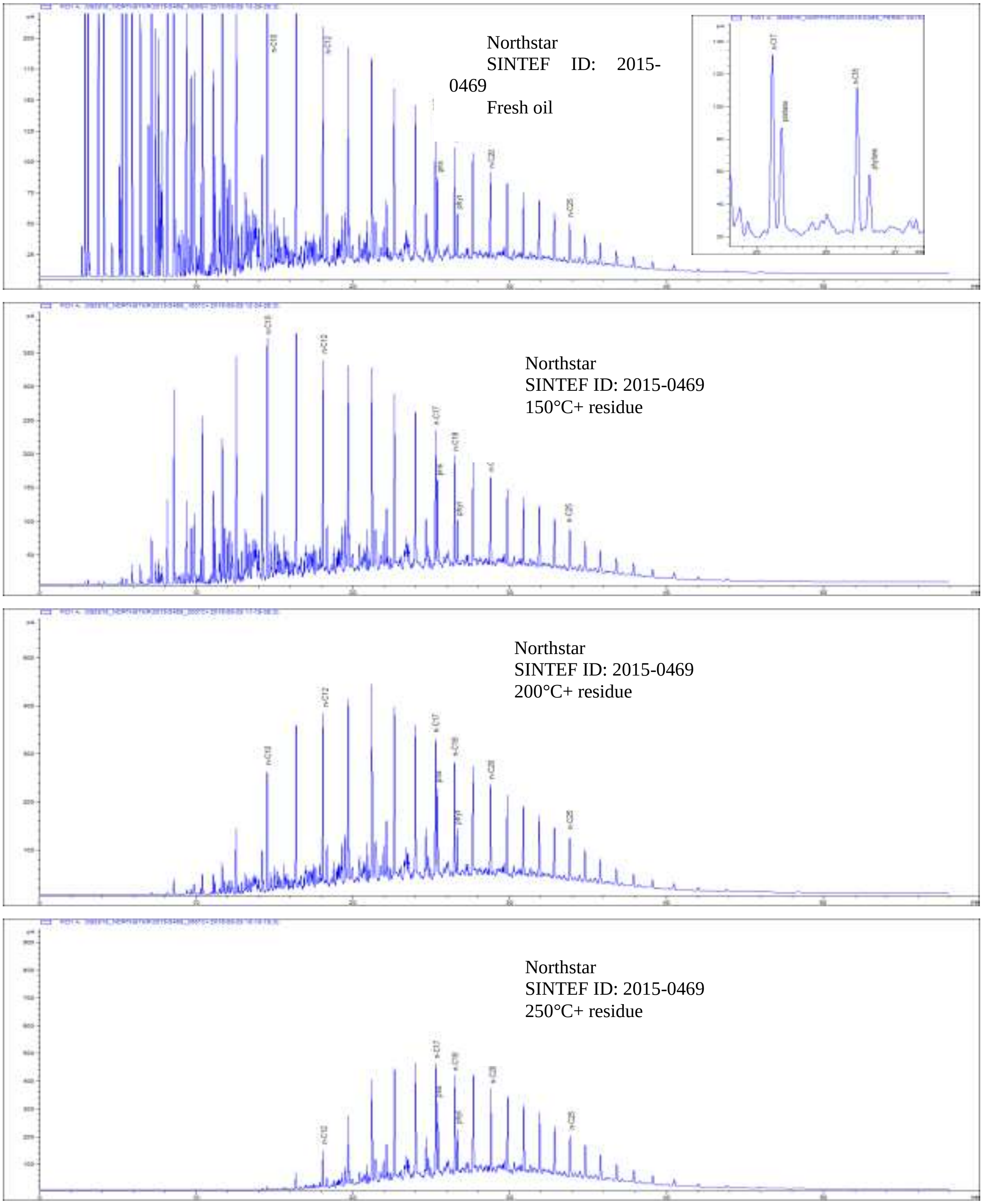


Figure 3.5. GC/FID chromatograms of the fresh and its evaporated residues of Northstar crude oil (SINTEF ID: 2015-0469)

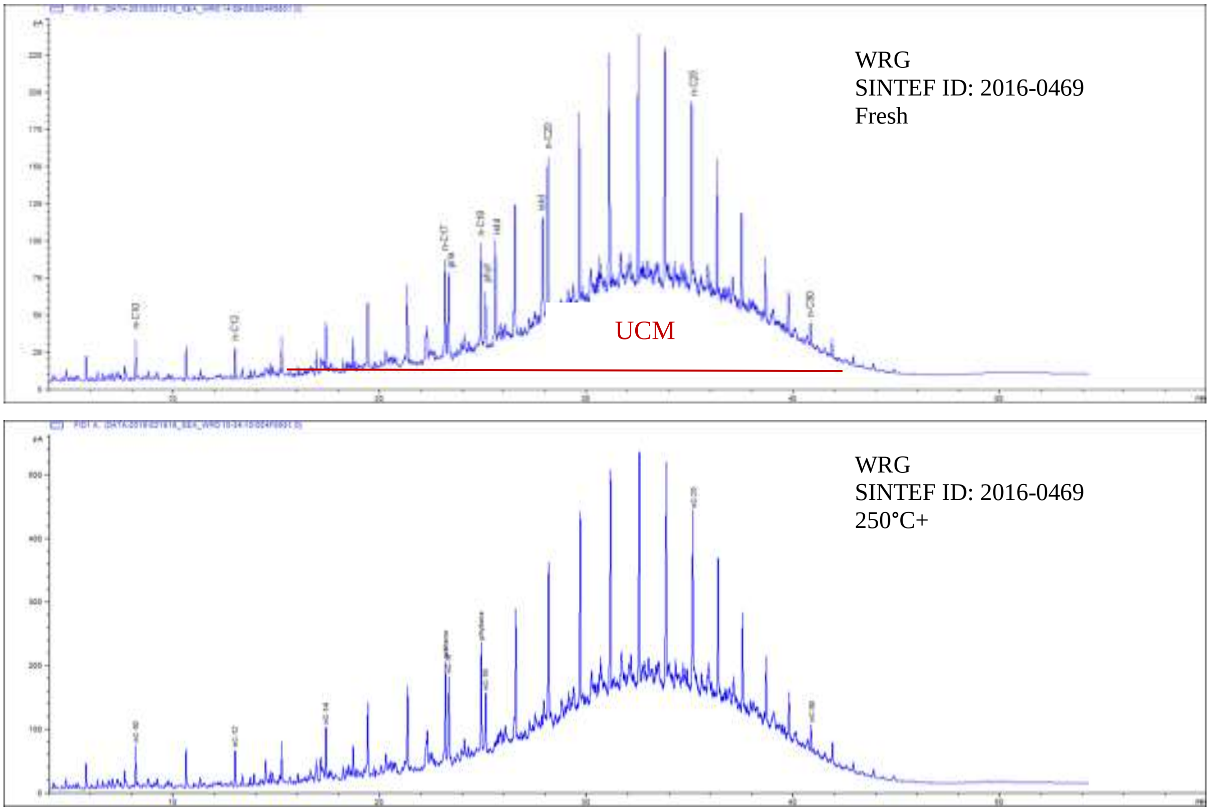


Figure 3.6. GC/FID chromatogram of the fresh Wide Range Gasoil (SINTEF ID: 2016-0106)

3.2.2 Asphaltene and wax content

The chemical properties of asphaltene and wax contents of Alpine crude oil and the two refined products of ADO and MGO (Year One), and Kuparuk, Northstar and Wide Range Gasoil (Year Two) are given in Table 3.7. Kuparuk exhibits a high content of asphaltenes compared with the other oils, and is considered as an asphaltenic crude with paraffinic features. Alpine, Kuparuk and Northstar crude oils have all low to medium content of wax. The lack of lighter components explain the low evaporative loss of Wide Range Gasoil (WRG) and the fresh oil is therefore assumed to correspond to the 250 °C+ residue, whilst the fresh oils of ADO and MGO correspond to the 150°C+ residue.

Table 3.7

Asphaltene ("hard") and wax content of Alpine, ADO MGO (Year One), and Kuparuk, Northstar and WRG (Year Two)

Oil type	Residue	"Hard"* asph. (wt.%)	Wax (wt.%)
Alpine SINTEF ID 2015-0258	Fresh	0.46	2.05
	150°C+	0.58	2.61
	200°C+	0.68	3.07
	250°C+	0.78	3.51
ADO** SINTEF ID 2014-0491	Fresh~150°C+	0.03	0.04
	200°C+	0.04	0.05
	250°C+	0.06	0.08
MGO* SINTEF ID 2014-0492	Fresh~150°C+	0.03	1.96
	200°C+	0.04	2.16
	250°C+	0.05	2.70
Kuparuk SINTEF ID 2015-0259	Fresh	4.74	1.32
	150°C+	5.21	1.44
	200°C+	5.46	1.51
	250°C+	5.94	1.64
Northstar SINTEF ID 2014-0469	Fresh	0.03	1.74
	150°C+	0.05	2.77
	200°C+	0.06	3.47
	250°C+	0.09	4.82
WRG*** SINTEF ID 2016-0106	Fresh~250°C+	0.05	4.84

** Hard asphalthenes: Precipitation of asphaltene using n-heptane (nC$_7$)*
*** The fresh oils of ADO and MGO correspond to the 150°C+ residue.*
**** The fresh oil of WRG corresponds to the 250°C+ residue.*

3.2.3 Physical properties of fresh and weathered residues

The physical properties of Alpine crude oil and the refined diesel oils of ADO and MGO (Year One) and Kuparuk and Northstar crude oils and the refined WRG (Year Two) are listed in Table 3.8 and Table 3.9.

Table 3.8

Physical properties of Alpine crude oil and refined products of ADO and MGO (Year One)

Oil type	Residue	Evap. (vol. %)	Res. (wt. %)	Dens. (g/mL)	Flash point (°C)	Pour point (°C)	Visc. mPa.s 10°C $10\ s^{-1}$	IFT (ini.) (mN/m)	IFT (eq.) (mN/m)
Alpine	Fresh	0	100	0.832	-	<-36	8	30	15
	150 °C +	25.5	78.5	0.877	40	0	43	30	14
	200°C+	37.9	66.8	0.896	87	9	204	28	13
	250°C+	46.6	58.4	0.906	113	12	688	30	15
ADO*	Fresh~ 150 °C+	0	100	0.830	59	<-36	5	24	12
	200 °C +	15.9	84.7	0.835	74	<-36	6	23	9.5
	250 °C +	47.5	53.4	0.845	107	-33	10	21	8.3
MGO*	Fresh~ 150 °C+	0	100	0.849	62	<-36	7	27	17
	200 °C +	9.7	90.9	0.854	78	<-36	9	29	13
	250 °C +	28.5	72.8	0.864	108	-30	14	28	11

** The fresh oil of ADO and MGO corresponds to the 150°C+ residue.*

- = Not analyzed

Table 3.9

Physical properties of Kuparuk and Northstar crude oils and refined products WRG (Year Two)

Oil type	Residue	Evap (vol. %)	Res. (wt. %)	Dens. (g/mL)	Flash point (°C)	Pour point (°C)	Visc. mPa.s 10°C $10\ s^{-1}$	IFT (ini.) (mN/m)	IFT (eq.) (mN/m)
Kuparuk	Fresh	0	100	0.917	-	-33	143	19	7
	150 °C +	11	92	0.941	57	-27	630	20	8
	200°C+	16	87	0.950	81	-21	1242	21	9
	250°C+	23	80	0.962	115	-12	4420	26	11
Northstar	Fresh	0	100	0.779	-	-9	1	29	10
	150 °C +	42	63	0.838	33	9	20	30	8
	200 °C +	54	50	0.852	71	15	249	30	7
	250 °C +	68	36	0.869	116	21	409	31	9
WRG*	Fresh~ 250 °C +	0	100	0.892	106	-24	85	19	12

** The fresh oil of WRG corresponds to the 250°C+ residue.*

- = Not analyzed

Distillation curve (True Boiling Point Curve -TBP)

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

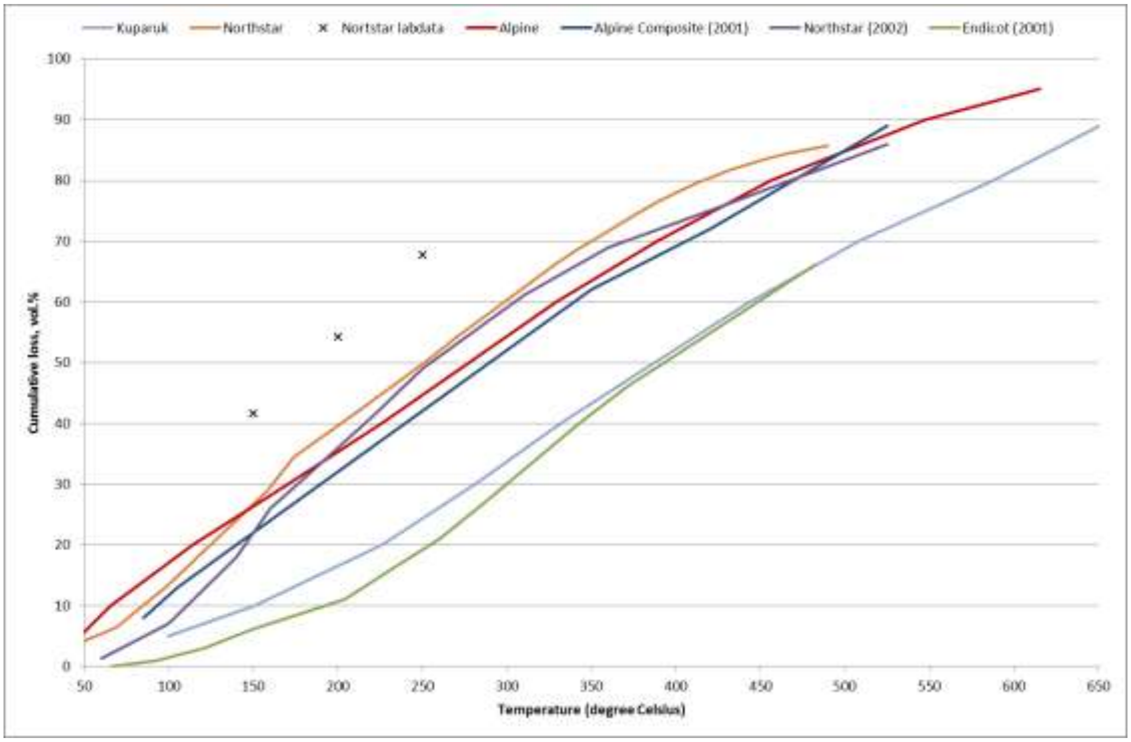


Figure 3.7. Distillation curves of Alpine, Kuparuk and Northstar crude oils in comparison with previously tested oils from Alaska North Slope (Leirvik *et. al*., 2002). Northstar lab data is based on the topped oil, and the TBP is therefore adjusted to fit the lab data as input to model tools

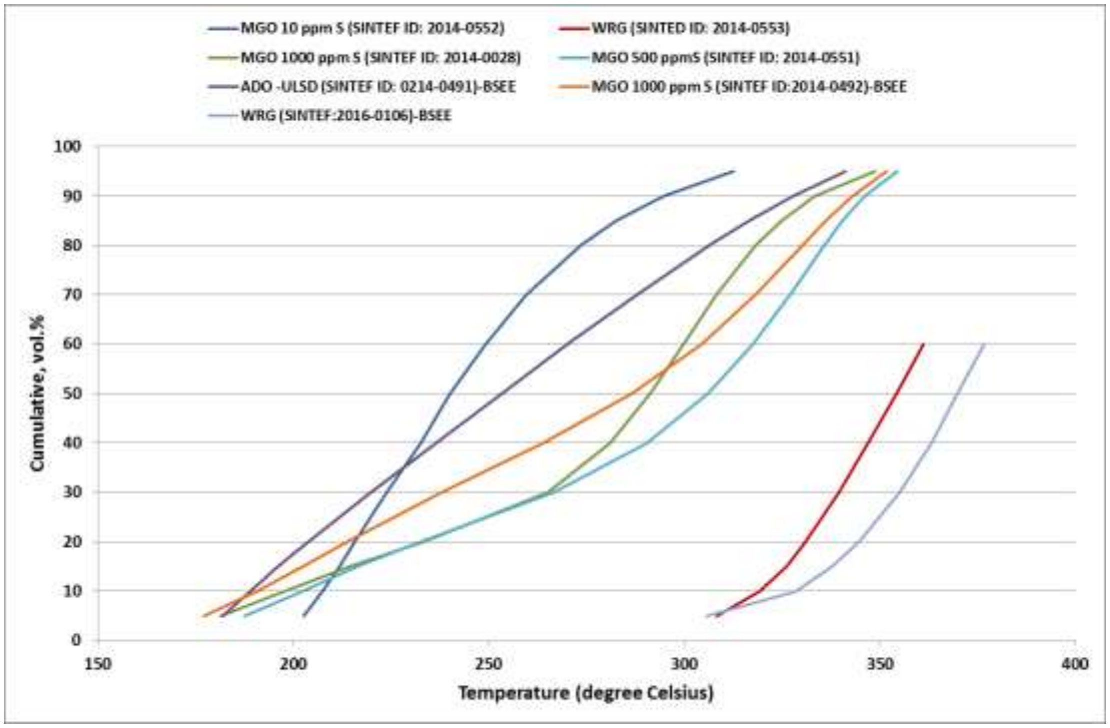


Figure 3.8. Distillation curves of WRG (Year Two) in comparison of ADO and MGO (Year One), and other refined products of marine gas oil and wide range gas oil (Sørheim and Daling, 2015)

3.3 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, section A.1.3. 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. In general, residues of 150°C+, 200°C+ and 250°C+ are made for each oil in order to produce data for stability, viscosity, water uptake and effectiveness of application of an emulsion breaker. Four cylinders of each residue of each oil, e.g., 150°C+, are 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).

