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Project No: Bunker project

'BUNKER FUEL WEATHERING STUDY'

Report By:

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ACKNOWLEWLEGEMENT

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Australian Government
Australian Maritime Safety Authority

CONTENTS

GLOSSARY

Bunker Fuel
A heavy fuel oil or diesel used as a ships fuel. Heavy fuel oil is typically supplied in three viscosity grades 180, 280 and 380 cSt.

Cutter Stock
Diluent added to residue to meet residual fuel (bunker fuel) specifications for viscosity and sometimes sulphur content. Typically cracked gas oil is used.

Evaporation
A process that causes some volatile components of an oil/fuel to be transferred to the atmosphere. Lighter hydrocarbons evaporate more rapidly than heavy components.

Front End Loss
The front-end loss is defined as the loss of hydrocarbons with boiling points less than tetradecane (nC14, 255^{o}C). This is obtained from the Gas Chromatographic data.

Gas Chromatography
An analytical technique used to separate complex mixtures. Can be used to obtain a boiling distribution range of oil for identification purposes.

HAVR
Heat Assisted Volume Reduction. A technique used in the laboratory to produce large volumes of weathered oils.

MacKay Chamber
A chamber used to artificially weather oils under simulated sea state conditions. Salinity, seawater temperature, air temperature and wind speed can all be adjusted to simulate local environmental conditions.

Pour Point
This is the temperature (^{o}C) at which the oil becomes fluid (liquid).

Residue
A refinery term for the bottoms from a crude oil distilling unit, vacuum flasher, thermal cracker, or visbreaker. This material is typical used to produce heavy bunker fuels.

Viscosity
Viscosity is a measure of a fluid's resistance to flow. It is also a function of temperature and weathering and has units of centistokes (cSt).

Volumetric Loss
The total volumetric loss is determined by comparing the chromatographic profile of the weathered oils with the fresh bunker fuel oils. This is obtained from the Gas Chromatographic data.

1. INTRODUCTION

A vast number of oil spills in Australian waters are due to bunker fuels. There is currently very little data available on how bunker fuels weather in Australian waters. The movement of oil spilt on the sea is effected by environmental conditions, which may in turn cause changes in the properties of the oil spill. Oil weathering studies can provide physical and chemical data on how bunker oils change over time (including volumetric loss) and can provide an estimate as to how long they have been on the water. This data can be used as an input to improve modelling capabilities. This will potentially reduce the time window for tracking suspect vessels and improve the ability of source identification. A Research and Development project on the weathering of bunker fuels in Australian waters was established by Australian Maritime Safety Authority (AMSA) and the National Plan Environment Working Group. Leeder Consulting was requested to carry out the following.

- Carry out summer and winter weathering studies on four bunker fuels in a MacKay chamber (MNS) over a 96 hour period.
- Carry out simulated distillations on the fresh and weathered oils to determine both front end and total volumetric loss.
- Prepare heat assisted volume reduced (HAVR) oils for physical testing purposes.
- Carry out physical testing on the fresh and weathered oils.
- Carry out whole oil and biomarker analysis on the fresh and weathered oils.
- Produce a video on the MacKay (MNS) chamber weathering trials.

On the 25th of October 2004 a range of bunker fuels were received for testing. A list of the oil samples received by Leeder Consulting can be found in Appendix 1 of this report.

2. BUNKER FUELS

The term ‘bunker’ has its origins in the use of coal as a fuel. Coal was stored in bunkers on land and when coal fired steamships took over from sail, ‘bunkers’ became the term used for both the fuel and the space used to store it on board. Around the early 1900’s ships began to burn oil. Oil was easier to handle than coal, however the term ‘bunker’ was retained. The refuelling of ocean-going ships, known as bunkering, is probably one of the least familiar aspects of the petroleum industry. Bunker fuel can be broadly divided into two types- heavy fuel oil and gasoil (marine diesel).

Bunker Fuel, also known as Bunker C, No.6 Oil, Resid or High Sulphur Fuel Oil is essentially based on the “bottom of the barrel” from the refining of petroleum. As such, its properties are to a great extent dependent on the nature and source of the crude oil from which it is produced and the refining processes employed. The heavy fuel oil is derived from refinery bottoms or residues after all other fractions have been extracted from a crude oil feedstock. These crude feedstocks vary from refinery to refinery and also from week to week at each refinery. The refinery bottoms material will vary in chemical composition from refinery to refinery as they will vary in the type of plant and its operation. The residue has a typical viscosity of around 400-450 centistokes (cst) and it can be blended with lighter products to produce a range of fuel oil grades.

There are two principal grades of marine bunker fuel in general use based on their viscosity measured at 50^{o}C, namely IFO 180 cSt and IFO 380 cSt. Each of these has two sub-grades dependent on the allowable contents of vanadium, carbon residue and ash. The full specifications for these can be found in the ISO fuel specification number ISO 8217.

Each refinery in Australia and overseas produces bunker fuels that are chemically different to each other. The reason for this is a combination of different crude oil feedstocks, cutter stock and different plant that are used at each refinery.

3. OPERATIONAL ASSESSMENT

A systematic assessment of an oil's physical and chemical properties can provides a number of benefits to those agencies and operators that are charged with oil spill management, including clean-up and source identification. These assessment studies are typically undertaken in a three-stage assessment process which includes physical and chemical testing of the fresh oils, weathering studies of the oil (followed by physical and chemical testing), and finally dispersant testing on both the fresh and weathered oils. The scope of this study allowed for a two stage approach. The two stages carried out are described below.

3.1 Stage 1 – Physical and chemical characterisation of fresh oil

Fresh oils can be characterised in order to determine their likely behaviour at sea, probable amenability to dispersants and other response methods, and to gauge the likely weathering properties of the oil. This stage is, in many respects, a preliminary one and supplies data, which enables the accurate scoping and design of the assessment program. A basic assessment of oil's physical and chemical characteristics can encompass:

- Simulated Distillation by Gas Chromatography.
- Viscosity (at three temperatures).
- Pour point.
- Whole oil and biomarker analysis.

The laboratory methods used to undertake these tests are described in volume five of the American Society for Testing Materials (ASTM) manual. The whole oil and biomarker analysis provides a chemical fingerprint of the oil and this data can be used for source identification. The simulated distillation, viscosity and pour point can be used for modelling purposes of the fresh bunker fuel.

3.2 Stage 2 – Weathering Properties of the test oil

In this stage, the test oil is weathered in the MacKay (MNS) chamber under various environmental conditions. Water temperature, salinity, air temperature and wind speed can all be set to simulate local environmental conditions. Simulated distillation is performed on the weathered oils in order to determine the front end loss and total volume loss, by evaporation and or dissolution. The duration of the weathering would depend on a number of factors, including likely spill trajectories, response times and clean-up capabilities. Once the weathering has been completed larger volumes of the weathered oil are produced by a process of heat assisted volume reduction (HAVR). These larger samples are then analysed to determine viscosity, pour point, whole oil analysis and simulated distillation.

4. PHYSICAL PROPERTIES OF BUNKER FUEL

The physico-chemical properties of oil types determines the nature of changes that will occur as each oil is exposed to the environment after being spilled (weathering) and subsequently whether the spilled oil can be effectively cleaned-up or treated with dispersants. The basic oil properties are also important as input data for oil spill modelling. Oil characteristics and changes due to weathering are determined through a combination of laboratory analysis and numerical modelling. The relationship between the laboratory testing and modelling components is illustrated in figure 1 below.

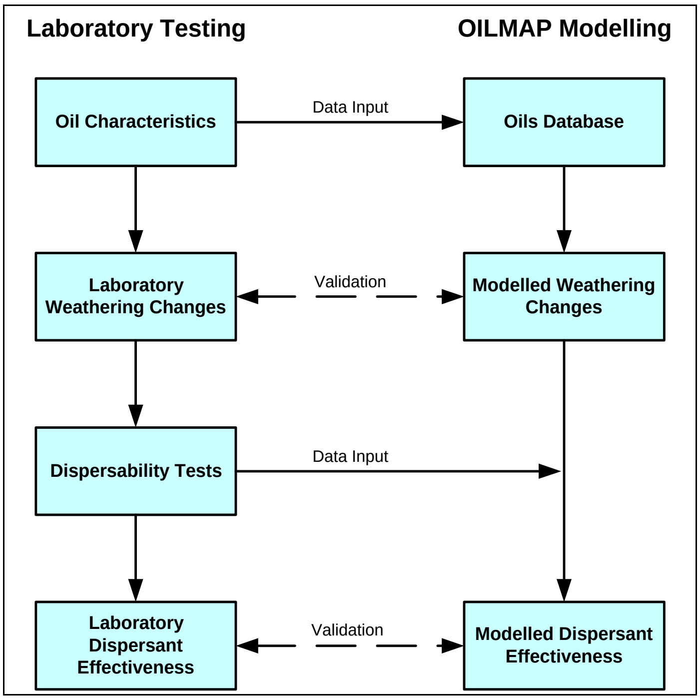

Figure 1: Relationship between Laboratory Testing and Modelling
(Produced by Dr B. King, ASA, Australia)

Some of the most important characteristics for modelling oil's behaviour are its API gravity or density, kinematic viscosity (a measure of a fluid's resistance to flow) and pour point (NOAA 1994). These factors provide the best estimation of the way in which the viscosity of the oil will change over time and at different temperatures.

5. CHANGES DUE TO WEATHERING

The weathering process that occurs when oil is spilled at sea is highly dependent on the environmental conditions prevailing at the time. For example, increasing wind speed and wave action causes greater evaporation and loss of light components, resulting in an increase in the viscosity and density of the remaining oil and can also lead to the formation of oil/water emulsions. The weathering of spilled oil is determined primarily by:

- oil composition;
- oil slick thickness;
- temperature of the sea water and air; and
- wind speed and sea state.

5.1 Climatic Data Review

It is important to have an understanding of the environmental conditions at the site of any potential spill, so that these conditions can be approximated during laboratory weathering of oils. In this way, laboratory test results will most accurately predict the changes that will occur in the field. Climatic data under which the bunker fuels were to be tested was supplied to Leeder Consulting by Dr Trevor Gilbert of AMSA. The following environmental conditions were adopted for laboratory tests:

Conditions	**Units**	**Summer**	**Winter**
Wind speed	knots	20 knots	5 knots
Sea temperature	°C	30°C	12°C
Air temperature	°C	30°C	14°C
Salinity	$^{o}/oo$	31	31

The weathering conditions can be found in Appendix 2 of this report.

5.2 Weathering Analysis

(i) Oil Preparation

Four bunker fuels were selected for this study. The bunker fuels were 180cSt, 280cSt and 380cSt sourced from Australian ports and a 280cSt bunker fuel sourced from Singapore. A sub-sample of the four bunker fuels supplied to Leeder Consulting were heated in a sealed container in an air oven to 50°C and then thoroughly mixed. The oils were then tested for a range of physical parameters as requested. These were density, pour point and kinematic viscosity at three temperatures. Viscosity was performed at three temperatures so that a straight line could be drawn through these points. Viscosities for a range of temperatures can then be extrapolated from this line.

(ii) Weathering

The Mackay chamber[1] (MNS), developed by Donald Mackay of Environment Canada, was used in this study to simulate weathering processes (see Figure 2) at sea. The Mackay test is the world-recognised standard for the weathering of petroleum oils and has stringent control over conditions such as water temperature, wind velocity, salinity, wave energy etc. The oil was heated to above its pour point until it was liquid. A 10mL aliquot of the fresh liquid oil was added to the Mackay apparatus, which contained 10 litres of seawater. The bunker fuel oils were subjected to laboratory weathering under average Australian summer and average Australian winter conditions in the Mackay apparatus for 96 hours. Sub-samples of oil were collected from the chamber at times ranging from 9 hours to 96 hours from the commencement of the weathering study. These sub-samples were analysed by Gas Chromatography to determine the front end and volumetric loss for each of the oils.

During the Mackay weathering, notes were taken on the visual appearance of the oil and how it was behaving in the chamber. These observations along with the front end and volumetric loss are found in Appendix 4 of this report.

The distillation characteristics, determined by gas chromatography, of the fresh and weathered samples were used to determine both the total volumetric loss and the front-end loss.

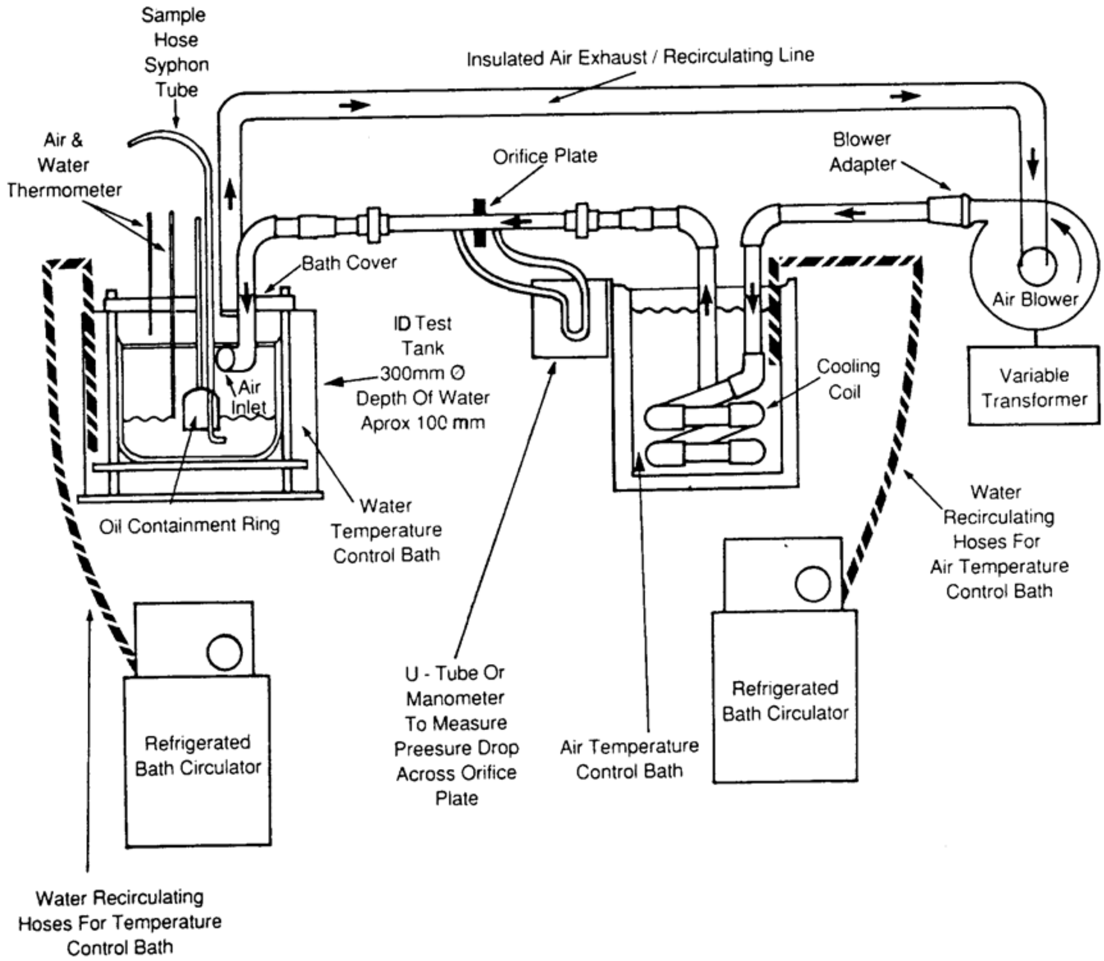

Figure 2: Mackay (MNS) test apparatus

The front-end loss is defined as the loss of hydrocarbons with boiling points less than tetradecane (nC14, 255^{o}C). The total volumetric loss was determined by comparing the chromatographic profile of the weathered oils with the fresh bunker fuel oils.

After the weathering was completed in the MacKay chamber, larger volumes bunker oils were prepared with corresponding characteristics for physical testing purposes. Large volumes of weathered oils were generated by heating the oil and applying an air purge to reduce the volume. This process is called heat assisted volume reduction (HAVR). The bunker fuel oil was heated and air purged until the appropriate volume reduction was obtained.

All of the physical data generated from testing the fresh and weathered oils is presented in Appendix 3 of this report.

After four hours of weathering at sea, simulated in the MacKay chamber, the pour point (temperature at which an oil becomes a liquid) of the bunker oils were found to have increased to a temperature above the winter water temperature (Appendix 3). Once the pour point of the oil exceeds the seawater temperature, the oil can be regarded as a solid non-spreading oil and dispersant effectiveness will be very low. As would be expected, both the pour point and kinematic viscosity of the bunker fuel oils were found to increase with time as the oil weathered (see Appendix 3). All of the chromatograms obtained from the Gas Chromatography analysis of the fresh and weathered oils are presented in Appendix 5 of this report.

5.3 Chromatographic Profiling

Gas Chromatographic (GC) profiling of both the fresh and weathered bunker fuel samples allows the overall chemical characteristics of the oils to be determined. Both qualitative and quantitative analysis was undertaken. The data generated from the chromatographic analysis can be used for oil spill source identification purposes.

Whole oil analysis of the fresh and weathered bunker fuel oils was performed by Gas Chromatography using a Flame Ionisation detector (GC-FID)[2]. The analytical column employed was a non-polar thirty metre (30m) J&W DB-1 fused silica capillary column with a 0.25mm internal diameter and a 0.25µm film thickness. Results from this analysis are presented in Appendix 4.

Gas Chromatographic-Mass Spectrometric (GC-MS) analysis of biomarkers enables the determination of various ratios that can be used for oil spill source identification purposes. Biomarkers are biochemical fossils that occur in sedimentary rocks and crude oils. These compounds encode information about the geological age and origins of organic matter to the point where the specific oil field where the petroleum products originated can be identified. In this study the GC/MS analysis has identified specific biomarker ratios that are characteristic of the bunker fuel oil source. The weathering study has also enabled use to determine the stability of specific biomarker compounds in weathered oils. The methodology employed was that described in the NORDTEST[3] biomarker testing regime. Biomarker profiles for triterpanes, steranes, along with polycyclic aromatic hydrocarbons (PAHs) such as alkylated phenanthrenes and alkylated dibenzothiophenes were determined. These profiles and biomarker ratios are presented in Appendix 4 and 5 of this report. The analytical column employed was a thirty metre (30m) J&W DB-5MS fused silica capillary column with a 0.25mm internal diameter and a 0.25µm film thickness. The biomarker fingerprints can be used to update the National Oil on the Sea Identification Database[3] (NOSID) as developed by the National Plan.