3.3.1 Water uptake

Emulsification is the mixing of seawater droplets into spilled oil at the water's surface (water-in-oil emulsion), forming a weathered oil product that tends to be relatively resistant to other weathering processes such as evaporation, and also increased the total volume of oil due to the uptake of water into the oil. Highly emulsified oil can be more difficult to recover and also be difficult to chemically disperse.

Alpine Crude Oil

The Alpine crude oil formed water-in-oil (w/o) emulsions mixing with seawater as shown in Figure 3.9 The oil showed both a rapid and high water uptake for all the residues. The tabulated water uptake as a function of time and the calculated $T_{1/2}$ values is shown in Table 3.10.

Figure 3.9. The rotating cylinders of water-in-oil emulsion of Alpine crude oil after 24 hours of rotation at 10 °C

Table 3.10

Water uptake of the evaporated residues of Alpine crude oil at 10 °C

Mixing time	*150°C+ (Vol. % water)	*200°C+ (Vol. % water)	*250°C+ (Vol. % water)
Start	0	0	0
5 min	33	28	15
10 min	45	39	23
15 min	54	45	25
30 min	69	54	37
1 hour	77	63	78
2 hours	91	69	79
4 hours	90	78	79
6 hours	89	82	79
24 hours	84	81	79
$T_{1/2}$	0.16	0.23	0.38

** Depending on weather situation and release rate, the residues correspond to approximately 0.5-1 hour, 0.5-1 day and 0.5-1 week of weathering on the sea surface.*

ADO and MGO

Neither the ADO nor the MGO emulsified when mixed with seawater, where no water uptake during the testing in the rotational cylinders was measured, as shown in Figure 3.10. The stability and effectiveness of emulsion breaker was therefore not evaluated for these oils.

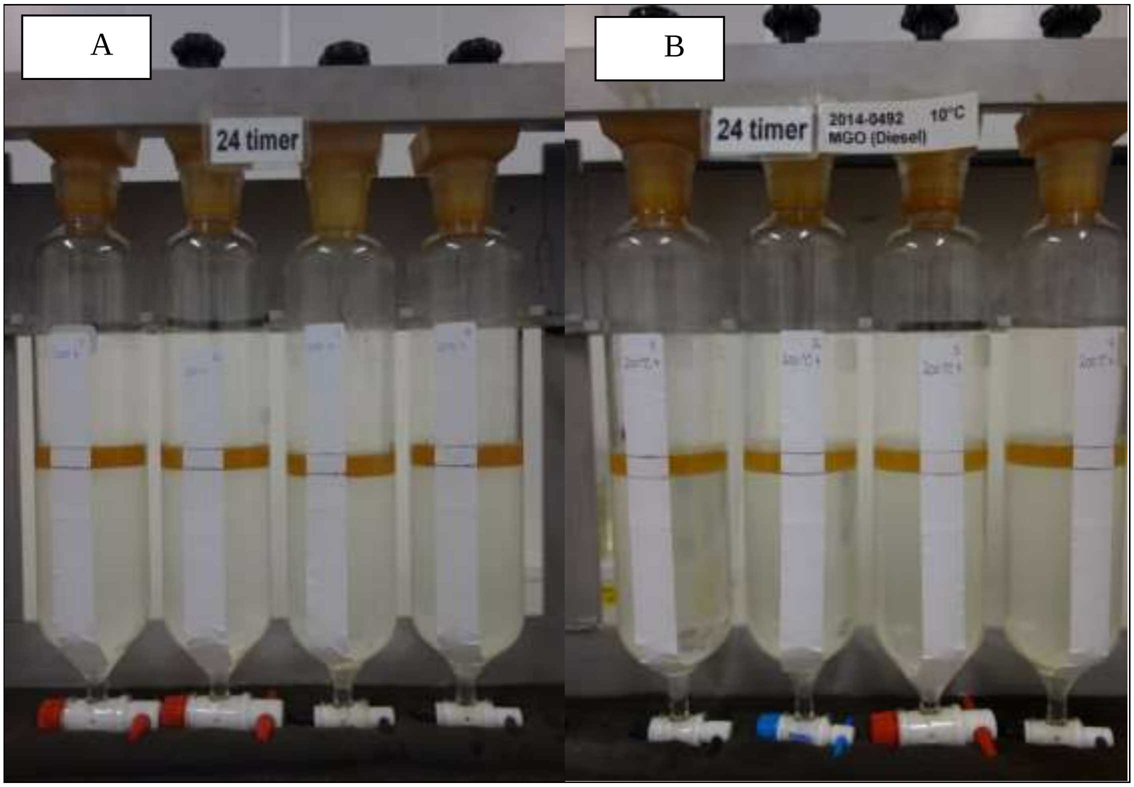


Figure 3.10. The rotating cylinders of ADO (left) and MGO (right) after 24 hours of rotation at 10°C. No emulsification was observed for ADO and MGO

Kuparuk Crude Oil

The Kuparuk crude oil formed water-in-oil (w/o) emulsions mixing with seawater as shown in Figure 3.11 after 24 hours of rotation. The oil showed a slow emulsification rate and relatively low maximum water uptake after 24 hours, as shown in Table 3.11.

Figure 3.11. The rotating cylinders of water-in-oil emulsion of Kuparuk crude oil after 24 hours of rotation at 10 °C, given as example for the 200 and 250°C+ residue

Table 3.11

Water uptake of the evaporated residues of Kuparuk crude oil at 10 °C.

Mixing time	*150°C+ (Vol. % water)	*200°C+ (Vol. % water)	*250°C+ (Vol. % water)
Start	0	0	0
5 min	8	3	2
10 min	13	7	4
15 min	19	7	4
30 min	31	18	7
1 hour	41	26	12
2 hours	48	33	12
4 hours	52	40	14
6 hours	55	43	14
24 hours	58	49	21
$T_{1/2}$	0.52	1.10	1.50

* *Depending on weather situation and release rate, the residues are corresponding to approximately 0.5-1 hour, 0.5-1 day and 0.5-1 week of weathering on the sea surface.*

Northstar Crude Oil

Northstar crude oil showed almost no emulsification for the 150°C+ residue where the emulsified residue almost corresponded to the water-free fresh oil, whilst the 250 °C+ residue developed a very high water uptake, but the emulsion was unstable with large water droplets and easily released water when settled under static conditions. Figure 3.12 shows the rotating cylinders of water-in-oil (w/o) emulsion of Northstar crude oil after 24 hours rotation time at 10 °C.

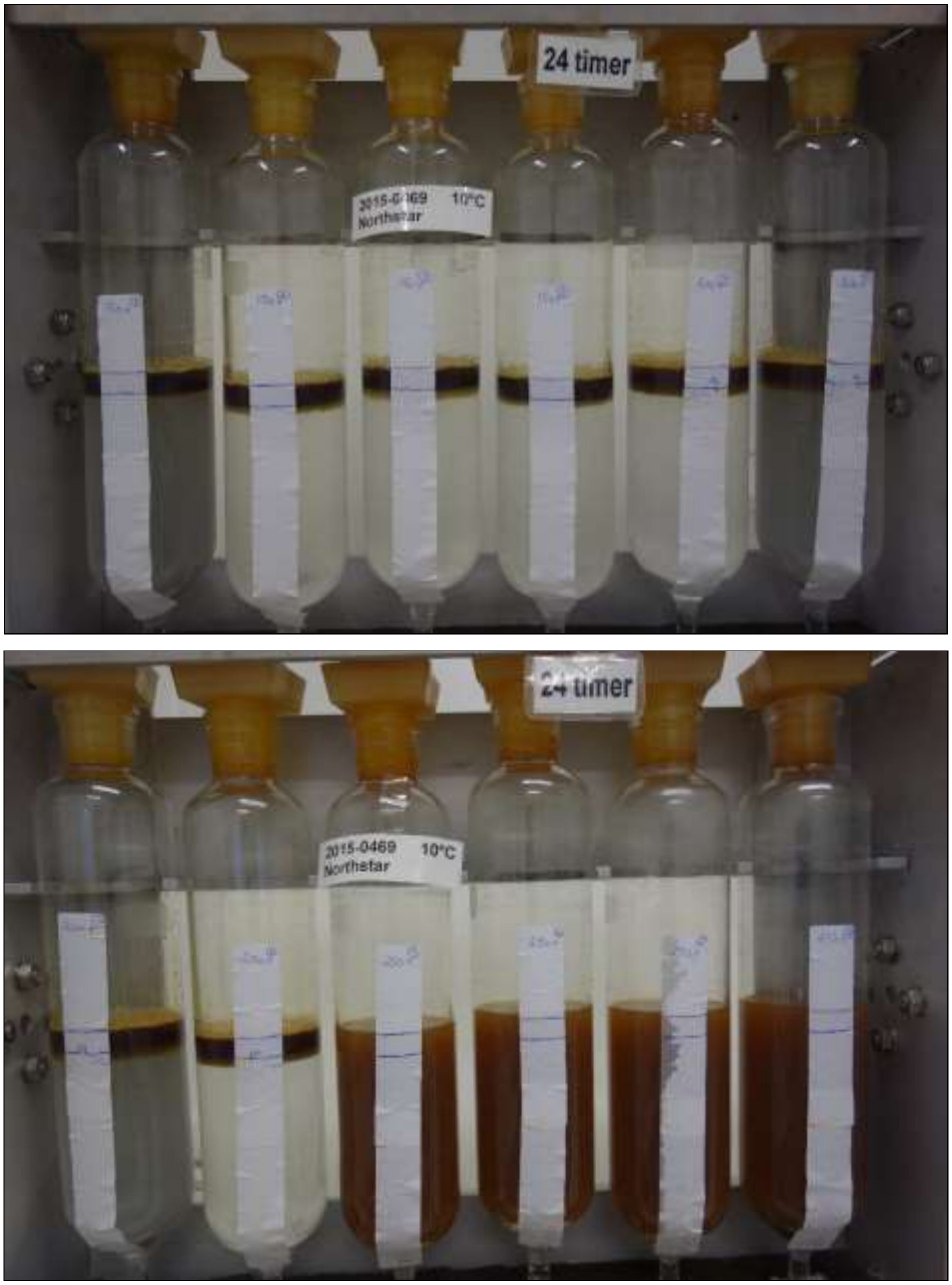


Figure 3.12. The rotating cylinders of water-in-oil emulsion of Northstar crude oil after 24 hours of rotation at 10 °C, given as example for the 150 and 200°C+ residues above, and for the 200 and 250°C+ residue, below.

Table 3.12

Water uptake of the evaporated residues of Northstar crude oil at 10 °C.

Mixing time	*150°C+ (Vol. % water)	*200°C+ (Vol. % water)	*250°C+ (Vol. % water)
Start	0	0	0
5 min	3	47	81
10 min	3	44	88
15 min	3	44	89
30 min	3	39	90
1 hour	3	33	90
2 hours	3	33	90
4 hours	3	31	90
6 hours	3	26	90
24 hours	3	26	90**
$T_{1/2}$	0.01	0.01	0.03

** Depending on weather situation and release rate, the residues are corresponding to approximately 0.5-1 hour, 0.5-1 day and 0.5-1 week of weathering on the sea surface.*

***~ 90 vol. % due to supersaturation in rotating cylinders and the very high water uptake is unlikely to happen in a spill situation at sea.*

Wide Range Gasoil (WRG)

The Wide Range Gasoil product showed emulsifying properties at 10 °C, but the oil formed very unstable emulsions with large water droplets, and the emulsion was quickly broken upon standing (within 1 hour), where most of the water was separated from the oil phase, as shown in Figure 3.13 below.

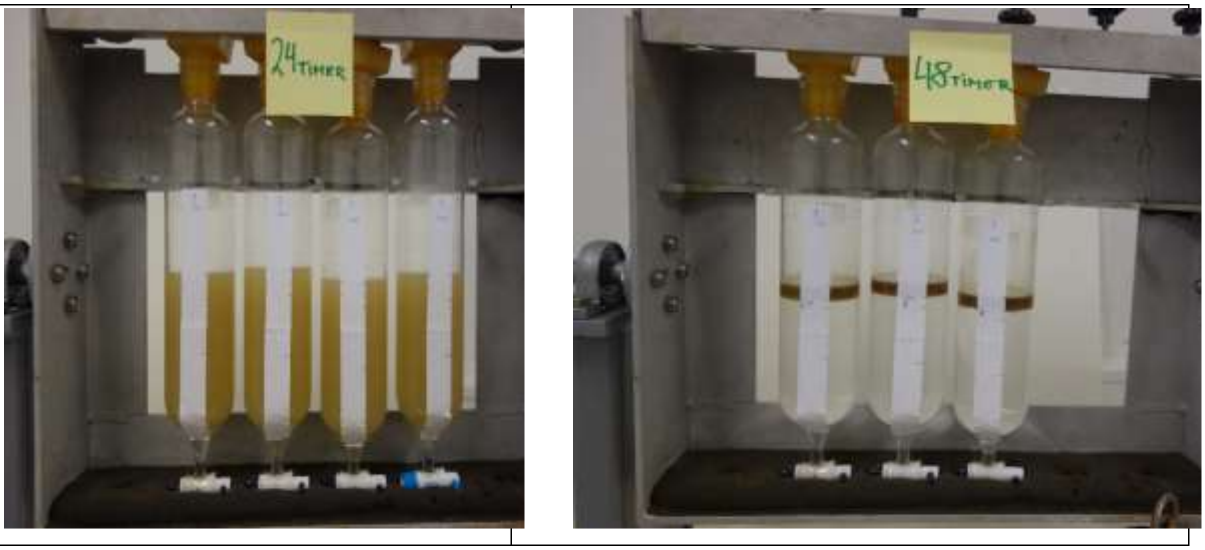


Figure 3.13. Unstable emulsion formation of WRG after 24 hours large droplet incorporated in the oil phase (left) and totally broken emulsion (left) after 48 hours without emulsion breaker

Table 3.13

Water uptake of the fresh oil of WRG at 10 °C

Mixing time	Fresh oil~250 °C+ residue (Vol. % water)
Start	0
5 min	41
10 min	82
15 min	91
30 min	91
1 hour	91
2 hours	91
4 hours	91
6 hours	91
24 hours	91*
$T_{1/2}$	0.15

**Unstable emulsion after 24 hours rotation. The emulsion was easily broken due to large droplet incorporated in the oil phase. 91 vol. % due to supersaturation- the very high water uptake is unlikely to happen in a spill situation at sea.*

3.3.2 Stability and efficiency of emulsion breaker

Overall, the findings of stability and the efficiency of emulsion breakers is important in a mechanical recovery situation because separating the oil from water enables optimal use of available storage facilities/tankers. The emulsified oil volume decreases considerably with treatment of an emulsion breaker as water is removed.