6. RESULTS

6.1 Physical Properties of the Fresh Bunker Fuels

The unweathered bunker fuel samples were analysed with the following results.

		180 cSt	280 cSt	380 cSt	280 cSt
Test	**Units**	Fremantle	Fremantle	Fremantle	Singapore
Pour Point	°C	18	9	18	-3
Kinematic Viscosity at 60°C	cSt	79.4	133.4	121.5	157.1
Kinematic Viscosity at 80°C	cSt	38.7	55.4	40.8	59.7
Kinematic Viscosity at 100°C	cSt	19.2	27.9	25.5	32.8

6.2 Physical Properties of the Weathered Bunker Fuels

The four bunker fuels were weathered in the MacKay Chamber. The results obtained for the weathered oils are presented in Appendix 3 of this report.

6.3 Whole Oil and Biomarker Analysis

The results obtained from the whole oil and biomarker analysis is presented in Appendix 4 and 5 of this report. All whole oil chromatograms are presented in Appendix 5 of this report.

7. DISCUSSION

7.1 Weathering

Four bunker fuels sourced from Australia and Singapore were weathered in the MacKay chamber under summer and winter conditions. Environmental condition from Northern and Southern Australia can vary considerably between summer and winter. Taking this large variation around the country into account, it was decided that two weathering conditions be selected to represent the extremes of the kind of weathering that might typically be expected in Australian waters.

During the weathering trial in the Mackay chamber, the four bunker oils were not incorporated into the water column by mechanical dispersion. The oils remained on the surface of the water column for the duration of the weathering study (96 hours).

7.2 Physical Properties

The pour points for the unweathered bunker fuels were found to be very different. The 280cSt bunker fuel obtained from Singapore was found to have a pour point of -3°C while the three Australian bunker fuels sourced from Fremantle, Western Australia were found to have pour points above 8°C. This suggests that the physical properties of weathered bunker oil cannot be predicted by knowing the initial grade of bunker fuel and the weathering conditions alone – the source of the oil, the blending and cutting of the oil will also affect the weathering process. This is highlighted by differences in weathering between the two bunker fuels of the same grade, but different sources (Fremantle 280cSt and Singapore 280cSt).

After nine hours of weathering the pour point for all bunker fuels was found to be higher than the winter seawater temperature. The 380cSt oil in particular would be solid at all possible sea temperatures after only nine hours of weathering. A similar trend applies to the other bunker fuels. The pour point of the Singapore oil, initially -3°C, exceeds the seawater temperature after nine hours. This has an impact on the various clean-up options for a spilled bunker fuels.

All of the bunker fuels were found to have lost on average 30% by volume over the 96 hour weathering period under both summer and winter conditions.

Even after the most extreme weathering (temperature and wind speed), approximately 70% of the bunker fuels remained as a solid residue on the waters surface. Weathered bunker oils at this stage resembled solid wax patties. The initial rate (first 10 hours) at which the volumetric loss occurs, however, is highly dependant on the weathering conditions.

A volumetric loss of 25% of the Fremantle 180cSt oil, for example, took 48 hours of winter weathering, but only 9 hours of summer weathering. Laboratory conditions must therefore approximate 'real world' conditions as closely as possible in any investigative work.

The viscosities for the bunker fuels were found to increase on average by two orders of magnitude over the 96 hour period, although this can vary. The Fremantle 180cSt oil, for example, when weathered under summer conditions, gave a viscosity ten times higher than the same oil weathered under winter conditions. Once the cutter solvent (used to adjust the viscosity of the bunker fuel) has been lost from the bunker fuel its pour point and viscosity rapidly increases. This was observed to be the case for all four bunker fuels. The data obtained could be used to update the data currently on hand for modelling purposes of bunker fuel spills in Australian waters.

The changes in the oils physical properties as the bunkers weathers, could affect response options as the window of opportunity to respond to bunker spills is very limited even under favourable sea temperatures e.g. dispersant use.

7.3 Whole Oil and Biomarker Data

The whole oil and biomarker analysis was performed on all oils and the various ratios reported in Appendix 4. These analyses are typically carried out to provide post spill information on the type of oil present in the environment and also to possibly identify the source of the oil spill.

Whole oil analysis is carried out by Gas Chromatography with a Flame Ionisation Detector (GC-FID) and is typically used to obtain a boiling distribution range for an oil sample. The whole oil analysis is useful for fresh and slightly weathered oils as the boiling range distribution of the oil will change over time. Large variations can be seen in the whole oil data for the same oil from the weathering trials over the 96 hour period as the volatile components were lost from the sample through evaporative loss. This study has identified that the whole oil analysis on its own is limited in its ability to be used for source identification purposes of weathered oils.

The biomarker analysis is performed by Gas Chromatography-Mass Spectrometry and focuses on stabile biomarker compounds present in the oil.

A range of publications are available that provide a detailed description of biomarker compounds, their sources and usefulness in oil correlation studies. A detailed description of these is beyond the scope of this study.

These stabile biomarker compounds employed in oil fingerprinting analysis typically have high molecular weights, have very low water solubilities and are resistant to biodegradation. These biomarkers are extremely resistant to weathering and remain intact even in most severely degraded samples.

In this study, the ratios obtained for the biomarkers indicate only minimal variation between bunker fuel samples weathered over a 96 hour period. This demonstrates there ability to fingerprint bunker fuel samples that have been weathered in the environment under average summer and winter conditions for 96 hours.

A six year study on an oil mangrove in South Australia (ERA spill) indicated how stabile the biomarker compounds are to environmental weathering. The biomarker profiles (hopanes and steranes) on mangrove sediment collected over a six year period were found to still match the original heavy bunker fuel. A range of other scientific publications have shown how stabile many of these biomarker compounds are to environmental weathering.

8. REFERENCES

1. Mackay, D. and Szeto, F. (1982). Effectiveness of oil spill dispersants – Development of a Laboratory Method and Results for selected commercial products. Institute for Environmental Studies, University of Toronto, Pub. No. EE-16.

2. ASTM, Philadelphia, USA, D3328, Standard Test methods for the comparison of waterborne oils by Gas Chromatography.

3. Liv-Guri Faksness, Hermann M. Weiss, Per S. Daling. (2002). Revision of the Nordtest Methodology for Oil Spill Identification. Sintef Report no STF66 A02028

4. NOSID (National Oil on the sea database) database of oil hydrocarbon fingerprints produced by various government agencies (AMSA, AGSO, AGAL)

APPENDIX ONE

SAMPLES RECEIVED

The following bunker samples were received for the weathering study.

Fremantle 180 cSt, bunker fuel, 3/08/04

Fremantle 280 cSt, bunker fuel, 20/10/04

Fremantle 380 cSt, bunker fuel, 3/08/04

Singapore 280 cSt, bunker fuel, 21/01/05

APPENDIX TWO

WEATHERING CONDITION

Due to Australia's vast size (North to South), we have wide ranging weather conditions. For this study it was decided to use extremes temperatures for both summer and winter conditions.
The aim of using this approach was to cover a wide temperature range and determine how this affects the weathering process of the bunker fuels.

Conditions	*Units*	*Summer*	*Winter*
Wind speed	knots	20 knots	5 knots
Sea temperature	°C	30°C	12°C
Air temperature	°C	30°C	14°C
Salinity	^{o}/oo	31	31

APPENDIX THREE

PHYSICAL TESTING DATA

Physical Testing data for both fresh and weathered bunker fuel oil

Sample Description	Winter Weathering	Pour Point °C	Kinematic Viscosity at 60°C (cSt)	Kinematic Viscosity at 80°C (cSt)	Kinematic Viscosity at 100°C (cSt)	% Front End Loss	% Volumetric Loss
Fremantle,180cSt bunker	fresh	18	79.39	38.7	19.23	0	0
Fremantle,180cSt bunker	9 hrs	27	456.2	127.1	50.66	90	14
Fremantle,180cSt bunker	24 hrs	27	816.7	210.3	86.39	100	19
Fremantle,180cSt bunker	48 hrs	33	1562	359.5	128.4	100	24
Fremantle,180cSt bunker	96 hrs	33	1770	364.9	137.2	100	27

Sample Description	Summer Weathering	Pour Point °C	Kinematic Viscosity at 60°C (cSt)	Kinematic Viscosity at 80°C (cSt)	Kinematic Viscosity at 100°C (cSt)	% Front End Loss	% Volumetric Loss
Fremantle,180cSt bunker	fresh	18	79.39	38.7	19.23	0	0
Fremantle,180cSt bunker	9 hrs	33	1488	392.2	142.7	100	25
Fremantle,180cSt bunker	24 hrs	33	1770	364.9	137.2	100	28
Fremantle,180cSt bunker	48 hrs	36	3322	595.0	205.8	100	31
Fremantle,180cSt bunker	96 hrs	45	18226	2161	560.0	100	34