Alpine Crude Oil

The emulsion stability of Alpine crude oil was studied by quantifying the amount of water released from the emulsion during 24 hours settling time. In addition, the efficiency of adding emulsion breaker (Alcopol O 60 %) to the emulsion was evaluated. The results are shown in Table 3.14. The results indicate that Alpine crude oil forms very stable water-in-oil emulsions when spilled at sea and weathered. The effect of applying chemical emulsion breaker was most efficient by using the highest dosage of 2000 ppm (0.2 wt. %).

Kuparuk Crude Oil

The emulsion stability of Kuparuk was studied by quantifying the amount of water released from the emulsion during 24 hours settling time and the efficiency of adding emulsion breaker (Alcopol O 60 %) to the emulsion was evaluated. The effect of applying the highest dosage of 2000 ppm (0.2 wt. %) was slightly more efficient compared with the lower dosage of 500 ppm of the emulsion breaker. The results are shown in Table 3.15.

Northstar Crude Oil

The emulsion stability of Northstar was studied by quantifying the amount of water released from the emulsion during 24 hours settling time. In addition, the efficiency of adding emulsion breaker (Alcopol O 60 %) to the emulsion was evaluated. Northstar formed loose emulsions that were easily broken with the lowest dosage of 500 ppm of the emulsion breaker. The results are shown in Table 3.16.

Wide Range Gasoil

The stability of WRG emulsion was studied by quantifying the amount of water released from the emulsion during 24 hours settling time. In addition, the efficiency of adding emulsion breaker (Alcopol O 60 %) to the emulsion was evaluated. The emulsion was easily broken with or without the addition of emulsion breaker; i.e. the effect of adding emulsion breaker was insignificant. The results are shown in Table 3.17.

Table 3.14

Stability of Alpine emulsions (no emulsion breaker) and efficiency of emulsion breaker at 10 °C

Residue	Emulsion breaker	Water-in-oil emulsion (vol.%) at 10 ºC		
		Reference	24 hours *	Stability ratio**
150ºC+	none	84	86	1.00
200ºC+	none	81	80	0.95
250ºC+	none	79	77	0.94
150ºC+	Alc. O 60 % 500 ppm	84	-	-
200ºC+	Alc. O 60 % 500 ppm	81	71	0.57
250ºC+	Alc. O 60 % 500 ppm	79	72	0.70
150ºC+	Alc. O 60 % 2000 ppm	84	12	0.02
200ºC+	Alc. O 60 % 2000 ppm	81	35	0.12
250ºC+	Alc. O 60 % 2000 ppm	79	39	0.17

- Not measured

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

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

Table 3.15

Stability of Kuparuk emulsions (no emulsion breaker) and efficiency of emulsion breaker at 10 °C

Residue	Emulsion breaker	Water-in-oil emulsion (vol.%) at 10 ºC		
		Reference	24 hours *	Stability ratio**
150°C+	none	58	6	0.05
200°C+	none	49	17	0.21
250°C+	none	21	19	0.87
150°C+	Alc. O 60 % 500 ppm	58	12	0.10
200°C+	Alc. O 60 % 500 ppm	49	12	0.14
250°C+	Alc. O 60 % 500 ppm	21	17	0.75
150°C+	Alc. O 60 % 2000 ppm	58	12	0.10
200°C+	Alc. O 60 % 2000 ppm	49	6	0.07
250°C+	Alc. O 60 % 2000 ppm	21	9	0.37

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

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

Table 3.16

Stability of Northstar emulsions (no emulsion breaker) and efficiency of emulsion breaker at 10 °C

Residue	Emulsion breaker	Water-in-oil emulsion (vol.%) at 10 ˚C				
		Ref.	24 hours *	Stability ratio**	24 hours + 10 rotations ***	Stability ratio***
150°C+	none	3	3	-	3	-
200°C+	none	26	19	0.67	19	0.67
250°C+	none	90	90	0.93	51	0.11
150°C+	Alc. O 60 % 500 ppm	3	3	1.00	3	1.00
200°C+	Alc. O 60 % 500 ppm	26	3	0.10	3	0.10
250°C+	Alc. O 60 % 500 ppm	90	23	0.03	23	0.03
150°C+	Alc. O 60 % 2000 ppm	3	3	1.00	3	1.00
200°C+	Alc. O 60 % 2000 ppm	26	12	0.38	6	0.19
250°C+	Alc. O 60 % 2000 ppm	90	14	0.02	14	0.02

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

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

*** *w/o emulsion after 24 hours rotation and 24 hours settling + 10 rounds of rotation is expected to be most reliable with respect to a field operation.*

Table 3.17

Stability of WRG (no emulsion breaker) and efficiency of emulsion breaker at 10 °C

Residue	Emulsion breaker	Water-in-emulsion (vol. %) at 10 ˚C		
		Reference	24 hours*	Stability ratio*
Fresh	none	91	6	0.01
Fresh	Alc. O 60 % 500 ppm	91	14	0.02
Fresh	Alc. O 60 % 2000 ppm	91	0	0.00

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

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

3.3.3 Viscosity of water-free residues and emulsified residues

Alpine Crude Oil

Table 3.18 gives the viscosities of water-free residues and the corresponding residues after emulsification at 10 °C with 50 vol. %, 75 vol. % and the maximum water. As a non-Newtonian fluid, the viscosities of Alpine oil residues and emulsions are dependent on the shear rate; 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. In general, Alpine shows an increasing emulsion viscosity with increasing degree of weathering (evaporating and water uptake).

Table 3.18

Viscosity of Alpine water-free residue and their emulsified residues at 10 °C

Residue	Water content (vol. %)	Viscosity (m.Pas)	
		10 s^{-1}	100 s^{-1}
Fresh	0	8	7
150°C+	0	43	39
200°C+	0	204	159
250°C+	0	688	447
150°C+	50	358	281
200°C+	50	1128	736
250°C+	50	2386	1370
150°C+	75	2214	825
200°C+	75	5760	1885
250°C+	75	10481	3266
150°C+	83	24104	3802
200°C+	80	26059	5485
250°C+	77	33720	3650

ADO and MGO

The viscosities of the water free residues of ADO and MGO are given in Table 3.8. None of these oils showed emulsifying properties. The refined products also behaved as a Newtonian fluid, where the viscosity is not dependent on its shear rate.

Kuparuk and Northstar Crude Oils

The viscosities of the water free 150, 200 and 250°C+ residues and the corresponding emulsions are shown in Table 3.19 and Table 3.20 for Kuparuk and Northstar. The viscosity of Northstar for maximum water content of the 250°C+ residue was regarded as uncertain due to the low stability of the emulsion.

Wide Range Gasoil

The viscosities of the water free residues of WRG is given in Table 3.9. The emulsion of WRG was very unstable, and the very low viscosities measured were not tabulated.

Table 3.19

Viscosity of Kuparuk water-free residue and their emulsified residues at 10 °C

Residue	Water content (vol. %)	Viscosity (m.Pas) (10 s^{-1})	Viscosity (m.Pas) (100 s^{-1})
Fresh	0	143	134
150°C+	0	630	613
200°C+	0	1242	1230
250°C+	0	4420	4410
150°C+	50	3799	1978
200°C+	50	7380	3379
250°C+	50	22497	1867
150°C+	75	6546	767
200°C+	65*	14306	2736
250°C+	27*	9758	4977
150°C+	60	4979	2049
200°C+	52	7045	2975
250°C+	23	8497	4524

** The residue did not reach 75 % vol. water uptake and hence influence the viscosities.*

Table 3.20

Viscosity of Northstar water-free residue and their emulsified residues at 10 °C

Residue	Water content (vol. %)	Viscosity (m.Pas) (10 s^{-1})	Viscosity (m.Pas) (100 s^{-1})
Fresh	0	1	2
150°C+	0	20	10
200°C+	0	249	57
250°C+	0	409	152
150°C+	< 50*	16	8
200°C+	<50*	81	24
250°C+	<50*	60	39
150°C+	<75*	14	8
200°C+	<75*	55	18
250°C+	<75*	104	33
150°C+	3	17	8
200°C+	6	87	25
250°C+	-	-	8

**The residue did not reach 50 and 75 % vol. water uptake.*
- Unstable emulsion

4. MESO-SCALE FLUME LABORATORY TESTING RESULTS

The description of the meso-scale flume is given in Appendix A.2. This section is organized by oil type and provides an overview of the tabulated results of the meso-flume testing, visual observations, and estimated mass balance of each of the six oils that were tested.

The estimated mass balance of each oil is presented for each oil in Figures 4.1, 4.3, 4.6, 4.8, 4.10, 4.12.

The main processes of the mass balance for oil spilled at sea are:
- Evaporative loss
- Surface oil
- Dispersed oil into the water column

In addition, the mass balances from the flume basin also includes the estimated parameters:
- Amount of oil sampled
- Amount of oil sticking to the flume wall

The meso-scale testing provides valuable operational information about the oil's behavior. The flume testing is therefore considered a supplement to the bench-scale laboratory testing. The experimental results obtained for Alpine crude oil, ADO and MGO (refined products) from Year One and Kuparuk and Northstar crude oils, and WRG (refined product) from Year Two conducted at 10 °C are presented below.

4.1 ALPINE CRUDE OIL

An overview of the tabulated results from the meso-scale flume testing is given in Table 4.1 for Alpine crude oil.

Table 4.1

Tabulated results from the meso-scale weathering experiment of Alpine crude oil at 10ºC

Sample no	Time (hours)	Water content (vol. %)	Evaporative loss (wt. %)	Viscosity (m.Pas) 10 s^{-1}	Oil in water ppm*
1	0.5	7	20	NA	69
2	1	28	23	49	62
3	2	32	26	NA	62
4	4	34	29	173	65
5	6	57	31	329	45
6	12	69	33	762	34
7	24	70	35	1587	19
8	48	63	37	2296	17
9	72	56	39	2683	19
1st application of dispersants: 49.3g Corexit 9500 (DOR = 1:71)					
3 min. disp. 1	-	-	-	-	188
10 min. disp. 1	-	-	-	-	188
60 min. disp. 1		-	-	-	201
2nd application of dispersants: 60.6g Corexit 9500 (DOR = 1:56)					
3 min. disp. 2	-	-	-	-	374
10 min. disp. 2	-	-	-	-	334
30 min. disp. 2	-	-	-	-	352
120 min. disp. 2	-	-	-	-	340

- = no measured data. **ppm=parts per million* *NA: Not applicable*

Mass Balance of Alpine Crude Oil

The amount of oil evaporated, oil on surface, naturally dispersed and sampled oil was calculated, and the oil adsorbed to the flume walls was estimated by weight. Figure 4.1 shows the estimated mass balance before applying dispersant agent into the flume, whilst Table 4.2 shows an example of tabulated values of the estimated mass balance after 24 hours weathering.

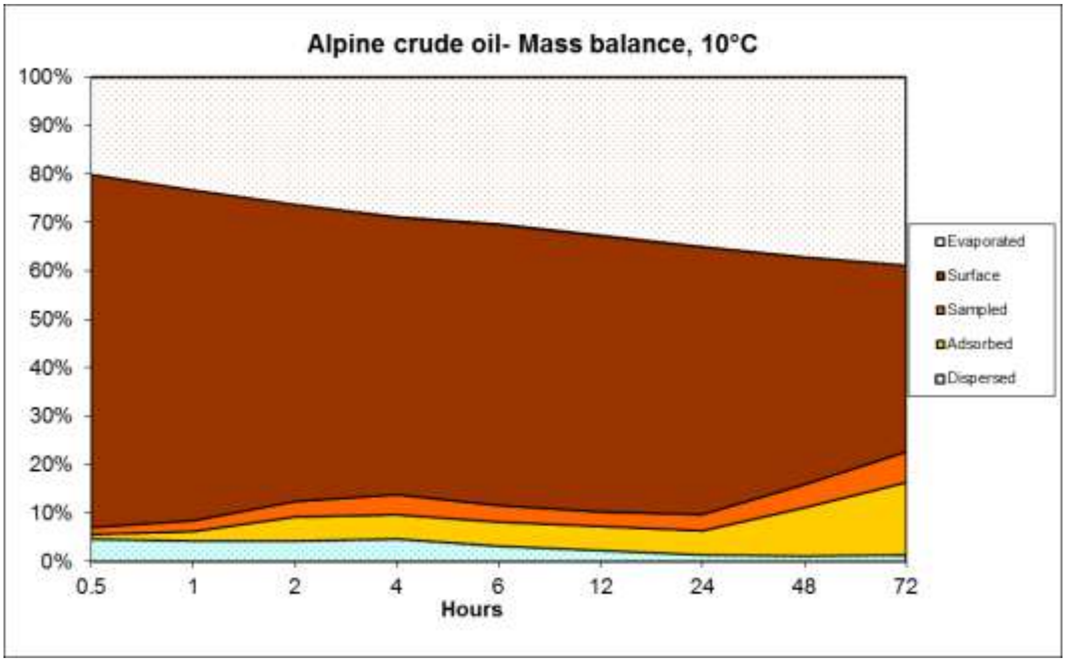


Figure 4.1. Estimated mass balance for Alpine crude oil in the meso-scale flume basin at 10°C, before dispersant application.

Table 4.2

Tabulated values of the estimated mass balance for Alpine crude oil. Example after 24 hours weathering in the meso-scale flume

Mass balance (% of initial oil) after 24 hours	Alpine crude oil Test temperature (10 °C)
Evaporated	35
Oil on water surface	55
Dispersed oil	1
Sampled amount of oil*	3
Oil adsorbed to the flume walls*	5

**Estimated values*

Visual observations of Alpine crude oil

A selection of pictures taken during the flume experiment at 10 °C is presented below. Figure 4.2 shows the visual observation of Alpine crude oil before and after treatment by dispersant. Artificial sunlight simulated using a solar simulator (see Figure A3) was turned on for photographing, but otherwise turned off during the weathering time (no photo-oxidation). Note: The oil/emulsion can therefore be significantly lighter in appearance /color with the solar simulator turned on.

Sample 0 (Start): The oil spread evenly in a thin dark brown film on the surface.

Samples 1-3 (First 2 hours): Thin dark brown film on the surface. No emulsification observed.

Samples 4-5 (4-6 hours): The oil film was getting thicker and had slightly started to emulsify.

Sample 6 (12 hours): The oil is emulsifying.

Sample 7 (24 hours): The oil appeared much thicker as a "real" water-in-oil emulsion. The appearance /color of the emulsion was now a little bit lighter brown than the 12 hours sample.

Sample 8 (48 hours): Stable homogeneous w/o-emulsion. Minor amount of the emulsion was now adsorbed to the flume wall. The appearance of the emulsion was even lighter brown compared with the previous samples.

Sample 9 (72 hours): Less observed changes from the 48 hours weathering. The emulsion became a little thicker and more elastic.

***In-situ* chemical dispersion of Alpine crude oil.**

After 72 hours of weathering in the flume, the dispersant Corexit 9500 was sprayed on the remaining w/o-emulsion (*in-situ* application). Approximately 40 % of the total volume of oil (approx. 8.8 liters) was available for chemical dispersion. The treatment of Corexit 9500 was sprayed twice on the surface with a dosage-to-oil ratio (DOR) of 1:71 and a dosage-to-emulsion ratio (DER) of 1:167 in the first application, giving a cumulative DOR of 1:33 and DER of 1:100 with the second application.

The first application of Corexit 9500 showed visually some effect on the surface oil/emulsion as the dispersant broke up the emulsion into smaller patches and resulted in less water content and a lower viscous emulsion. However, some resurfacing of larger droplets of the dispersed oil was observed. The second application of dispersant was considered to be very effective on the remaining emulsion with minor observed surface oil after 30 minutes. The emulsion was broken into even smaller droplets and was therefore easily dispersed into the water column. No resurfacing of oil on the surface was visually observed after 2 hours. The concentration of oil dispersed into the water column increased approximately 10 times after the first application and approximately 20 times after the second application compared with no treatment by dispersant.