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Sample Description	Winter Weathering	Pour Point °C	Kinematic Viscosity at 60°C (cSt)	Kinematic Viscosity at 80°C (cSt)	Kinematic Viscosity at 100°C (cSt)	% Front End Loss	% Volumetric Loss
Fremantle,280cSt bunker	fresh	9	133.4	55.41	27.97	0	0
Fremantle,280cSt bunker	9 hrs	24	750.9	194.3	70.65	88	13
Fremantle,280cSt bunker	24 hrs	27	1829	399.1	140.8	100	19
Fremantle,280cSt bunker	48 hrs	30	3386	657.5	190.8	100	22
Fremantle,280cSt bunker	96 hrs	39	8972	1605	371.0	100	28

Sample Description	Summer Weathering	Pour Point °C	Kinematic Viscosity at 60°C (cSt)	Kinematic Viscosity at 80°C (cSt)	Kinematic Viscosity at 100°C (cSt)	% Front End Loss	% Volumetric Loss
Fremantle,280cSt bunker	fresh	9	133.4	55.41	27.97	0	0
Fremantle,280cSt bunker	12 hrs	27	1562	342.5	113.2	100	21
Fremantle,280cSt bunker	24 hrs	33	4491	770.7	212.3	100	24
Fremantle,280cSt bunker	48 hrs	38	10872	1591	362.0	100	27
Fremantle,280cSt bunker	96 hrs	40	10978	1606	373.0	100	28

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Sample Description	Winter Weathering	Pour Point °C	Kinematic Viscosity at 60°C (cSt)	Kinematic Viscosity at 80°C (cSt)	Kinematic Viscosity at 100°C (cSt)	% Front End Loss	% Volumetric Loss
Singapore,280cSt bunker	fresh	-3	157.1	59.66	32.84	0	0
Singapore,280cSt bunker	9 hrs	21	1943	464.8	165.5	86	15
Singapore,280cSt bunker	24 hrs	39	16684	2341	590.8	100	23
Singapore,280cSt bunker	48 hrs	43	25461	3714	867.5	100	27
Singapore,280cSt bunker	96 hrs	45	27461	3798	887.5	100	29

Sample Description	Summer Weathering	Pour Point °C	Kinematic Viscosity at 60°C (cSt)	Kinematic Viscosity at 80°C (cSt)	Kinematic Viscosity at 100°C (cSt)	% Front End Loss	% Volumetric Loss
Singapore,280cSt bunker	fresh	-3	157.1	59.66	32.84	0	0
Singapore,280cSt bunker	9 hrs	27	2921	641.6	204.7	100	19
Singapore,280cSt bunker	24 hrs	43	25361	3701	857.2	100	26
Singapore,280cSt bunker	48 hrs	45	28730	3784	877.8	100	28
Singapore,280cSt bunker	96 hrs	57	194206	20622	2802	100	32

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Sample Description	Winter Weathering	Pour Point °C	Kinematic Viscosity at 60°C (cSt)	Kinematic Viscosity at 80°C (cSt)	Kinematic Viscosity at 100°C (cSt)	% Front End Loss	% Volumetric Loss
Fremantle,380cSt bunker	fresh	18	121.5	50.78	25.53	0	0
Fremantle,380cSt bunker	9 hrs	27	951.6	242.5	89.32	92	12
Fremantle,380cSt bunker	24 hrs	33	3726	699.6	234.6	100	22
Fremantle,380cSt bunker	48 hrs	36	5796	987.8	296.9	100	26
Fremantle,380cSt bunker	96 hrs	42	9572	1538	422.1	100	29

Sample Description	Summer Weathering	Pour Point °C	Kinematic Viscosity at 60°C (cSt)	Kinematic Viscosity at 80°C (cSt)	Kinematic Viscosity at 100°C (cSt)	% Front End Loss	% Volumetric Loss
Fremantle,380cSt bunker	fresh	18	121.5	50.78	25.53	0	0
Fremantle,380cSt bunker	9 hrs	33	3726	699.6	234.6	100	21
Fremantle,380cSt bunker	24 hrs	36	5796	987.8	296.9	100	25
Fremantle,380cSt bunker	48 hrs	42	9870	1638	432.1	100	29
Fremantle,380cSt bunker	96 hrs	45	20893	2757	670.0	100	31

APPENDIX FOUR

WHOLE OIL AND BIOMARKER DATA

Abbreviation	Biomarker
PAHs/PAH groups	
C2-dbt	C2-dibenzothiophenes
C2-phe	C2-phenanthrenes/anthracenes
C3-dbt	C3-dibenzothiophenes
C3-phe	C3-phenanthrenes/anthracenes
1-MP	1-methylphenanthrene
2-MP	2-methylphenanthrene
4-MD	4-methyldibenzothiophene
1-MD	1-methyldibenzothiophene
Retene	Retene
C4-phe	C4-phenanthrenes/anthracenes
Pentacyclic triterpanes	
27Ts	18α(H)-22,29,30-trisnorhopane
27Tm	17α(H)-22,29,30-trisnorhopane
28ab	17α(H),21β(H)-28,30-bisnorhopane
25nor30ab	17α(H),21β(H)-25-norhopane
29Ts	18α(H)-30-norneohopane
30O	18α(H)-oleanane
30G	Gammacerane
29ab	17α(H),21β(H)-30-norhopane
30d	15α-methyl-17α(H)-27-norhopane (diahopane)
30ab	17α(H),21β(H)-hopane
32abS	17α(H),21β(H)-22S-bishomohopane
Diasteranes and Steranes	
27dbS	13β(H),17α(H), 20S-cholestane (diasterane)
27dbR	13β(H),17α(H), 20R-cholestane (diasterane)
27bbR	5a(H),14b(H),17b,20R-cholestane
27bbS	5a(H),14b(H),17b,20S-cholestane
29aaS	24-ethyl-5a(H),14a(H),17a,20S-cholestane
29bbR	24-ethyl-5a(H),14b(H),17b,20R-cholestane
29bbS	24-ethyl-5a(H),14b(H),17b,20S-cholestane
29aaR	24-ethyl-5a(H),14a(H),17a,20R-cholestane
Triaromatic Steroids	
C21TA	C21-triaromatic steroid hydrocarbon
SC26TA	C23,20S-triaromatic steroid hydrocarbon
SC28TA	C28,20S-triaromatic steroid hydrocarbon
RC27TA	C27,20R-triaromatic steroid hydrocarbon
RC28TA	C28,20R-triaromatic steroid hydrocarbon
Whole oil analysis	
C16	n-hexadecane
C17	n-heptadecane
C18	n-octadecane
nor	Norpristane
pris	Pristane
phy	Phytane

Ratio	Meaning
C2-dbt/C2-phe	100 × C2-dbt / (C2-dbt + C2-phe)
C3-dbt/C3-phe	100 × C3-dbt / (C3-dbt + C3-phe)
2-MP/1-MP	100 × 2-MP / (2-MP + 1-MP)
4-MD/1-MD	100 × 4-MD / (4-MD + 1-MD)
Retene/C4-phe	100 × Retene / (Retene + C4-phe)
%27Ts	100 × 27Ts / (27Ts + 27Tm)
%28ab	100 × 28ab / (28ab + 30ab)
%25nor30ab	100 × 25nor30ab / (25nor30ab + 30ab)
%29Ts	100 × 29Ts / (29Ts + 30ab)
%30O	100 × 30O / (30O + 30ab)
%30G	100 × 30G / (30G + 30ab)
%29ab	100 × 29ab / (29ab + 30ab)
%30d	100 × 30d / (30d + 30ab)
%32abS	100 × 32abS / (32abS + 32abR)
%27dia	100 × (27dbS + 27dbR) / (27dbS + 27dbR + 27bbS + 27bbR)
%29aaS	100 × 29aaS / (29aaS + 29aaR)
%29bb	100 × (29bbR + 29bbS) / (29bbR + 29bbS + 29aaR + 29aaS)
%27bbSTER	100 × 27bb(S+R) / (27bb(S+R) + 28bb(S+R) + 29bb(S+R))
%28bbSTER	100 × 28bb(S+R) / (27bb(S+R) + 28bb(S+R) + 29bb(S+R))
%29bbSTER	100 × 29bb(S+R) / (27bb(S+R) + 28bb(S+R) + 29bb(S+R))
%TA21	100 × C21TA / (C21TA + RC28TA)
%TA26	100 × SC26TA / (SC26TA + SC28TA)
%TA27	100 × RC27TA / (RC27TA + RC28TA)
C16/nor	C16 / nor
C17/pris	C17 / pris
C18/phy	C18 / phy
Pris/phy	Pris / phy