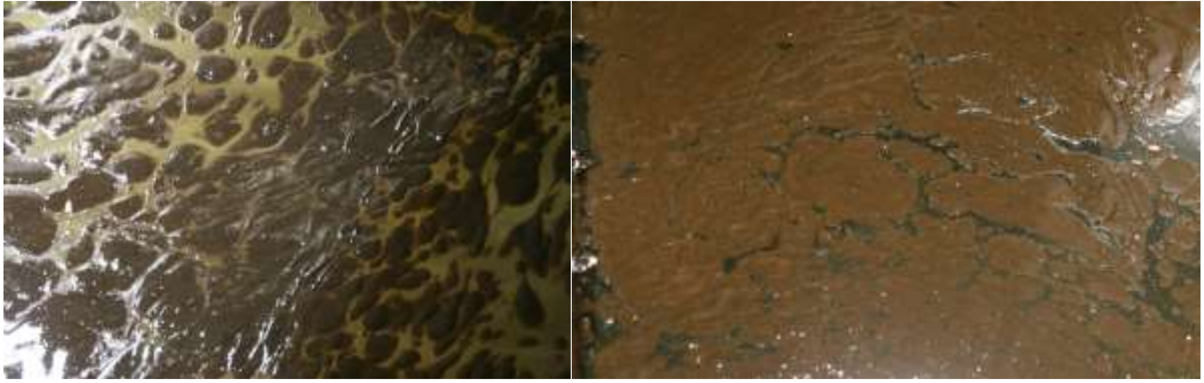
Sample 2 – 1 hour after application of Alpine crude oil.

Sample 5 – 6 hours. The oil is starting to emulsify slightly.

Sample 6 – 12 hours. Emulsion formation.

Sample 7 – 24 hours

Sample 8 – 48 hours



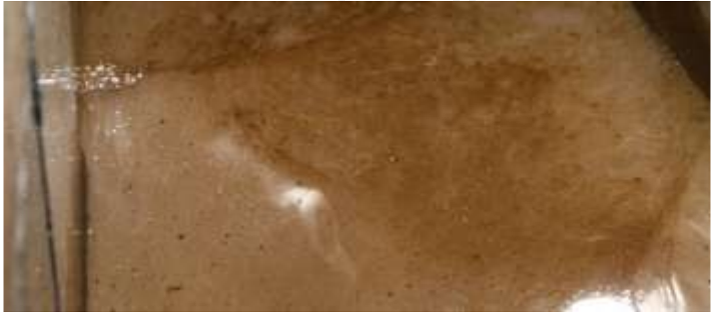
Sample 9 – 72 hours. Stable w/o-emulsion.

3 minutes after first dispersant application.

10 minutes after first dispersant application.

1 hour after first dispersant application. The slick is broken into smaller patches and the emulsion is now less viscous with less water content. Some resurfacing of the dispersed oil was observed.

3 minutes after second dispersant application. The dispersion process is ongoing.



10 minutes after second dispersant application. The major surface of oil/emulsion is dispersed into the water column.

30 minutes after second dispersant application. Only small patches left on the surface.

2 hours after second dispersant application. Hardly any observed oil/emulsion left on the surface.

Figure 4.2. Visual observation of Alpine crude oil before and after treatment by dispersant

4.2 REFINED PRODUCT ADO

An overview of the tabulated results from the meso-scale flume testing is given in Table 4.3 for ADO.

Table 4.3

Results from the meso-scale weathering experiment of ADO.

Sample no	Time (hours)	Water content (vol. %)	Evaporative loss (wt. %)	Viscosity (mPa.s) 10 s^{-1}	Oil in water ppm*
1	0.5	0	3	4	165
2	1	0	5	4	162
3	2	0	8	5	167
4	4	0	14	5	209
5	6	0	18	5	252
6	12	0	24	5	262
7	24	0	32	7	359
8	48	14	42	9	-
9	72	19	47	296	*480***
1st application of dispersants: 10 g Corexit 9500 (DOR = 1:33)					
3 min. disp. 1	-	-	-	-	***
2nd application of dispersants: 10 g Corexit 9500 (DOR = 1:29)					
3 min. disp. 2	-	-	-	-	***

*- = no measured data.   *ppm=parts per million   **estimated from visual observation*

**** An increase of 85 ppm dispersed oil was observed after application of dispersant. This corresponds to an oil amount of approximately 400 g and correlates well with the visual observations.*

For water samples of dispersed oil, GC/FID was used to quantify oil in water from the water samples. The response factor for the fresh oil was used to calculate 'Oil-in-water ppm' for the first six samples. 'Oil-in-water ppm' for the last samples was calculated using the 250°C+ residue response factor.

Mass Balance of ADO

The amount of oil evaporated, oil on surface, dispersed and sampled oil was calculated, and the oil adsorbed to the flume walls was estimated. Figure 4.3 shows the mass balance before applying dispersant agent into the flume, whilst Table 4.4 shows values for the mass balance of ADO during weathering in the flume experiment after 24 hours.

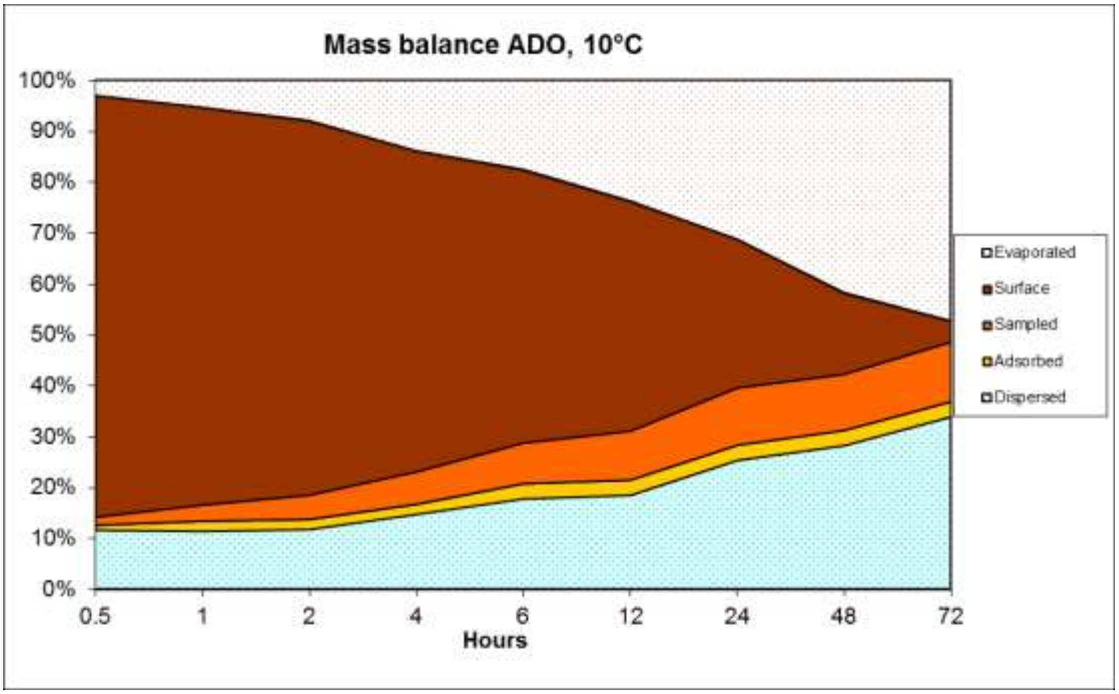


Figure 4.3. Estimated mass balance for ADO in the meso-scale flume basin at 10°C, before dispersant application.

Table 4.4

Tabulated values of the estimated mass balance for ADO.

Example after 24 hours weathering in the meso-scale flume

Mass balance (% of initial oil)	ADO Test temp temperature 10 °C
Evaporated	31
Oil on water surface	29
Dispersed oil	25
Sampled amount of oil	12
Oil adsorbed to the flume walls	3

Visual observations of ADO

A selection of pictures taken during the flume experiment at 10 °C are presented for ADO. Figure 4.5 shows the visual observation of ADO before and after treatment with dispersant agent (Corexit 9500). Artificial sunlight simulated using a solar simulator (see Figure A3) was turned on for photographing, but otherwise turned off during the weathering time (no photo-oxidation).

Sample 0 (Start): Initially the diesel has little appearance of color and spreads evenly on the surface in a thin transparent layer.

Sample 1 (0.5 hour): After 30 minutes the diesel changed its appearance/color to very light brown. The diesel was still evenly distributed on the surface. No emulsification observed.

Sample 2 (1 hour): Slightly browner than the last sample. Otherwise no significant change.

Sample 3 (2 hours): Slightly browner than the last sample. Otherwise no significant change.

Sample 4 (4 hours): Slightly browner than the last sample. Otherwise no significant change

Sample 5 (6 hours): Slightly browner than the last sample. Otherwise no significant change.

Sample 6 (12 hours): After 12 hours the diesel oil had become darker in color and there was minor oil on the surface. Some foam was observed, as a mixture of air, water and diesel which was not stable.

Sample 7 (24 hours): The diesel and water has now been mixed to a loose emulsion, which was very unstable and broke within 15 minutes after sampling, however, slightly more stable than the previous sample (P6).

Sample 8 (48 hours): In the time between P7 (24 hours) and P8 (48 hours) most of the oil had been mixed in to the water column and there is not much left on the surface. The remaining residue did not form a traditional emulsion, but more like a "slimy material" that seemed to be stable and did not separate approx. 30 minutes after sampling. However, when these samples were left over night at the ambient testing temperature, most of the water had been drained off.

Sample 9 (72 hours): Almost all of the surface oil was naturally dispersed into the water column. Approximately 300 mL of "slimy material" was left on the surface. These samples did not break up when left over the weekend at room temperature.

The change in appearance/color during the weathering (0.5 - 48 hours) in the flume basin of the ADO is shown in Figure 4.4.

Figure 4.4. The oil-samples Sample 1 (0.5 hour) – Sample 8 (48 hours) from left to right with observed changes in the color appearance over time

In-situ chemical dispersion on ADO

First application: The remaining surface residue estimated to 300 mL was dispersed using 10 grams of Corexit 9500 with a dispersant-to-oil ratio, DOR of 1:33 (sampling after 3 minutes).

Second application: Some resurfacing of oil was observed, and the estimated 100 mL remaining surface residue was treated with an additional 10 grams of dispersant, which gave a cumulative DOR of 1:17. The remaining residue was then totally dispersed into the water column.

Sample 0 (Start)–Application of ADO – Natural dispersion started immediately when wave action was turned on.

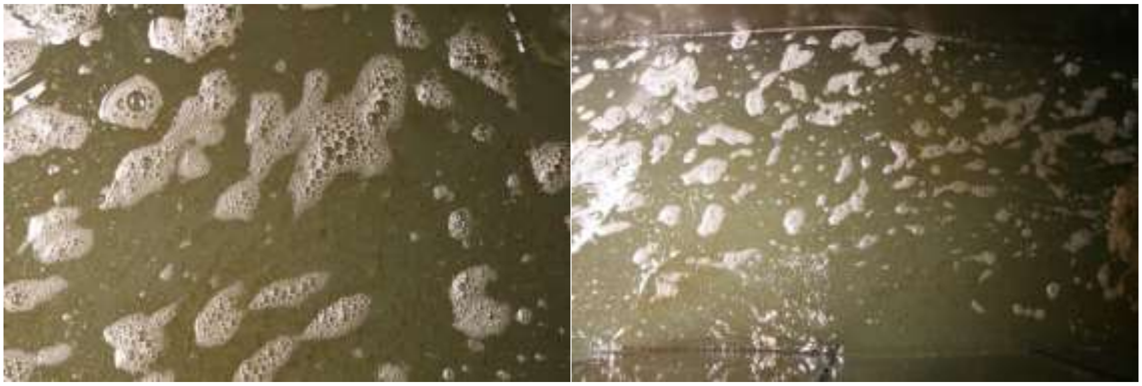
Sample 1 –30 min.

Sample 2 –1 hour

Sample 3 –2 hours

Sample 4 –4 hours

Sample 5 –6 hours



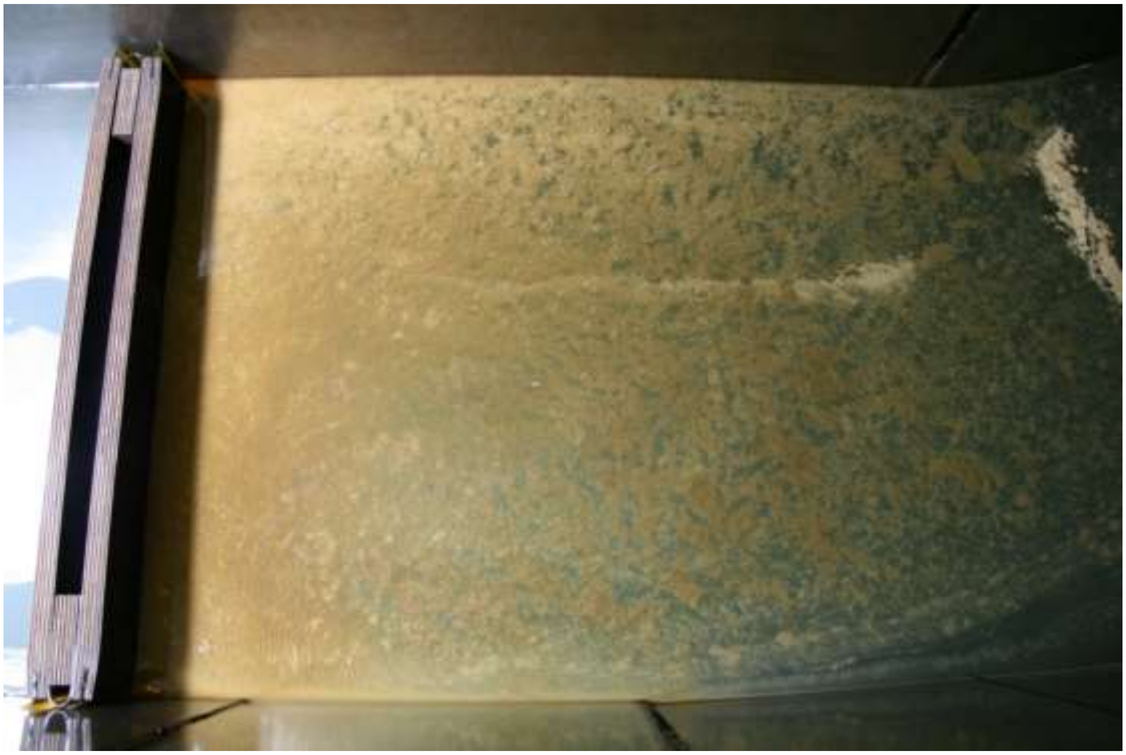
Sample 6 –12 hours

Sample 7 –24 hours

Sample 8 –48 hours: Minor residue left on the surface.

Sample 9 –72 hours: Collecting oil for surface residue prior to applying the dispersant (Corexit 9500).

Prior to the first dispersion – Estimating 300 mL of the residue described as a "slimy material" that was available for chemical dispersion.



Prior to the second dispersion –Estimating 100 mL available for chemical dispersion.

After the second dispersion – The residue totally dispersed into the water column.

Figure 4.5. Visual observation of ADO before and after treatment by dispersant

4.3 REFINED PRODUCT MGO

An overview of the tabulated results from the meso-scale flume testing is given in Table 4.5 for MGO.

Table 4.5

Results from the meso-scale weathering experiment of MGO

Sample no	Time (hours)	Water content (vol. %)	Evaporative loss (wt. %)	Viscosity (mPa.s) 10 s^{-1}	Oil in water ppm*
1	0.5	0	1	8	136
2	1	0	3	8	127
3	2	0	4	9	137
4	4	0	7	9	135
5	6	0	10	9	171
6	12	1	13	11	251
7	24	4	17	12	342
8	48	28	24	-	*850***

- = no measured data. **ppm=parts per million* ***estimated from visual observation*

For water samples of dispersed oil, GC/FID was used to quantify oil-in-water from the water samples. The response factor for the fresh oil was used to calculate 'Oil in water ppm' for the first six samples. 'Oil in water ppm' for the last samples was calculated using the 250°C+ residues response factor.

Mass Balance of MGO

The amount of oil evaporated, oil on surface, dispersed and sampled oil was calculated, and the oil adsorbed to the flume walls was estimated. Figure 4.6 shows the estimated mass balance for MGO, and Table 4.6 shows tabulated values for the mass balance after 24 hours of weathering in the flume.

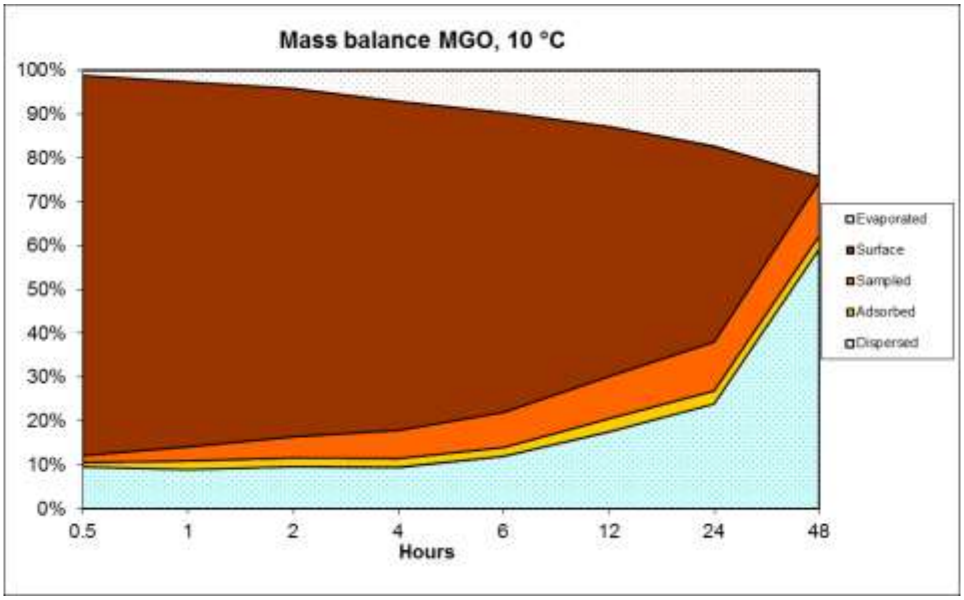


Figure 4.6. Estimated Mass balance for MGO in the meso-scale flume basin at 10°C.

Table 4.6

Tabulated values of the estimated mass balance for MGO. Example after 24 hours weathering in the meso-scale flume

Mass balance (% of initial oil) after 24 hours	Test temperature 10 °C, MGO
Evaporated	17
Oil on water surface	45
Dispersed oil	24
Sampled amount of oil	11
Oil adsorbed to the flume walls	3

Visual observations of MGO

A selection of pictures taken during the flume experiment at 10 °C are presented. Figure 4.7 shows the visual observation of MGO. Artificial sunlight simulated using a solar simulator (see Figure A3) was turned on for photographing, but otherwise turned off during the weathering time (no photo-oxidation).

Sample 0 (start): The MGO has a light yellow color and spreads evenly on the surface in small "bubbles". MGO has a blue tint appearance/color under the solar simulator.

Samples 1- 3 (0.5-2 hours): Light yellow color. It was no emulsification and the MGO spread evenly on the surface. Some natural dispersion and some foam were observed.

Sample 4 (4 hours): The yellow coloring becomes a little darker and more foam was observed. The oil sample has now formed a very loose "emulsion" that broke easily with very low viscosity.

Samples 5 - 6 (6-12 hours): Slightly darker yellow appearance/color – some brown "bubbles".

Sample 7 (24 hours): The water was now whiter /shady, and not much of the diesel remained on the surface and the "bubbles" of oil could visually be observed in the water column. The loose emulsion was a little harder to break, but still it breaks at the test temperature.

Sample 8 (48 hours): No oil remained on the surface and no sampling was necessary.

In-situ chemical dispersion on MGO

Approximately, only 50 mL of the MGO residue remained on the surface. This residue was further collected using a stopper and the wave machine was turned off. The sample was "mixed" with a slimy consistency (similar observation as for the ADO) that didn’t break easily at the test temperature (10 °C). The experiment was finalized without dispersants application because there was very little surface oil remaining after two days of weathering in the flume basin.


Sample 0 - Application of MGO (note that the diesel appears blue with the solar simulator).


Sample 1 –30 minutes


Sample 2 –1 hour


Sample 3 – 2 hours

Sample 4 – 4 hours

Sample 5 – 6 hours

Sample 6 – 12 hours

Sample 7 –24 hours

Sample 8 –48h: no MGO left on the surface – no need for dispersant application.

Figure 4.7. Visual observation of MGO

4.4 KUPARUK CRUDE OIL

An overview of the tabulated results from the meso-scale flume testing is given in Table 4.7 for Kuparuk crude oil.

Table 4.7

Results from the meso-scale weathering experiments of Kuparuk crude oil

Sample no	Time (hours)	Water content (vol. %)	Evaporative loss (wt. %)	Viscosity (mPa.s) 10 s^{-1}	Oil in water ppm
1	0.5	25	6.4	709	423
2	1	43	10.1	2531	286
3	2	46	11.2	3953	261
4	4	61	12.6	6775	125
5	6	68	13.3	8128	106
6	12	70	14.5	10407	60
7	24	72	15.5	11268	69
8	48	68	17.0	14859	57
9	72	65	17.2	17949	77
1st application of dispersants: 61.6 g Corexit 9500 (DOR = 1:98)					
3 min. disp. 1	-	-	-	-	227
10 min. disp. 1	-	-	-	-	219
30 min. disp. 1	-	-	-	-	237
2nd application of dispersants: 58.4 g Corexit 9500 (DOR = 1:103)					
3 min. disp. 2	-	-	-	-	317
10 min. disp. 2	-	-	-	-	448
60 min. disp. 2	-	-	-	-	404
120 min. disp. 2	-	-	-	-	484

- = no measured data. **ppm=parts per million* ***estimated from visual observation*

Mass balance of Kuparuk crude oil

The amount of oil evaporated, oil on surface, naturally dispersed and sampled oil was calculated, and the oil adsorbed to the flume walls was estimated by weight. Figure 4.8 shows the estimated mass balance before applying dispersant agent into the flume, whilst Table 4.8 shows an example of tabulated values of the estimated mass balance after 24 hours of weathering.

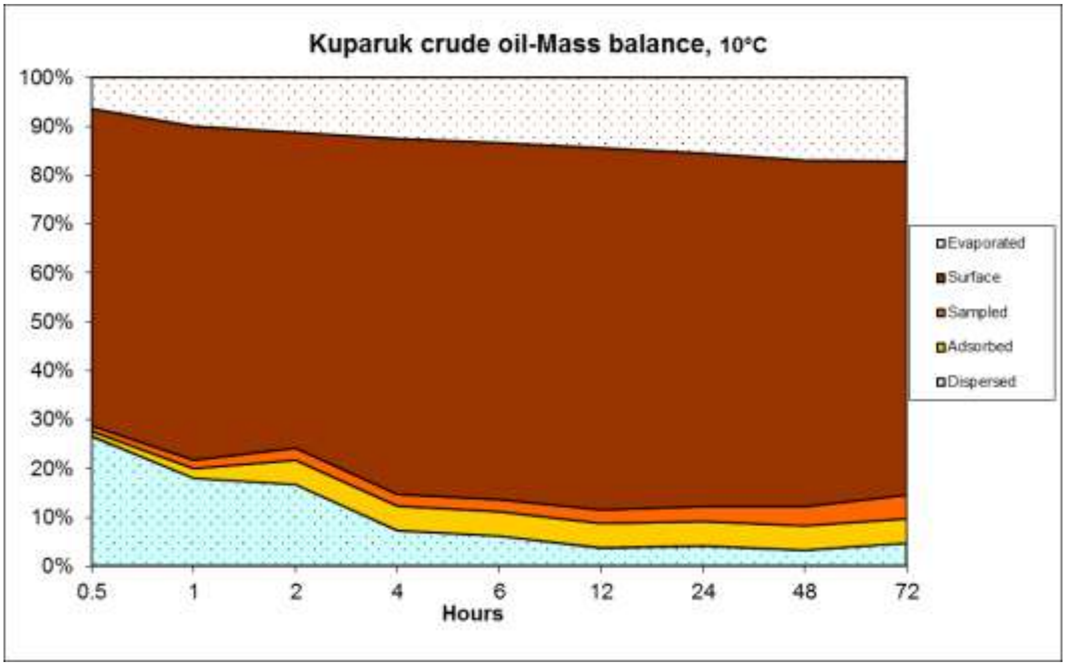


Figure 4.8. Estimated mass balance for Kuparuk crude oil in the meso-scale flume basin at 10°C, before dispersant application.

Table 4.8

Tabulated values of the estimated mass balance for Kuparuk crude oil after 24 hours weathering. Example after 24 hours weathering in the meso-scale flume

Mass balance (% of initial oil)	Test temperature 10 °C, Kuparuk crude oil
Evaporated	16
Oil on water surface	72
Dispersed oil	4
Sampled amount of oil	3
Oil adsorbed to the flume walls	5

Visual observations of Kuparuk crude oil

A selection of pictures taken during the flume experiment at 10 °C is presented. Figure 4.9 shows the visual observations of Kuparuk crude oil with and without dispersant application. Artificial sunlight simulated using a solar simulator (see Figure A3) was turned on for photographing, but otherwise turned off during the weathering time (no photo-oxidation).

Sample 0 (start): The oil spread evenly on the surface when applied onto the water surface.

Sample 1 (30 min.): The oil did not change significantly after 30 minutes of weathering. Low water uptake and low viscosity. Easily sampled with a separating funnel. Dark appearance. Most of the oil on the surface – minor observed natural dispersion. Thin continuous slick.

Sample 2 (1 hour): The oil seemed a bit "thicker" – higher water uptake and increased viscosity.

Samples 3 - 6 (2 -12 hours): The emulsion steadily got thicker with increased water uptake giving a higher viscosity. After 6 hours weathering, it was no longer possible to sample surface oil using separating funnel. Dark emulsion. Most of the oil is on the surface – minor observed natural dispersion.

Sample 7 (24 hours): The oil/emulsion seemed slightly thicker. Oil moves around the flume as balls/lumps of emulsion (diameter ≈ 5 cm) – not a continuous slick. Some emulsion stuck to the flume wall, but not more than expected for this kind of crude oil.

Sample 8 (48 hours): Little or no change visually from sample 7. Thick dark emulsion. Most of the emulsion stuck to the wall was now released onto the water surface.

Sample 9 (72 hours): Visually minor changes from Sample 7. Thick dark emulsion. Almost no emulsion observed on the flume wall.

In-situ **chemical dispersion on Kuparuk crude oil**

After 72 hours of weathering, the dispersant Corexit 9500 was sprayed on the remaining w/o-emulsion (*in-situ* application). Approximately 68 % of the total volume of oil (approx. 8.8 liters) was available for chemical dispersion as shown in Figure 4.8. Corexit 9500 was applied twice on the surface with a dosage-to-oil ratio (DOR) of 1:98 and a dosage-to-emulsion ratio (DER) of 1:250 in the first application, giving a cumulative DOR of 1:50 and DER of 1:100 in the second application.

First application: The dispersant (Corexit 9500) broke up the lumps of emulsion in to smaller more irregular bits. Some dispersion effect observed, but not much – most of the emulsion was still on the surface. After 1 hour, the emulsion started to re-form into balls/lumps again (diameter 3-5cm).

Second application: The dispersant broke the emulsion in to smaller patches (as observed in the first application), but still a high amount of emulsion was observed on the water surface. Some large droplets were observed in the water column, but those quickly resurfaced. After 30 minutes, the emulsion again formed lumps (diameter 2-4 cm). Visually the dispersion was not effective (the dispersant gives the emulsion a beautiful blue-green color under the solar simulator). 1 hour after the 2nd dispersant application the large lumps generated in the flume broke into smaller fractions/patches. The results indicated that Kuparuk is dispersible with Corexit 9500, but requires a higher dosage of dispersant (DOR > 1:50; DER > 1:100). Use of artificial turbulence applied on the slick after dispersant application in an oil spill situation may also increase the efficiency of dispersant use on this oil.


Sample 1– 30 minutes continuous slick


Sample 2 –1 hour continuous slick


Sample 3 –2 hours


Sample 4 –4 hours


Sample 5 –6 hours


Sample 6 –12 hours lump formation



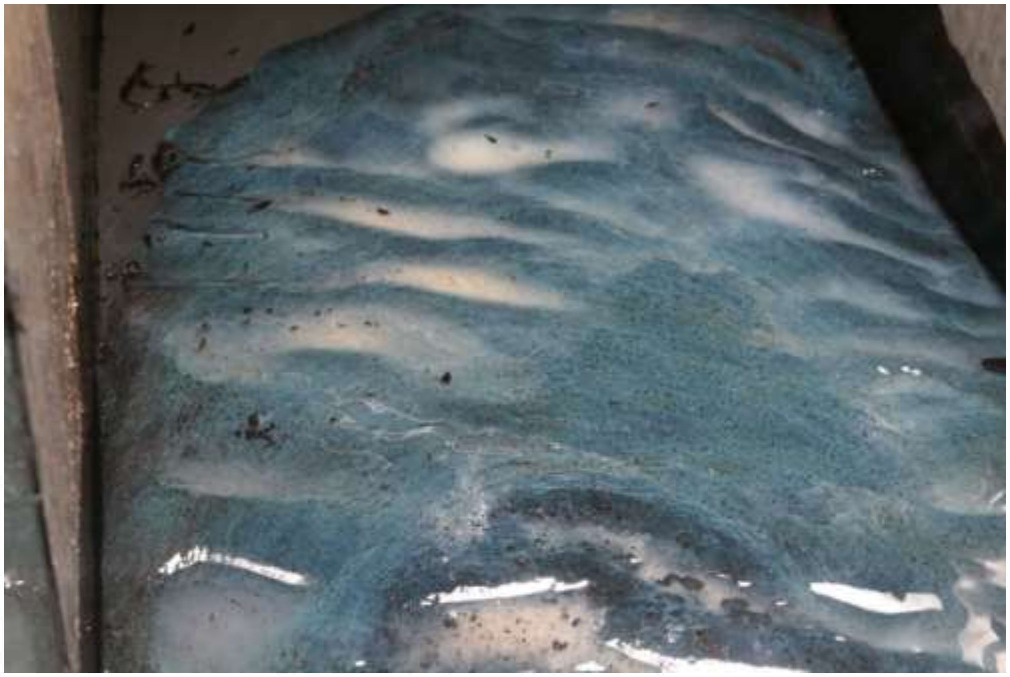
Sample 7 –24 hours


Sample 8 –48 hours (emulsion color changes due to direct exposure to solar simulator, right)


Sample 9 –72 hours weathering. The blackish lumps observed in the meso-scale flume are typical for asphaltenic crude oils.

3 minutes after first application of dispersant (broken up lumps)

30 minutes after first application of dispersant (reformed smaller lumps)



1 minute after second application of dispersant – picture taken under solar simulator

3 minutes after second application of dispersant – the emulsion breaks down to smaller lumps

1 hour after second application of dispersant – lumps reformed into larger lumps

2 hours after second application of dispersant – lump formation

Figure 4.9. Visual observations of Kuparuk Crude Oil with and without dispersant application

4.5 NORTHSTAR CRUDE OIL

An overview of the tabulated results from the meso-scale flume testing is given in Table 4.9 for Northstar crude oil.

Table 4.9

Results from the meso-scale weathering experiment of Northstar

Sample no	Time (hours)	Water content (vol. %)	Evaporative loss (wt. %)	Viscosity (mPa.s) 10 s^{-1}	Oil in water ppm
1	0.5	0	36.1	10	105
2	1	0	40.2	16	113
3	2	4	45.6	24	89
4	4	5	48.4	134	-
5	6	22	51.1	213	92
6	12	24	53.1	272	259
7	24	26	55.5	194	283
8	48	16	57.2	416	295
9	72	17	58.3	473	256
1st application of dispersants: g 55.6 Corexit 9500					
3 min. disp. 1	-	-	-	-	346
10 min. disp. 1	-	-	-	-	292
30 min. disp. 1	-	-	-	-	280
60 min. disp. 1	-	-	-	-	190

-= no measured data. **ppm=parts per million* ***estimated from visual observation*

Mass Balance of Northstar crude oil

Figure 4.10 shows values for the mass balance of Northstar crude oil during weathering in the flume experiment after 24 hours. Dispersed and sampled oil was calculated, and the oil adsorbed to the flume walls was estimated. Table 4.10 shows the estimated mass balance before applying dispersant agent into the flume.