Biomarker ratios, Fremantle 180cSt winter

Ratio	F 180 fresh	F 180 W 9	F 180 W 24	F 180 W 48	F 180 W 96
C2-dbt/C2-phe	23%	24%	24%	23%	23%
C3-dbt/C3-phe	25%	27%	23%	24%	25%
2-MP/1-MP	65%	65%	63%	66%	64%
4-MD/1-MD	61%	62%	65%	70%	66%
Retene/C4-phe	10%	9%	9%	9%	10%
%27Ts	67%	71%	71%	70%	70%
%28ab	0%	0%	0%	0%	0%
%25nor30ab	0%	0%	0%	0%	0%
%29Ts	42%	41%	44%	41%	42%
%30O	20%	21%	21%	24%	22%
%30G	19%	19%	19%	19%	20%
%29ab	0%	0%	0%	0%	0%
%30d	4%	5%	5%	5%	5%
%32abS	55%	54%	57%	56%	56%
%27dia	38%	38%	38%	35%	37%
%29aaS	67%	70%	71%	71%	71%
%29bb	35%	33%	39%	35%	34%
%27bbSTER	31%	30%	32%	31%	31%
%28bbSTER	21%	21%	22%	22%	23%
%29bbSTER	47%	48%	46%	48%	46%
%TA21	55%	51%	53%	54%	53%
%TA26	17%	16%	17%	18%	18%
%TA27	48%	46%	44%	48%	51%

Whole oil ratios

Ratio	F 180 fresh	F 180 W 9	F 180 W 24	F 180 W 48	F 180 W 96
C16/nor	4.95	4.90	5.06	4.76	4.76
C17/pris	1.75	1.83	1.84	1.97	1.81
C18/phy	6.23	6.36	6.93	6.81	6.53
Pris/phy	4.09	3.61	4.02	3.78	3.48

Biomarker ratios, Fremantle 180cSt summer

Ratio	F 180 fresh	F 180 S 9	F 180 S 24	F 180 S 48	F 180 S 96
C2-dbt/C2-phe	23%	24%	23%	22%	23%
C3-dbt/C3-phe	25%	25%	24%	24%	24%
2-MP/1-MP	65%	65%	66%	64%	62%
4-MD/1-MD	61%	70%	63%	66%	62%
Retene/C4-phe	10%	11%	10%	9%	7%
%27Ts	67%	71%	73%	75%	72%
%28ab	0%	0%	0%	0%	0%
%25nor30ab	0%	0%	0%	0%	0%
%29Ts	42%	41%	42%	43%	43%
%30O	20%	23%	22%	22%	22%
%30G	19%	19%	20%	20%	19%
%29ab	0%	0%	0%	0%	0%
%30d	4%	5%	4%	5%	4%
%32abS	55%	56%	57%	56%	55%
%27dia	38%	38%	37%	38%	35%
%29aaS	67%	69%	69%	71%	69%
%29bb	35%	34%	36%	33%	35%
%27bbSTER	31%	31%	29%	32%	30%
%28bbSTER	21%	22%	24%	21%	22%
%29bbSTER	47%	47%	48%	47%	48%
%TA21	55%	52%	55%	53%	54%
%TA26	17%	17%	15%	15%	18%
%TA27	48%	45%	45%	50%	50%

Whole oil ratios

Ratio	F 180 fresh	F 180 S 9	F 180 S 24	F 180 S 48	F 180 S 96
C16/nor	4.95	4.71	4.19	3.36	3.36
C17/pris	1.75	1.77	1.86	2.06	2.10
C18/phy	6.23	6.38	6.81	6.69	6.75
Pris/phy	4.09	3.63	3.42	2.66	2.10

Biomarker ratios, Fremantle 280cSt winter

Ratio	F 280 fresh	F 280 W 9	F 280 W 24	F 280 W 48	F 280 W 96
C2-dbt/C2-phe	28%	28%	27%	27%	29%
C3-dbt/C3-phe	28%	30%	29%	28%	29%
2-MP/1-MP	66%	68%	67%	67%	67%
4-MD/1-MD	65%	72%	72%	67%	68%
Retene/C4-phe	8%	9%	8%	8%	8%
%27Ts	56%	63%	58%	57%	58%
%28ab	0%	0%	0%	0%	0%
%25nor30ab	0%	0%	0%	0%	0%
%29Ts	38%	39%	37%	37%	39%
%30O	37%	35%	34%	33%	33%
%30G	19%	20%	20%	18%	18%
%29ab	0%	0%	0%	0%	0%
%30d	9%	10%	9%	9%	9%
%32abS	55%	57%	55%	54%	55%
%27dia	41%	39%	39%	41%	42%
%29aaS	69%	71%	72%	68%	69%
%29bb	32%	33%	29%	32%	37%
%27bbSTER	28%	30%	30%	27%	29%
%28bbSTER	26%	23%	26%	24%	22%
%29bbSTER	46%	47%	44%	49%	49%
%TA21	65%	64%	67%	66%	69%
%TA26	20%	18%	17%	21%	23%
%TA27	44%	40%	42%	42%	44%

Whole oil ratios

Ratio	F 280 fresh	F 280 W 9	F 280 W 24	F 280 W 48	F 280 W 96
C16/nor	5.43	5.68	5.76	5.31	5.11
C17/pris	2.62	2.73	2.64	2.62	2.63
C18/phy	5.98	5.81	5.90	5.84	6.05
Pris/phy	2.86	2.76	2.73	2.67	2.31

Biomarker ratios, Fremantle 280cSt summer

Ratio	F 280 fresh	F 280 S 9	F 280 S 24	F 280 S 48	F 280 S 96
C2-dbt/C2-phe	28%	29%	25%	26%	26%
C3-dbt/C3-phe	28%	28%	28%	29%	29%
2-MP/1-MP	66%	67%	66%	66%	67%
4-MD/1-MD	65%	66%	59%	65%	64%
Retene/C4-phe	8%	8%	6%	7%	7%
%27Ts	56%	60%	61%	66%	62%
%28ab	0%	0%	0%	0%	0%
%25nor30ab	0%	0%	0%	0%	0%
%29Ts	38%	40%	38%	35%	38%
%30O	37%	32%	35%	33%	36%
%30G	19%	20%	19%	18%	19%
%29ab	0%	0%	0%	0%	0%
%30d	9%	9%	9%	8%	8%
%32abS	55%	55%	57%	58%	55%
%27dia	41%	39%	38%	41%	36%
%29aaS	69%	73%	69%	70%	71%
%29bb	32%	30%	31%	28%	34%
%27bbSTER	28%	32%	28%	31%	30%
%28bbSTER	26%	21%	29%	24%	24%
%29bbSTER	46%	47%	43%	45%	46%
%TA21	65%	65%	65%	68%	68%
%TA26	20%	22%	18%	18%	19%
%TA27	44%	46%	41%	44%	45%

Whole oil ratios

Ratio	F 280 fresh	F 280 S 9	F 280 S 24	F 280 S 48	F 280 S 96
C16/nor	5.43	4.91	3.60	5.08	4.88
C17/pris	2.62	2.77	3.07	2.63	2.68
C18/phy	5.98	5.78	6.52	5.88	5.71
Pris/phy	2.86	2.32	2.57	2.44	2.28

Biomarker ratios, Fremantle 380cSt winter

Ratio	F 380 fresh	F 380 W 9	F 380 W 24	F 380 W 48	F 380 W 96
C2-dbt/C2-phe	25%	22%	24%	25%	24%
C3-dbt/C3-phe	26%	27%	26%	26%	27%
2-MP/1-MP	66%	65%	66%	63%	67%
4-MD/1-MD	67%	71%	64%	69%	67%
Retene/C4-phe	12%	12%	11%	12%	11%
%27Ts	77%	78%	78%	78%	76%
%28ab	0%	0%	0%	0%	0%
%25nor30ab	0%	0%	0%	0%	0%
%29Ts	42%	37%	39%	42%	43%
%30O	27%	26%	26%	28%	26%
%30G	16%	18%	16%	17%	16%
%29ab	0%	0%	0%	0%	0%
%30d	3%	3%	3%	5%	3%
%32abS	57%	56%	56%	56%	57%
%27dia	35%	34%	35%	34%	34%
%29aaS	62%	66%	66%	65%	65%
%29bb	35%	35%	33%	34%	35%
%27bbSTER	30%	29%	27%	28%	30%
%28bbSTER	20%	23%	22%	23%	22%
%29bbSTER	49%	48%	51%	50%	48%
%TA21	48%	48%	46%	46%	46%
%TA26	18%	17%	19%	18%	17%
%TA27	45%	44%	46%	45%	46%

Whole oil ratios

Ratio	F 380 fresh	F 380 W 9	F 380 W 24	F 380 W 48	F 380 W 96
C16/nor	5.06	4.96	5.14	4.79	4.47
C17/pris	1.93	1.98	1.93	1.95	1.95
C18/phy	6.55	6.61	6.75	6.72	6.84
Pris/phy	3.83	3.70	3.81	3.54	3.42

Biomarker ratios, Fremantle 380cSt summer

Ratio	F 380 fresh	F 380 S 9	F 380 S 24	F 380 S 48	F 380 S 96
C2-dbt/C2-phe	25%	23%	24%	24%	24%
C3-dbt/C3-phe	26%	25%	28%	27%	26%
2-MP/1-MP	66%	65%	68%	65%	64%
4-MD/1-MD	67%	71%	70%	66%	65%
Retene/C4-phe	12%	10%	13%	11%	9%
%27Ts	77%	75%	75%	75%	76%
%28ab	0%	0%	0%	0%	0%
%25nor30ab	0%	0%	0%	0%	0%
%29Ts	42%	40%	42%	44%	42%
%30O	27%	26%	27%	27%	28%
%30G	16%	15%	16%	17%	17%
%29ab	0%	0%	0%	0%	0%
%30d	3%	3%	4%	3%	3%
%32abS	57%	55%	58%	58%	58%
%27dia	35%	37%	41%	39%	39%
%29aaS	62%	65%	63%	65%	67%
%29bb	35%	35%	34%	34%	33%
%27bbSTER	30%	28%	29%	28%	29%
%28bbSTER	20%	22%	22%	22%	21%
%29bbSTER	49%	50%	49%	50%	49%
%TA21	48%	48%	47%	46%	46%
%TA26	18%	15%	16%	17%	17%
%TA27	45%	48%	43%	50%	41%

Whole oil ratios

Ratio	F 380 fresh	F 380 S 9	F 380 S 24	F 380 S 48	F 380 S 96
C16/nor	5.06	4.73	4.72	4.51	4.47
C17/pris	1.93	1.92	1.99	1.94	2.06
C18/phy	6.61	6.71	6.72	6.91	6.91
Pris/phy	3.56	3.82	3.45	3.46	3.16

Biomarker ratios, Singapore 280cSt winter

Ratio	S 280 fresh	S 280 W 9	S 280 W 24	S 280 W 48	S 280 W 96
C2-dbt/C2-phe	38%	38%	38%	38%	38%
C3-dbt/C3-phe	42%	42%	42%	42%	42%
2-MP/1-MP	66%	66%	66%	67%	66%
4-MD/1-MD	83%	84%	86%	85%	86%
Retene/C4-phe	22%	23%	23%	25%	23%
%27Ts	20%	23%	23%	22%	24%
%28ab	0%	0%	0%	0%	0%
%25nor30ab	2%	3%	2%	2%	2%
%29Ts	53%	52%	52%	54%	53%
%30O	9%	9%	9%	10%	10%
%30G	15%	15%	14%	15%	14%
%29ab	0%	0%	0%	0%	0%
%30d	0%	0%	0%	0%	0%
%32abS	59%	56%	58%	59%	57%
%27dia	29%	25%	27%	27%	22%
%29aaS	56%	60%	64%	58%	57%
%29bb	42%	43%	40%	41%	43%
%27bbSTER	36%	37%	35%	36%	34%
%28bbSTER	24%	24%	24%	24%	25%
%29bbSTER	40%	39%	41%	40%	41%
%TA21	0%	0%	0%	0%	0%
%TA26	37%	31%	33%	31%	33%
%TA27	52%	52%	55%	54%	54%

Whole oil ratios

Ratio	S 280 fresh	S 280 W 9	S 280 W 24	S 280 W 48	S 280 W 96
C16/nor	4.03	4.28	4.62	4.38	4.28
C17/pris	2.56	2.71	2.93	2.82	2.76
C18/phy	2.84	3.22	3.08	3.00	3.05
Pris/phy	1.41	1.46	1.32	1.37	1.37

Biomarker ratios, Singapore 280cSt summer

Ratio	S 280 fresh	S 280 S 9	S 280 S 24	S 280 S 48	S 280 S 96
C2-dbt/C2-phe	38%	38%	38%	36%	37%
C3-dbt/C3-phe	42%	42%	43%	40%	43%
2-MP/1-MP	66%	67%	66%	66%	65%
4-MD/1-MD	83%	85%	85%	86%	80%
Retene/C4-phe	22%	23%	23%	21%	19%
%27Ts	20%	23%	22%	22%	22%
%28ab	0%	0%	0%	0%	0%
%25nor30ab	2%	1%	2%	2%	2%
%29Ts	53%	53%	54%	54%	54%
%30O	9%	8%	8%	9%	10%
%30G	15%	15%	15%	14%	15%
%29ab	0%	0%	0%	0%	0%
%30d	0%	0%	0%	0%	0%
%32abS	59%	56%	59%	57%	58%
%27dia	29%	22%	25%	26%	26%
%29aaS	56%	59%	59%	60%	61%
%29bb	42%	44%	41%	41%	41%
%27bbSTER	36%	35%	37%	34%	36%
%28bbSTER	24%	26%	24%	26%	24%
%29bbSTER	40%	39%	39%	41%	40%
%TA21	0%	0%	0%	0%	0%
%TA26	37%	31%	33%	34%	32%
%TA27	52%	51%	56%	53%	54%

Whole oil ratios

Ratio	S 280 fresh	S 280 S 9	S 280 S 24	S 280 S 48	S 280 S 96
C16/nor	4.45	4.89	4.70	4.46	4.46
C17/pris	1.68	1.90	1.79	1.92	1.87
C18/phy	6.01	6.76	6.01	6.57	6.42
Pris/phy	3.72	3.73	3.54	3.27	3.21

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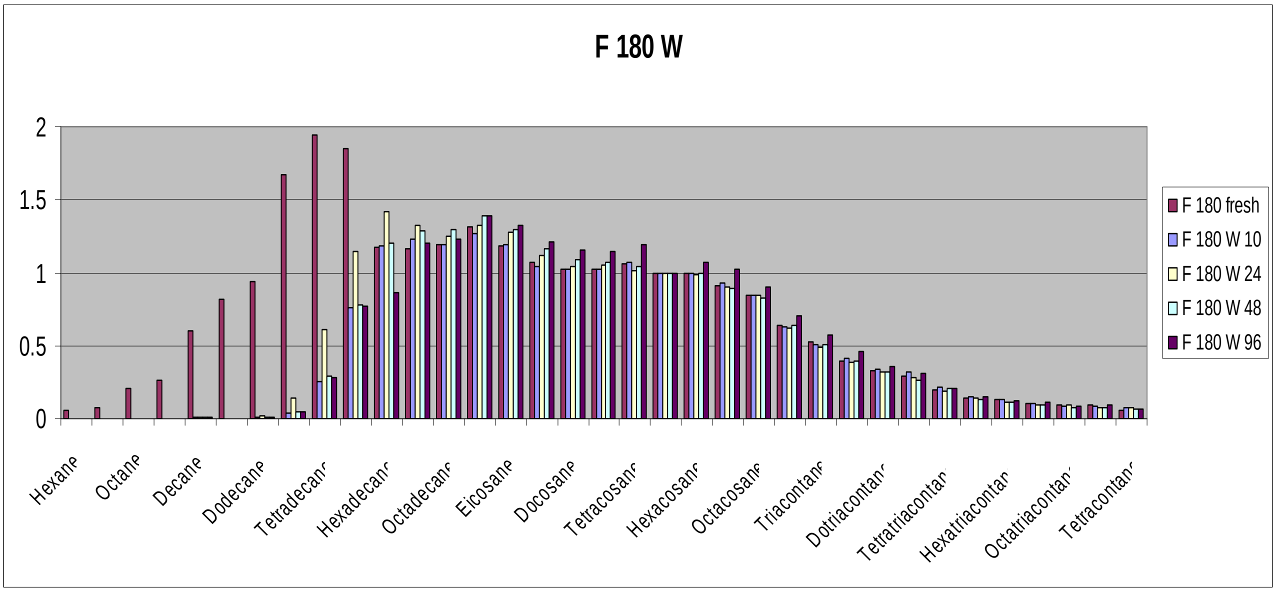
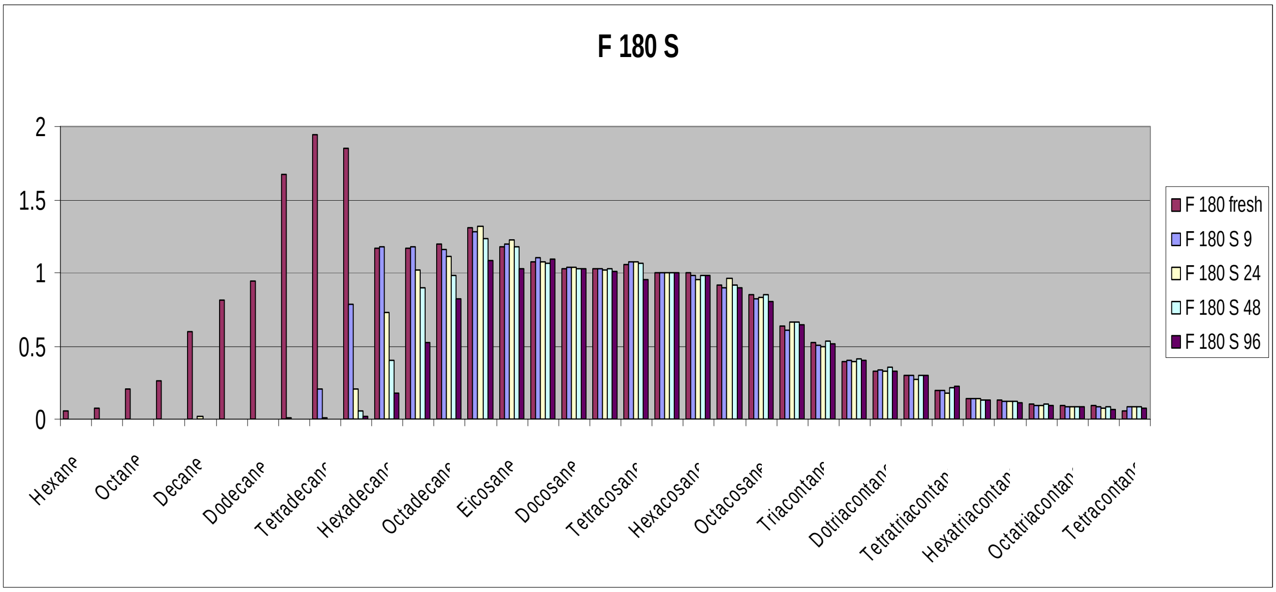
ALKANE PROFILES