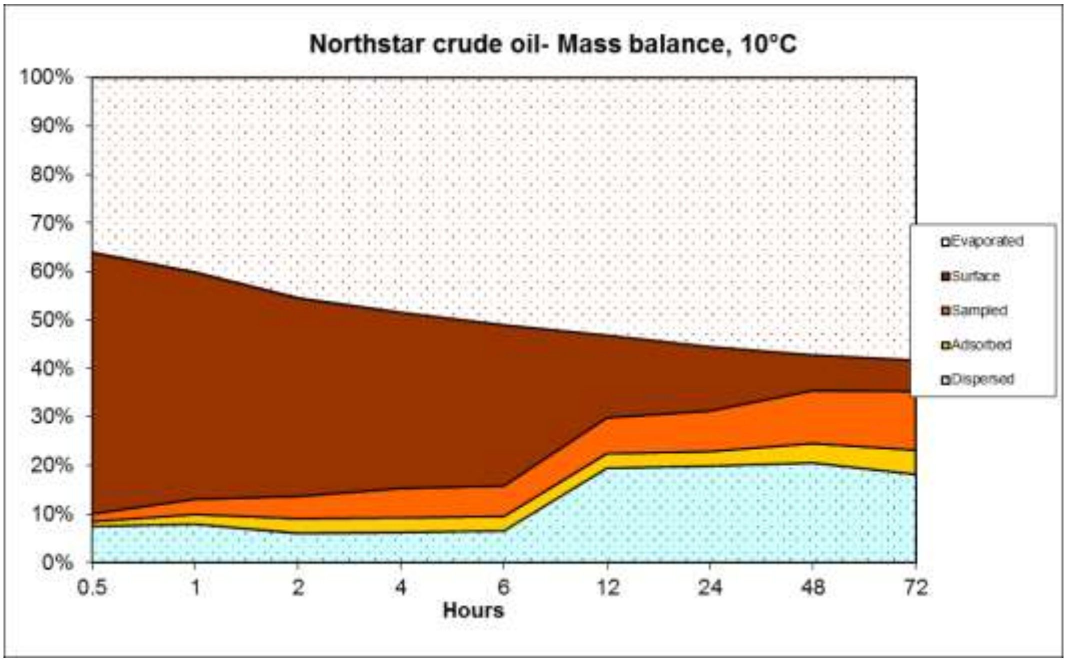


Figure 4.10. Estimated mass balance for Northstar crude oil in the meso-scale flume basin at 10°C, before dispersant application.

Table 4.10

Mass balance for Northstar during the meso-scale laboratory test at 10 °C (after 24 hours of weathering)

Mass balance (% of initial oil)	Test temperature 10 °C, Northstar crude oil
Evaporated	55
Oil on water surface	13
Dispersed oil	20
Sampled amount of oil	8
Oil adsorbed to the flume walls	3

Visual observations of Northstar crude oil

A selection of pictures taken during the flume experiment at 10 °C is presented. Figure 4.11 shows the visual observations of Northstar crude oil with and without dispersant application. Artificial sunlight simulated using a solar simulator (see Figure A3) was turned on for photographing, but otherwise turned off during the weathering time (no photo-oxidation).

Sample 0 (start): The oil spread evenly on the surface. Light brown color.

Samples 1 - 2 (1 hour): The oil starts to "emulsify" – did not form a true water-in-oil emulsion, only unstable "foam". Some natural dispersion.

Samples 3 - 4 (2-4 hours): Slightly more stable "emulsion", low water uptake so far more oil droplets were present in the water column.

Samples 5 - 6 (6-12 hours): The emulsion appeared darker, but the emulsion was not more stable.

Sample 7 (24 hours): Less oil on surface, more oil droplets in the water column.

Sample 8 (48 hours): Very little oil left on surface – surface sampling became more challenging.

Sample 9 (72 hours): Almost no oil on surface available for dispersant application.

In-situ **chemical dispersion on Northstar crude oil**

After 72 hours of weathering, the remaining oil was gathered and the dispersant (Corexit 9500) was applied onto the water surface on the remaining w/o-emulsion (*in-situ* application). The remaining emulsion dispersed easily into the water column. Less than 10 % of the total volume of oil (approx. 8.8 liters) was available for chemical dispersion, and Corexit 9500 was sprayed only once on the slick with a dosage-to-oil ratio (DOR) of 1:10 and a dosage-to-emulsion ratio (DER) of 1:12.

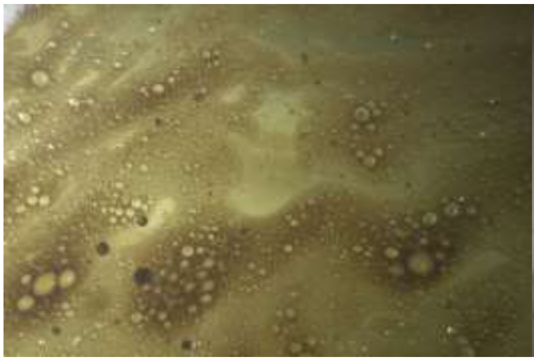

Sample 1 –30 minutes


Sample 2 –1 hour


Sample 3 –2 hours

Sample 4 –4 hours

Sample 4 –4 hours



Sample 5 –6 hours: "foam"

Sample 5 –6 hours

Sample 6 –12 hours

Sample 6 –12 hours


Sample 7 –24 hours


Sample 8 –48 hours


Sample 8 –48 hours


Sample 9 –72 hours

Oil before application of dispersant Oil 3 minutes after dispersant application (total dispersion)

Figure 4.11. Visual observations of Northstar Crude Oil without and with dispersant application

4.6 WIDE RANGE GASOIL (WRG)

An overview of the tabulated results from the meso-scale flume testing is given in Table 4.11 for Wide Range Gasoil (WRG).

Table 4.11

Results from the meso-scale weathering experiment of WRG 10 °C

Sample no	Time (hours)	Water content (vol. %)	Evaporative loss (wt. %)	Viscosity (mPa.s) 10 s^{-1}	Oil in water ppm*
1	0.5	58	0.5	465	38
2	1	76	0.9	367	48
3	2	79	1.9	183	73
4	4	83	2.1	207	177
5	6	82	2.8	355	212
6	12	85	4.1	746	148
7	24	80	4.8	978	418
8	48	72	5.8	709	946
1st application of dispersants: 20.4g Corexit 9500					
3 min. disp. 1	-	-	-	89	848
10 min. disp. 1	-	-	-	-	1237
30 min. disp. 1	-	-	-	-	1336
60 min. disp. 1		-	-	-	1191
120 min. disp. 1	-	-	-	-	1327

*-= no measured data. *ppm=parts per million*

Mass balance of Wide Range Gasoil (WRG)

Table 4.12 shows values for the mass balance of WRG during weathering in the flume experiment after 24 hours. The oil adsorbed to the flume walls was estimated. Figure 4.12 shows the estimated mass balance before applying dispersant into the flume.

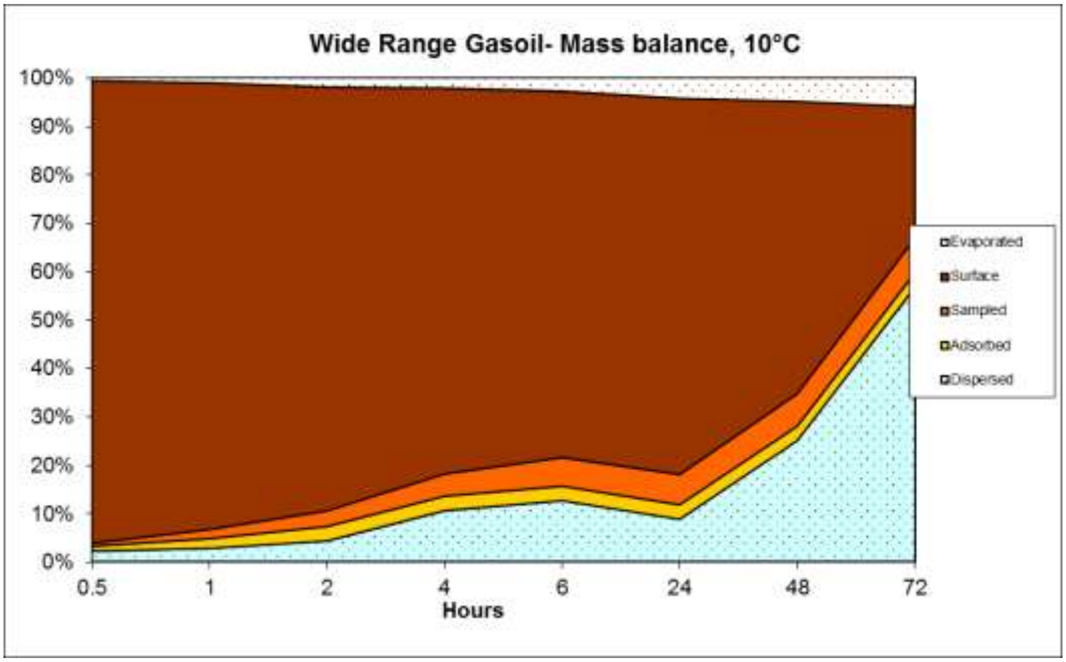


Figure 4.12. Estimated mass balance for Wide Range Gasoil (WRG) in the meso-scale flume basin at 10°C, before dispersant application

Table 4.12

Mass balance for WRG during the meso-scale laboratory test at 10 °C (after 24 hours of weathering)

Mass balance (% of initial oil)	Test temperature 10 °C, WRG
Evaporated	4
Oil on water surface	78
Dispersed oil	9
Sampled amount of oil	6
Oil adsorbed to the flume walls	3

Visual observations of Wide Range Gasoil (WRG)

A selection of pictures taken during the flume experiment at 10 °C are presented, below. Figure 4.13 shows the visual observations of WRG with and without dispersant application. Artificial sunlight simulated using a solar simulator (see Figure A3) was turned on for photographing, but otherwise turned off during the weathering time (no photo-oxidation).

Sample 0 (start): When applied onto the water surface, the oil seemed to solidify in contact with the water. Gray/brown color. Within a few minutes, the oil started to make a "foam" with the water.

Sample 1 (0.5 hour): The oil formed a light yellow "foam/emulsion" that covered half of the flume surface; some oil went into the water (droplet-size: 2-6 mm).

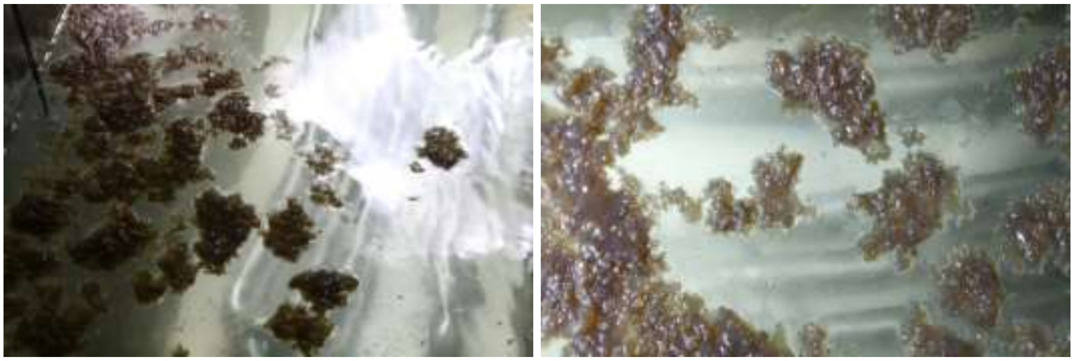
Samples 2-5 (1-6 hours): Minor change between 1 to 6 hours. The emulsion appeared a little more yellow and became seemingly thicker and more unstable.

Sample 6 (12 hours): The emulsion became even thicker and more yellow. Minor changes from 6 hours weathering.

Sample 8 (48 hours): The emulsion seemed smoother and more homogenous. Darker in color/ appearance. Still very unstable emulsion.

In-situ chemical dispersion on Wide Range Gasoil (WRG)

Corexit 9500 was decided to be applied in one 20.4 g application after 48 hours weathering with high dispersant to oil ratio (DOR). The "emulsion" broke up when the waves were switched off. 30 minutes after the application of dispersant the oil/emulsion was easily dispersed. It was estimated that 80 % of the oil was dispersed into the water column.



Sample 0 (start): Wax solidification in contact with water

Sample 1–30 minutes (L) Oil droplets in the water (R) "foam"/emulsion under solar simulator (solar simulator makes oil appear lighter)

Sample 2–1 hour: (L) "foam", (R) "foam"/emulsion under solar simulator

Sample 6–12 hours: (L) "foam", (R) "foam"

Sample 6–12 hours: (L) close-up of foam, (R) emulsion

Sample 7–24 hours: (L) close-up of foam, (R) emulsion

Sample 8–24 hours: (L) close-up of foam, (R) emulsion

Oil before application of dispersant

Oil seconds after application of dispersant

3 minutes after application of dispersant

10 minutes after application of dispersant

30 minutes after application of dispersant

120 minutes after application of dispersant

Figure 4.13. Visual observations of WRG with and without dispersant application

5. CONCLUSIONS

Overall, the bench-scale weathering studies yielded consistent data for input to oil weathering models. The experimental data from the meso-scale flume basin are considered supplemental to the bench-scale testing, in addition to providing valuable information related to potential field operations, such as the visual assessments of effectiveness after adding Corexit 9500 to five of the oils that had weathered for 72 hours. No dispersant was needed to chemically disperse MGO because no oil remained on the water surface after 48 hours. SINTEF recommends a total evaluation of the experimental data generated both by the bench-scale and meso-scale experiments to inform a more robust oil weathering prediction. As an example, for Alpine crude oil, the maximum water content could be adjusted or reduced from ~ 80 % vol. findings from the bench-scale testing to ~70 vol. % as observed in the flume basin. These differences will influence the predicted emulsion viscosity. For Kuparuk crude oil, the maximum water content from the flume testing was higher compared with the bench-scale testing, and therefore, could possibly be adjusted to match the findings from the flume basin. Adjustments of the experimental data to customize the most appropriate and best input data to oil weathering models were not a part of this project. Therefore, it should be considered to be part of the oil weathering modelling when evaluating the output predictions of the oil weathering properties.

6. QUALITY ASSURANCE

Scientific Quality Assurance (S-QA).

Senior scientist Per S. Daling at SINTEF has been responsible for the scientific quality assurance and signs the final report. Senior scientist at SINTEF CJ Beegle-Krause had contact with NOAA in connection to the ADIOS input data. The information from NOAA (Bill Lehr and Jeff Lankford, e-mails 2nd and 14th September, 2015 respectively) indicated that both ADIOS 2 and ADIOS 3 will run with only the density and viscosity, and missing fields are approximated by ASTM estimation formulas. *"For a crude oil you would need the data that for the API or a density value (units of measurement and temp), a viscosity either kinematic or dynamic along with related units of measurement and temp. For a refined product we need the distillation data. This would consist of a volume %, vapor or liquid temperature."*

When this project began ADIOS 3 was going to be released in 2015 (Version 2.0.11 of ADIOS 2 was posted on NOAA's website on 03/22/2016), and CJ Beegle-Krause (SINTEF) received a list of parameters from the ADOIS 3 SQL oil database. However, parameters that would be "nice to have" for ADIOS 3 were not possible to include in this project. SINTEF does not conduct these analyses on regular basis.

Data Management Quality Assurance (Data QA).

SINTEF Material and Chemistry's laboratories are certified according to NS-EN ISO 9001: 2008 (Quality Management System), ISO 14001:2004 (Environmental Management System), OHSAS 18001(Occupational Health and Safety Management System) and Regulations relating to Systematic Health, Environmental and Safety Activities in Enterprises (Norwegian Internal

Control Regulations), all which are international accepted standards for management of quality, environment and occupational health and safety.