Bunker Fuel Oil 180cSt



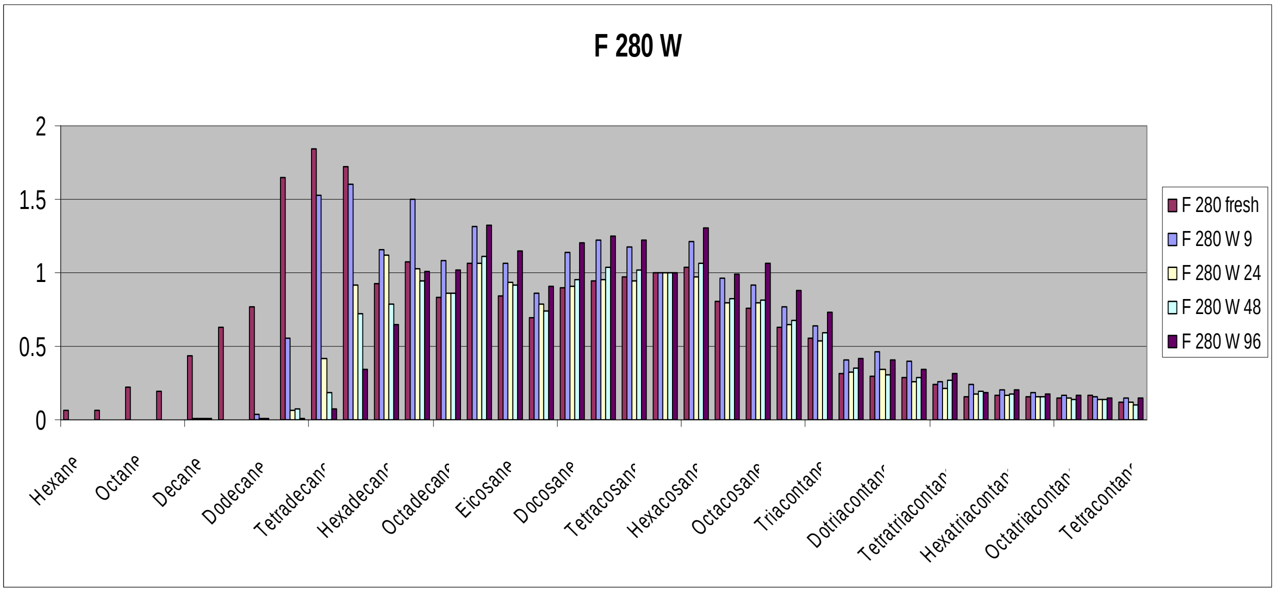


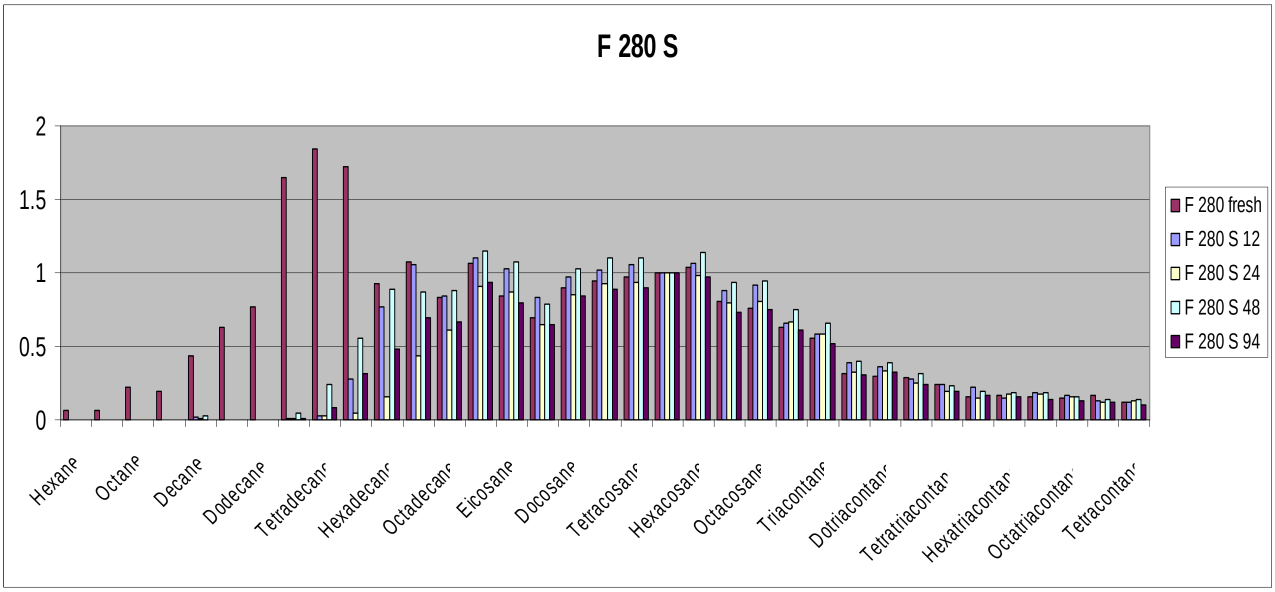
LEEDER
CONSULTING

Report No: M240943R1

ALKANE PROFILES

Bunker Fuel Oil 280cSt



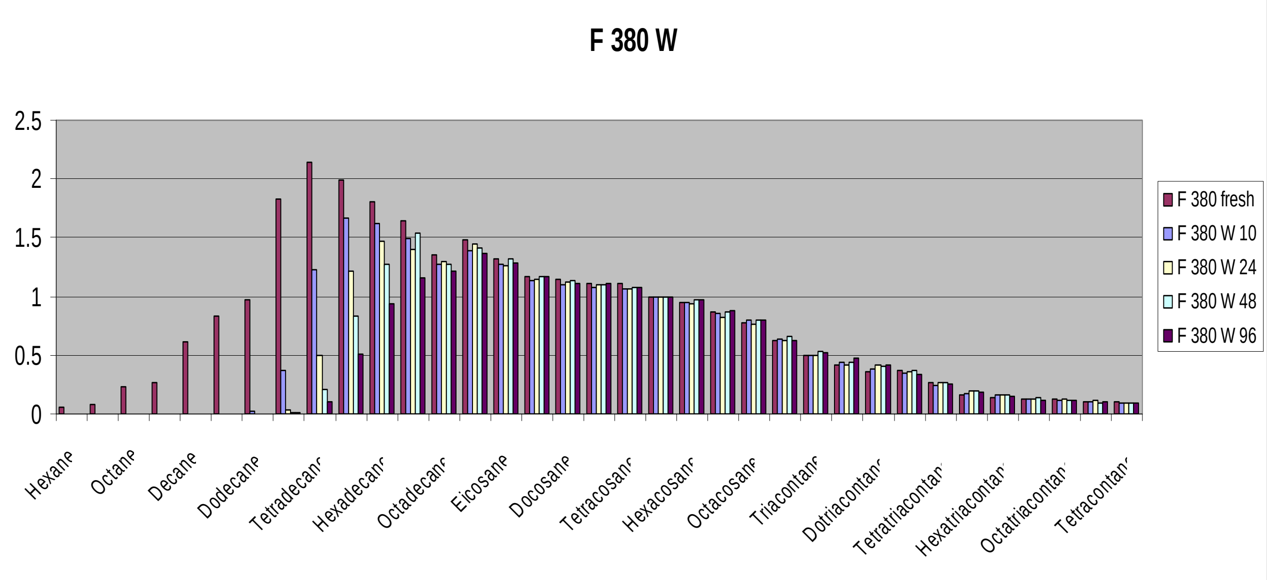


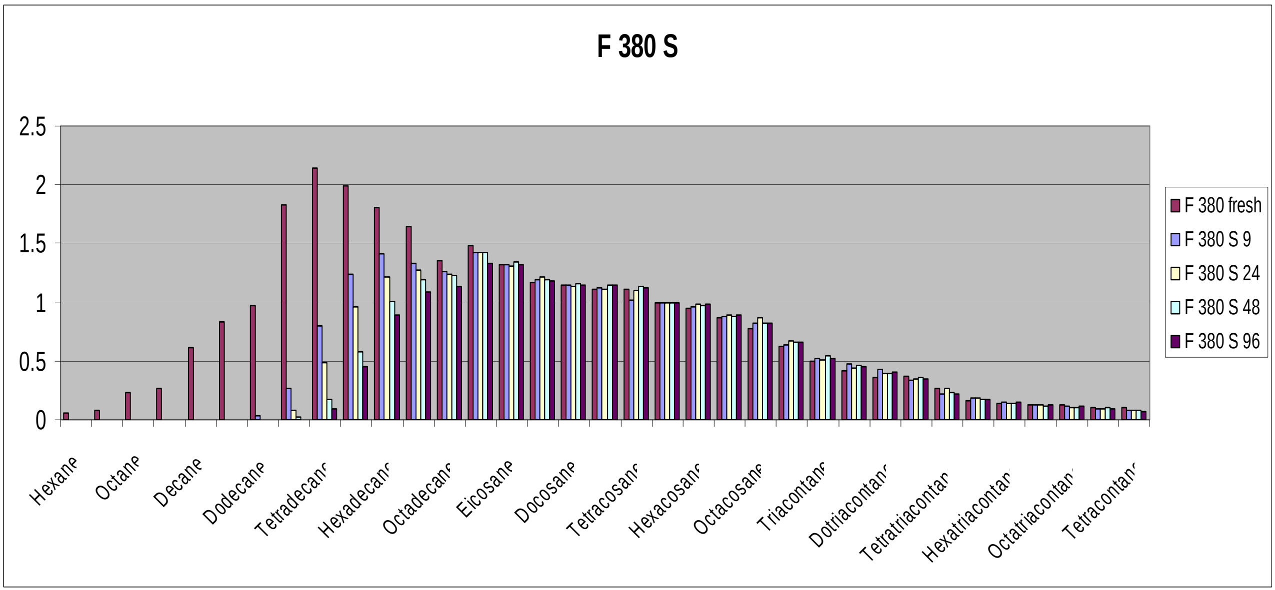
LEEDER
CONSULTING

Report No: M240943R1

ALKANE PROFILES

Bunker Fuel Oil 380cSt