The laboratory personnel have followed SINTEF laboratory SOP (Standard Operational Procedures). Samples and the obtained experimental data were also identified with unique identification numbers found in the laboratory database system and/or in the laboratory journals. Jon Olav Bjørgum (QA manager at SINTEF Materials and Chemistry) was responsible for SINTEF data management in this project, according to procedures in SINTEF ISO certificate management system to ensure chain of custody in laboratory reporting. Regular backups of all central servers in SINTEF are performed on a daily basis by SINTEF's CT service contractor, EVRY (www.evry.no).

7. REFERENCES

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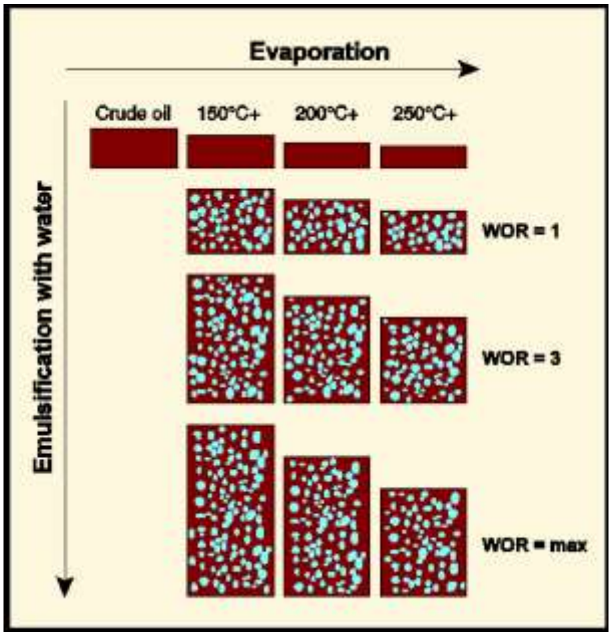
Appendix A

Experimental setup

The testing of the weathering properties was performed at 10 °C in accordance with the Client.

A.1 Bench-scale laboratory methodology

To isolate and map the various weathering processes at sea, the oil was exposed to a systematic, stepwise procedure developed at SINTEF (Daling et al., 1990). The weathering process 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.1.1 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 condensate 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.1.2 Physical and chemical analysis

The viscosity, density, pour point and flash point of the fresh and water-free residues was analyzed. 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
Interfacial tension (IFT)	-	Pendant drop method

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

The distribution of hydrocarbons ($n\mathrm{C}_5$-$n\mathrm{C}_{40}$) was analyzed using a Gas Chromatograph coupled with a Flame Ionization Detector (GC/FID). The Gas Chromatograph used was an Agilent 6890N with a 30m DB1 column.

A.1.3 Emulsification properties

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

- Relative water uptake (kinetics)
- Maximum water uptake
- Stability of the emulsion
- Effectiveness of emulsion breaker (Alcopol O 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.

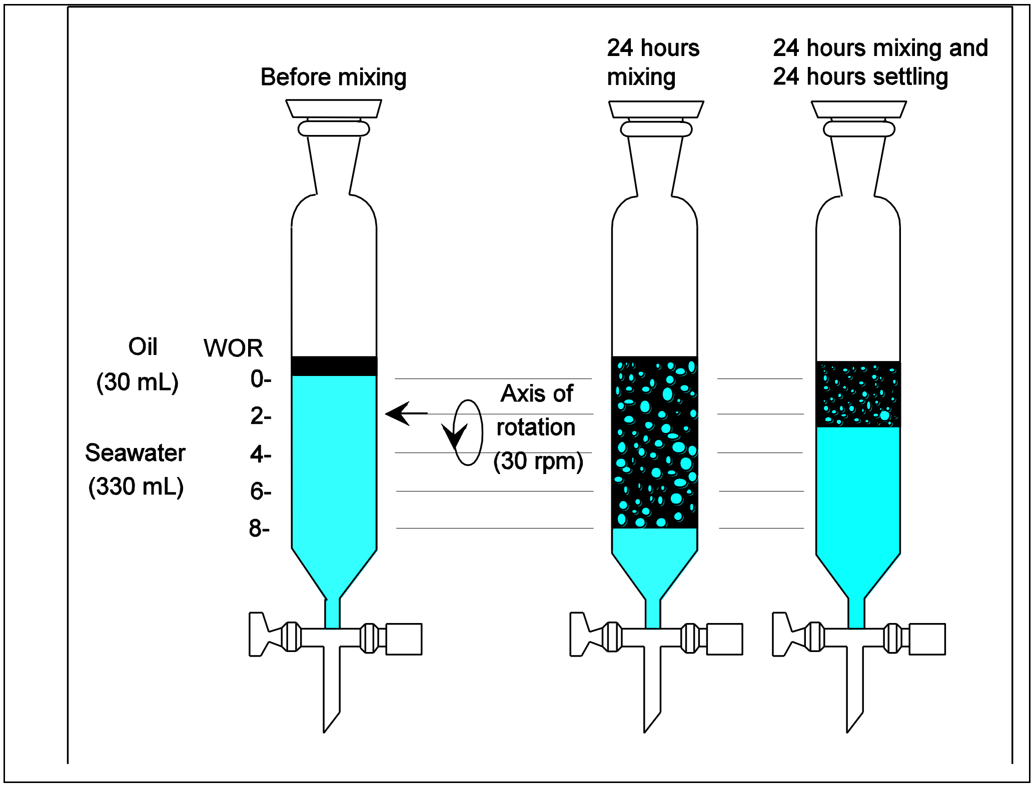


Figure A.2. Principle of the rotating cylinder after Mackay and Zagorski (1982)

A.2 Meso-scale flume basin

In an oil spill situation at sea, the weathering processes will occur simultaneously and affect each other. It is therefore very important to weather the oils under realistic conditions when studying their behavior when spilled on the sea surface.

A.2.1 Description of the flume basin

A meso-scale flume basin (Singsaas et al. 1993) located at SINTEF's Sealab is routinely used to simultaneously study the weathering processes under controlled conditions. A flume with an updated instrumentation was built in 2006, with a schematic drawing of the flume given in Figure A.3.

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

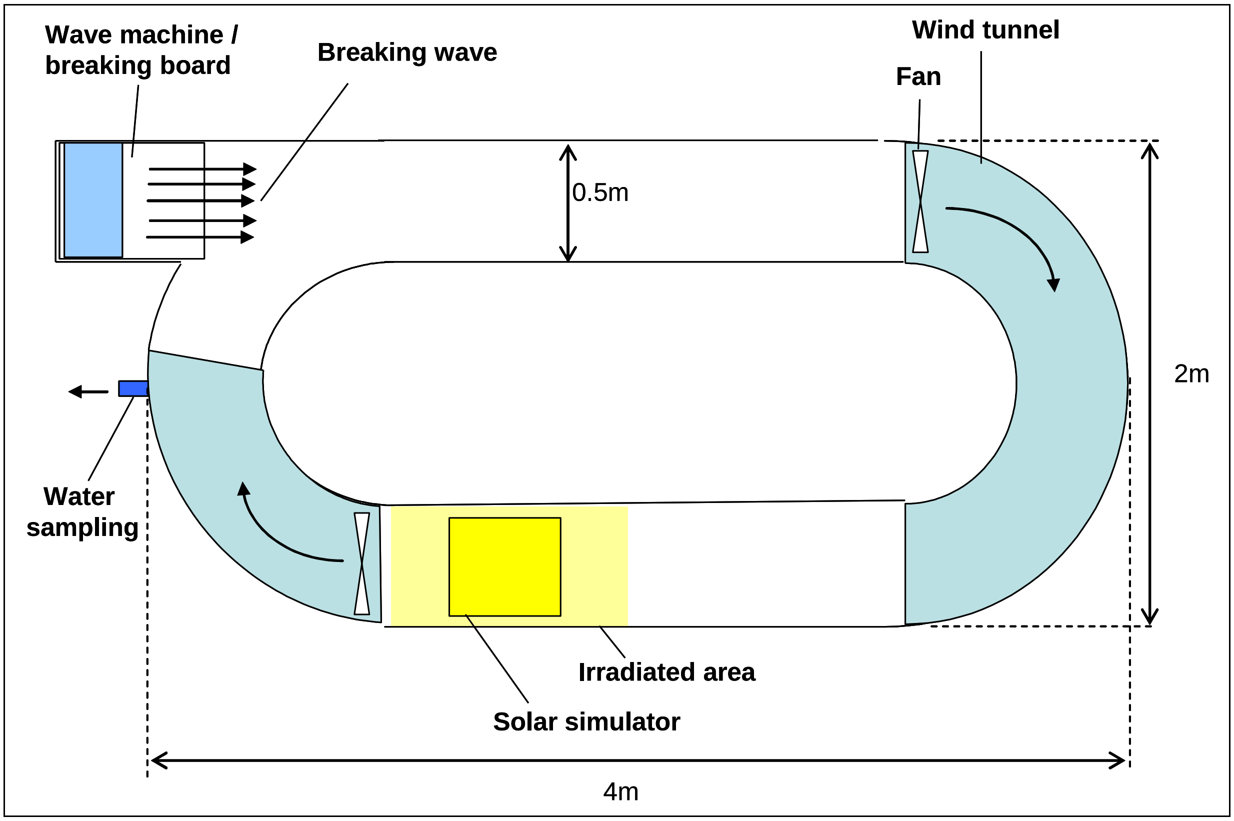


Figure A.3. Schematic drawing of the meso-scale flume

A.2.2 Oil weathering in the flume basin

The oil sample (~9 L) is carefully released on the seawater surface. In accordance to the standard procedure, the oil is normally weathered for three days in the flume. Samples of the surface oil are taken frequently during the first hours of the experiment and then once a day. The dispersant agent will normally be applied to the weathered oil *in-situ* after Day 3 of the experiment. Water samples are taken a few times during the weathering part of the experiment, and at a higher frequency after the dispersant application.

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

- Evaporative loss
- Density
- Water content
- Viscosity

Analysis was performed on a limited amount of samples for:

- Emulsion stability
- Oil concentration in the water column (droplets and dissolved components)

Samples of surface oil/emulsion

Samples of the surface oil/emulsion were taken using an aluminum tray and transferred to a 0.5 L separating funnel. The free water was removed after settling for 10 minutes in the climate room.

The oil phase was further handled for an analysis of viscosity, water content of emulsion and density.

Analytical methods for surface oil/emulsion

The methods used to determine the physical properties of the surface oil/emulsion are listed in Table A.3.

Table A.3

Methods used to determine the physical properties of the surface oil/emulsion.

Physical property	Analytical method	Instrument	Comments
Viscosity	McDonagh et al, 1995	Physica MCR 300	-
Water content	Adding approximately 2000 ppm emulsion breaker (Alcopol O 60%) to the sample and heating the vial. As the emulsion broke, the water height and the total height were measured.	Sample vials	The relative amount of water compared to the total sample volume was calculated.
Density	ASTM method D4052-81	Anton Paar, DMA 4500	Measured on water-free samples (after removal of the water with emulsion breaker and heat).
Evaporative loss	The density of the oil depends linearly on the vol. % of evaporative loss.	-	The evaporative loss was calculated based on the density.

Collection of water samples.

Water samples were taken at a depth of 50 cm through a tap in the basin wall into a Pyrex glass bottle (1 L). The sampled water was acidified with some droplets of 10% HCl (pH < 2), and the sampling position is shown in Figure A.3. Samples were extracted by liquid-liquid extraction with dichloromethane (DCM) and quantified by Ultra Violet (UV) spectrophotometer, unless otherwise specified in the report.

Appendix B

Table Format-Input to Oil Weathering Models

The obtained laboratory data are customized for input into oil weathering models (SINTEF OWM and ADIOS). The tabulated laboratory oil data for the six oils are given in Table B.1 –Table B.14. Note that the tabulated input data are derived from the standard bench-scale weathering study unless other specified.

Table B.1

Physical and chemical properties of the fresh oils for Alpine crude oil, ADO and MGO (Year One)

Summary properties of the fresh oil	Alpine SINTEF ID: 2015-0258	ADO SINTEF ID: 2014-0491	MGO SINTEF ID: 2014-0492
Density (60 F/15.5°C) g/mL	0.832	0.830	0.849
API ° **	38.4	38.8	35.1
Pour point (°C)	-36	-36	-36
Reference temperature (°C)	10	10	10
Viscosity at ref. temp. (mPa.s = cP) *	8	5	7
Asphaltenes (wt. %)	0.46	0.03	0.03
Flash Point (°C)	NA	59	62
Wax Content (wt. %)	2.05	0.04	1.96
IFT in (mN/m)	30	24	27
IFT eq (mN/m)	15	12	17
Dispersible for visc. <	NA	NA	NA
Not dispersible for visc. >	NA	NA	NA

** Measured at shear rate 10s-1 ** Calculated based on the measured densities*
NA: Not analyzed

Table B.2

Physical and chemical properties of the fresh oils for Kuparuk and Northstar crude oils and WRG (Year2)

Summary properties of the fresh oil	Kuparuk SINTEF ID: 2015-0259	Northstar SINTEF ID: 2015-0469	WRG SINTEF ID 2016-0106
Density (60 F/15.5°C) g/mL	0.917	0.779	0.892
API ° **	22.7	50.1	27.0
Pour point (°C)	-33	-9	-24
Reference temperature (°C)	10	10	10
Viscosity at ref. temp. (mPa.s = cP) *	143	1	85
Asphaltenes (wt. %)	4.74	0.03	0.05
Flash Point (°C)	NA	NA	106
Wax Content (wt. %)	1.32	1.74	4.84
IFT in (mN/m)	19	29	19
IFT eq (mN/m)	7	10	12
Dispersible for visc. <	NA	NA	NA
Not dispersible for visc. >	NA	NA	NA

** Measured at shear rate 10s-1 ** Calculated based on the measured densities NA: Not analyzed*

Table B.3

True boiling point (TBP) curve for Alpine crude oil

Temperature (°C)	Alpine crude oil (%)*
47	5
65	10
114	20
170	30
226	40
278	50
329	60
389	70
456	80
547	90
615	95

** TBP based on simulated distillation (SIMDIST).*
Source: Alpine COE-319 received from ConocoPhillips Alaska, Inc.

Table B.4

True boiling point (TBP) curve for ADO

Temperature (°C)	ADO Volume (%)*
182	5
189	10
196	15
204	20
220	30
237	40
253	50
270	60
288	70
307	80
317	85
328	90
341	95

**Source: ADO-ULSD from Esso Slagen Refinery, Norway*

Table B.5

True boiling point (TBP) curve for MGO

Temperature (°C)	MGO Volume (%)*
177	5
191	10
203	15
214	20
238	30
264	40
287	50
304	60
318	70
330	80
336	85
343	90
352	95

**Source: Marine Gas Oil (0.1 % S) from Esso Slagen Refinery, Norway*

Table B.6

True boiling point (TBP) curve for Kuparuk crude oil

Temperature (°C)	Kuparuk crude oil Volume (%)*
99	5
150	10
226	20
281	30
332	40
387	50
444	60
509	70
588	80
658	90
701	95

**Source: "CP1" Crude Assay SIMDIST from ConocoPhillips Alaska, Inc. (2001)*

Table B.7

True boiling point (TBP) curve for Northstar crude oil

Temperature (°C)	Northstar Volume (%)*
36	8.5
69	14.4
99	25.2
158	40.9
174	45.4
196	50.9
216	55.8
254	64.6
271	67.4
302	73.7
329	77.3
357	82.1
380	84.1
402	87.2
432	90.7
450	92.3

**Source: Northstar Assay Analysis from Hilcorp Alaska, LLC (9.17.13)*
The TBP is customized and adjusted to fit the laboratory data as input to OW model tools

Table B.8

True boiling point (TBP) curve for WRG

Temperature (°C)	WRG Volume (%)*
305.8	5
328.5	10
337.9	15
344.7	20
355	30
363.2	40
376.6	60
400**	80**
450**	100**

**Source: WRG TBP from Mongstad Refinery*
*** Estimated values to fit the input to OW model tools*

Table B.9

Summary lab weathering data of Alpine crude oil, 10 °C of fresh oil and its residues

Property	Fresh	150°C+	200°C+	250°C+
Boiling Point Temp. (°C)	-	198	260	309
Vol. topped (%)	0	25.5	37.9	46.6
Weight Residue (wt. %)	100	78.5	66.8	58.4
Density (g/mL)	0.832	0.877	0.896	0.906
API °	38.4	29.7	26.3	24.5
Pour point (°C)	-36	0	9	12
Flash Point (°C)	-	40	87	113
IFT in. (mN/m)	30	30	28	30
IFT eq. (mN/m)	15	14	13	15
Asphaltenes (wt. %)	0.46	0.58	0.68	0.78
Wax (wt.%)	2.05	2.61	3.07	3.51
*Viscosity of water-free residue (mPa.s =cP),	8	43	204	688
*Viscosity of 50% emulsion (mPa.s = cP)	-	385	1128	2386
*Viscosity of 75% emulsion (mPa.s = cP)	-	2214	5760	10481
*Viscosity of max water (mPa.s = cP)	-	24104	26059	33720
Max. water cont. (vol.%)	-	83	80	77
($T_{1/2}$) Halftime for water uptake (hrs.)	-	0.16	0.23	0.38
Stability ratio	-	1	0.95	0.94

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

- No data

Table B.10

Summary lab weathering data of ADO, 10 °C of fresh oil and its residues

Property	Fresh ~150°C+	200°C+	250°C+
Boiling Point Temp. (°C)	-	228	270
Vol. topped (%)	0	15.9	47.5
Weight Residue (wt. %)	100	84.7	53.4
Density (g/mL)	0.830	0.835	0.845
API °	38.8	37.8	35.8
Pour point (°C)	-36	-36	-33
Flash Point (°C)	59	74	107
IFT in. (mN/m)	24	23	21
IFT eq. (mN/m)	12	9.5	8.3
Asphaltenes (wt. %)	0.03	0.04	0.06
Wax (wt.%)	0.04	0.05	0.08
*Viscosity of water-free residue (mPa.s =cP),	5	6	10
*Viscosity of 50% emulsion (mPa.s = cP)	-	-	-
*Viscosity of 75% emulsion (mPa.s = cP)	-	-	-
*Viscosity of max water (mPa.s = cP)	-	-	-
Max. water cont. (vol.%)	0	0	0
($T_{1/2}$) Halftime for water uptake (hrs.)	0	0	0
Stability ratio	-	-	-

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

- No data

Table B.11

Summary lab weathering data of MGO, 10 °C of fresh oils and its residues

Property	Fresh ~150°C+	200°C+	250°C+
Boiling Point Temp. (°C)	-	241	281
Vol. topped (%)	0	9.7	28.5
Weight Residue (wt. %)	100	90.9	72.8
Density (g/mL)	0.849	0.854	0.864
API °	35	34	32.1
Pour point (°C)	-36	-36	-30
Flash Point (°C)	62	78	108
IFT in. (mN/m)	27	29	28
IFT eq. (mN/m)	17	13	11
Asphaltenes (wt. %)	0.03	0.04	0.05
Wax (wt.%)	1.96	2.16	2.70
*Viscosity of water-free residue (mPa.s =cP)	7	9	14
*Viscosity of 50% emulsion (mPa.s = cP)	-	-	-
*Viscosity of 75% emulsion (mPa.s = cP)	-	-	-
*Viscosity of max water (mPa.s = cP)	-	-	-
Max. water cont. (vol.%)	0	0	0
($T_{1/2}$) Halftime for water uptake (hrs.)	0	0	0
Stability ratio	-	-	-

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

- No data

Table B.12

Summary lab weathering data of Kuparuk crude oil, 10 °C of fresh oils and its residues

Property	Fresh	150°C+	200°C+	250°C+
Boiling Point Temp. (°C)	-	227	262	312
Vol. topped (%)	0	10.7	15.6	23.3
Weight Residue (wt. %)	100	91.6	87.4	80.4
Density (g/mL)	0.917	0.941	0.950	0.962
API °	22.7	18.7	17.3	15.4
Pour point (°C)	-33	-27	-21	-12
Flash Point (°C)	-	57	81	115
IFT in. (mN/m)	19	20	21	26
IFT eq. (mN/m)	7	8	9	11
Asphaltenes (wt. %)	4.74	5.21	5.46	5.94
Wax (wt.%)	1.32	1.44	1.51	1.64
*Viscosity of water-free residue (mPa.s =cP)	143	630	1242	4420
*Viscosity of 50% emulsion (mPa.s = cP)	-	3799	7380	22497
*Viscosity of 75% emulsion (mPa.s = cP)	-	6546	-	-
*Viscosity of max water (mPa.s = cP)	-	4979	7045	8497
Max. water cont. (vol.%)	-	60	52	23
($T_{1/2}$) Halftime for water uptake (hrs.)	-	0.5	1.1	1.5
Stability ratio	-	-	0.21	0.87

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

- No data

Table B.13

Summary lab weathering data of Northstar crude oil, 10 °C of fresh oils and its residues

Property	Fresh	150°C+	200°C+	250°C+
Boiling Point Temp. (°C)	-	181	238	297
Vol. topped (%)	0	42.6	54.2	67.7
Weight Residue (wt. %)	100	62.8	50.1	36.1
Density (g/mL)	0.779	0.837	0.852	0.869
API °	50.1	37.5	34.5	31.2
Pour point (°C)	-9	9	15	21
Flash Point (°C)	-	33	71	116
IFT in. (mN/m)	29	30	30	31
IFT eq. (mN/m)	10	8	7	9
Asphaltenes (wt. %)	0.03	0.05	0.06	0.09
Wax (wt.%)	1.74	2.77	3.47	4.82
*Viscosity of water-free residue (mPa.s =cP)	1	20	249	409
*Viscosity of 50% emulsion (mPa.s = cP)	-	-	-	-
*Viscosity of 75% emulsion (mPa.s = cP)	-	-	-	-
*Viscosity of max water (mPa.s = cP)	-	17	87	410**
Max. water cont. (vol.%)	-	3	6	30**
($T_{1/2}$) Halftime for water uptake (hrs.)	-	0.01	0.01	0.03
Stability ratio	-	-	0.67	0.11

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

*** Adjusted to increase the expected viscosity emulsion and water uptake based on the meso-scale flume basin. However, the bench-scale testing indicated that Northstar forms unstable emulsions with low viscosities and high water uptake of ~ 80 % for the 250°C+ residue. In case of a spill, the oil might therefore show a high water uptake with low viscosities at sea, but this is also depending on the release conditions/scenario. Overall, Northstar is a "low-emulsifying" crude oil that expects to form unstable emulsions with low viscosities when spilled at sea at 10 °C.*

- No data

Table B.14

Summary lab weathering data of WRG, 10 °C of fresh oil due to lack of lighter components with boiling point lower than 250 °C

Property	Fresh~250°C+
Boiling Point Temp. (°C)	-
Vol. topped (%)	0
Weight Residue (wt. %)	100
Density (g/mL)	0.892
API °	27
Pour point (°C)	-24
Flash Point (°C)	106
IFT in. (mN/m)	19
IFT eq. (mN/m)	12
Asphaltenes (wt. %)	0.05
Wax (wt. %)	4.84
*Viscosity of water-free residue (mPa.s =cP)	85
*Viscosity of 50% emulsion (mPa.s = cP)	-
*Viscosity of 75% emulsion (mPa.s = cP)	-
*Viscosity of max water (mPa.s = cP)	
Max. water cont. (vol.%)**	70
($T_{1/2}$) Halftime for water uptake (hrs.)	0.15
Stability ratio	0.01

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

**: *Based on the maximum water uptake from the meso-scale flume basin experiment. ~ 90 vol. % from the bench-scale laboratory testing is too high and not evident in a spill situation. Note that WRG exhibits unstable emulsion that easily break with mechanically stress and/or under static conditions.*

\- *No data*

Appendix C

Categorization Map of Alaska North Slope Crude Oils

A semi-quantitative categorization map of crude oils is developed into four main groups of oil; *paraffinic, waxy, naphthenic,* and *asphaltenic* oils, based on their typically physio-chemical properties, as described below. The categorization of crude oils from Alaska North Slope for Year One and Two (2016) and previous studies of crude oils from this region are illustrated in Figure C 1. The previous studies were part of the OCS Study MMS 98-0031 for MMS (Leirvik et al., 2002), and an older SINTEF study funded by MSRC in 1993. The categorization map (Figure C 1) illustrates the span in physio-chemical properties within the Alaska North Slope crude oils (blue and yellow circles) that can be quite wide, and may change as a function of production time.

Paraffinic crude oils

Paraffinic crude oils are often characterized by low to medium density, which reflects high content of light and saturated components, such as paraffins (alkanes). Paraffinic crudes differ mainly from the waxy crudes with a lower wax content (typically < 6 wt. %), hence the pour point of the fresh crude is often lower compared with waxy crude oils. Paraffinic crudes are characterized with medium to high evaporation loss, with rapid and high water uptake and normally form stable w/o-emulsions. Rapid initial evaporative loss will result in a relative increase of physiochemical properties like pour point, asphaltene and the wax content. Hence, the asphaltenes (polar surface-active components) may contribute, together with the wax, to the high stability usually observed of the w/o-emulsions formed.

Waxy crude oils

Waxy crude oils often exhibit high pour points due to large content of wax components (typically > 6 wt.%). These oils have a tendency to solidify producing elastic properties on the sea surface, particularly observed at low seawater temperatures. Solidification is pronounced if the seawater temperature typically is 10-15 ºC below the pour point. Waxy crude oils typically exhibit a light to medium evaporative loss. The water uptake can vary extensively, whereas the w/o- emulsions can be very stable or even highly unstable depending on the content of stabilizing and polar surface-active components like the asphaltenes and resins.

Naphtenic crude oils

Typically, naphtenic oils exhibit disrupted *n*-alkane (paraffins) patterns due to high degree of biodegradation of the oil in the reservoir. The content of paraffins are therefore normally low in for these oils, and have low pour points with corresponding low wax content. Such biodegraded crude oils may have high densities and a high degree of UCM (Unresolved Complex Mixture) consisting of a wide range of complex components, such as resins and naphthenes. Other naphtenic crude oils can be only slightly biodegraded and exhibit e.g. paraffinic features. Hence, the evaporative loss among this naphtenic crude can vary extensively, depending on its physical properties. Naphthenic crudes may form unstable w/o-emulsions with very low viscosities, but can also exhibit properties towards asphaltenic features and form stable w/o-emulsions. The water uptake may vary among the naphtenic crudes, but generally, they form emulsions with both low water content (typically 30-50 vol. %) and a relatively slow water uptake rate compared with paraffinic crudes.

Asphaltenic crude oils

Typically, features of asphaltenic oils are the high content of heavy components like asphaltenes and resins (typically > 0.8 wt. %), while the content of lighter components is correspondingly low. This is reflected by high density (typically > 0.9 g/ml) and low evaporation loss. The asphaltenic crudes often exhibit low pour points due to the high asphaltene content preventing wax precipitation and formation of a wax lattice structure. Compared with paraffinic and waxy crudes the asphaltenic crudes usually have both a slower and a lower maximum water uptake. The asphaltenic crude oils form stable, highly viscous and persistent blackish water-in-oil emulsions with expected long life time on the sea surface. The high stability is caused by the stabilization of the w/o-emulsification by the polar material in the oil.

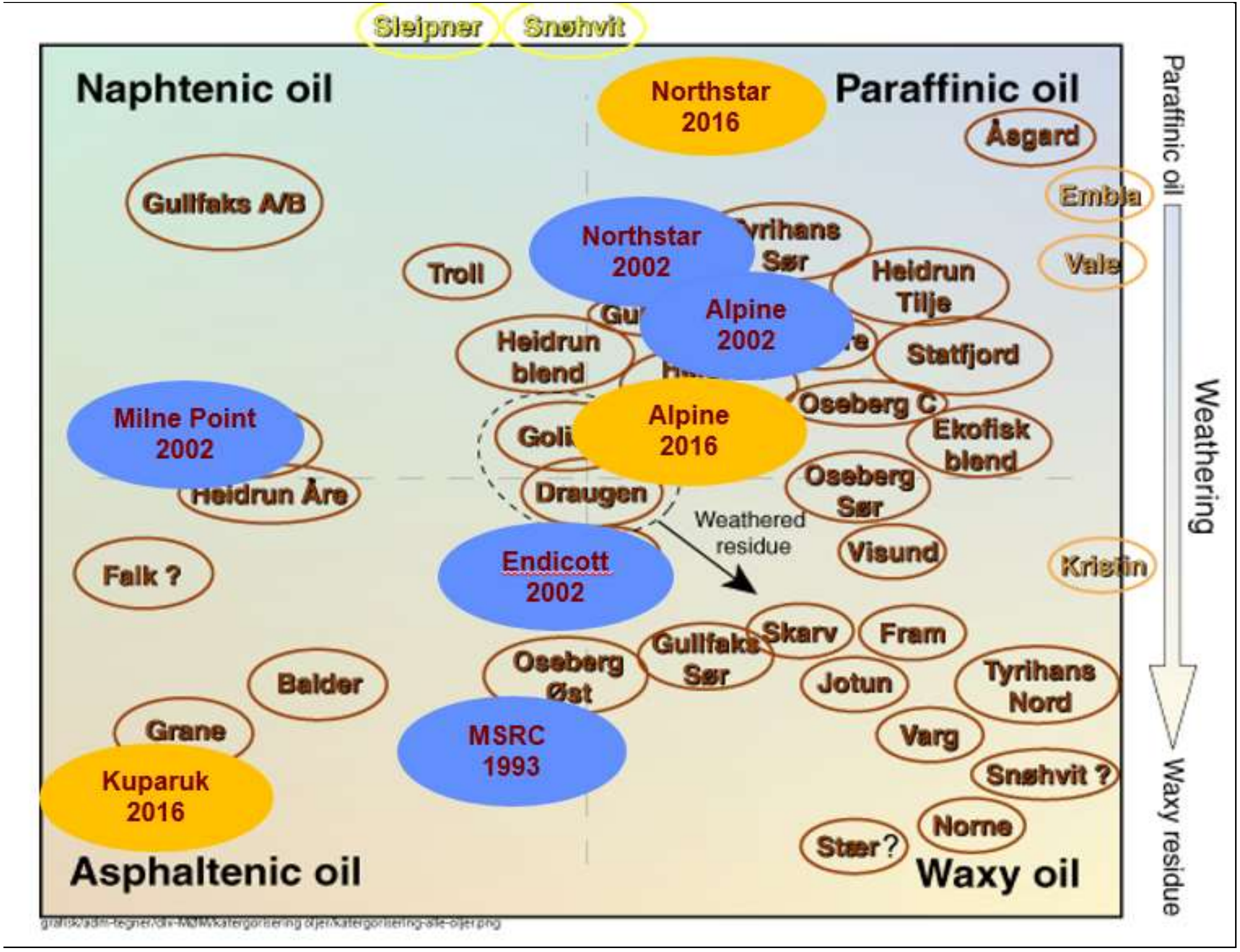


Figure C 1. Categorization of Alaska North Slope crude oils into four main groups; Naphtenic, Paraffinic, Waxy, and Asphaltenic oils. The oils in yellow circles are crude oils from Alaska North Slope from this project (Year One and Two), while the blue circles indicate crude oils from the same region from previous projects at SINTEF for comparison.

The Department of the Interior Mission

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering sound use of our land and water resources; protecting our fish, wildlife, and biological diversity; preserving the environmental and cultural values of our national parks and historical places; and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to ensure that their development is in the best interests of all our people by encouraging stewardship and citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in island territories under US administration.

The Bureau of Ocean Energy Management

As a bureau of the Department of the Interior, the Bureau of Ocean Energy (BOEM) primary responsibilities are to manage the mineral resources located on the Nation's Outer Continental Shelf (OCS) in an environmentally sound and safe manner.

The BOEM Environmental Studies Program

The mission of the Environmental Studies Program (ESP) is to provide the information needed to predict, assess, and manage impacts from offshore energy and marine mineral exploration, development, and production activities on human, marine, and coastal environments.