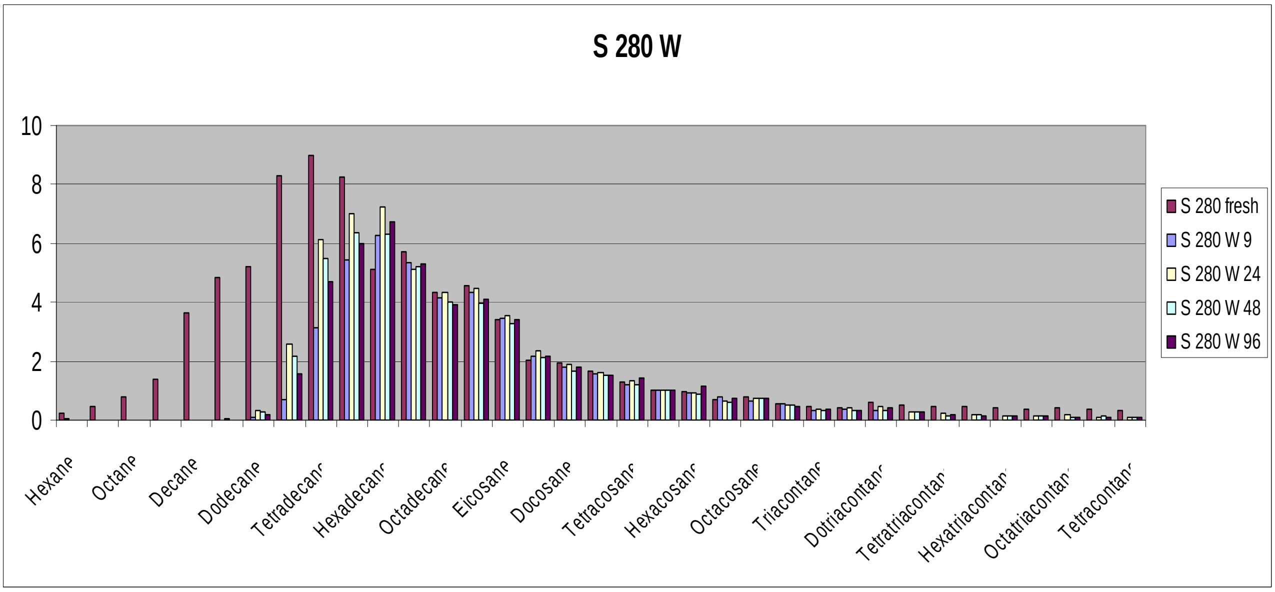


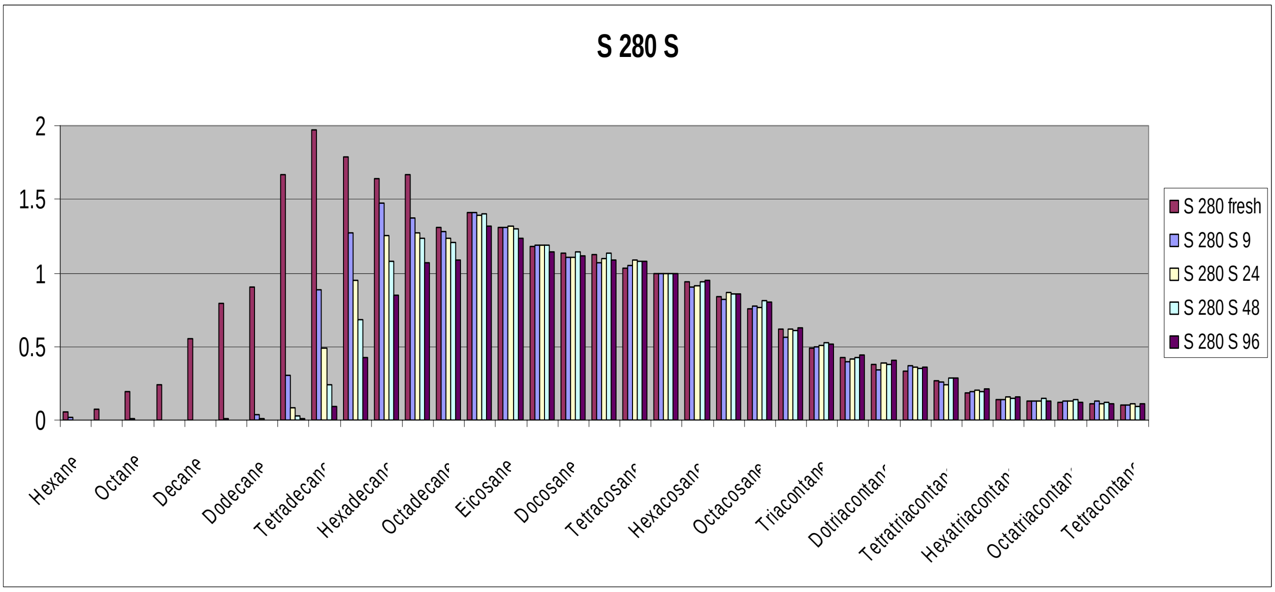
LEEDER
CONSULTING

Report No: M240943R1

ALKANE PROFILES

Bunker Fuel Oil Singapore 280cSt





APPENDIX FIVE

WHOLE OIL CHROMATOGRAMS

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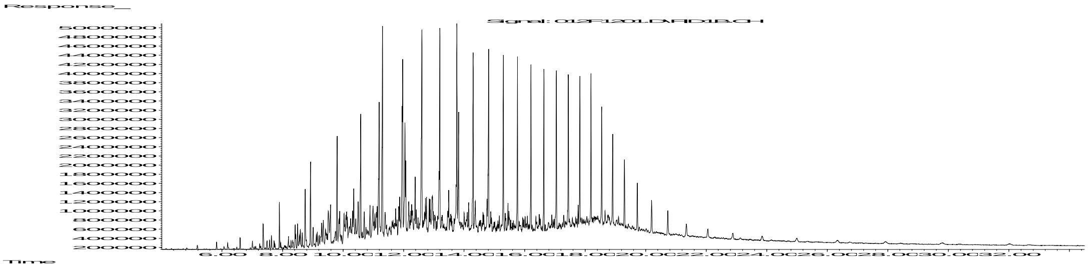
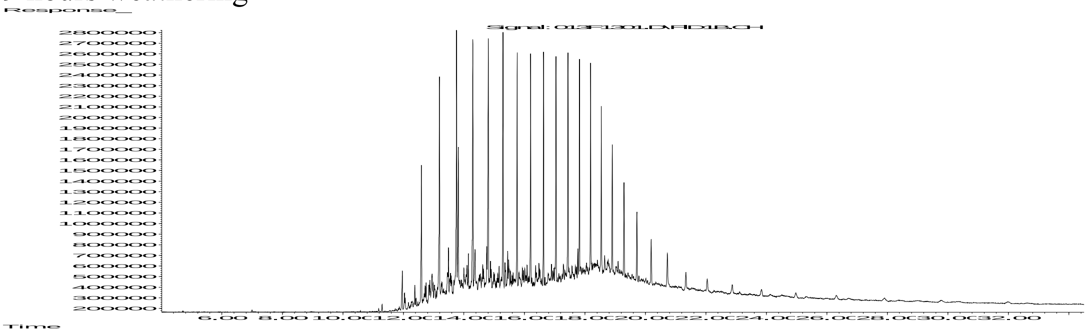
Fremantle 180cSt, winter

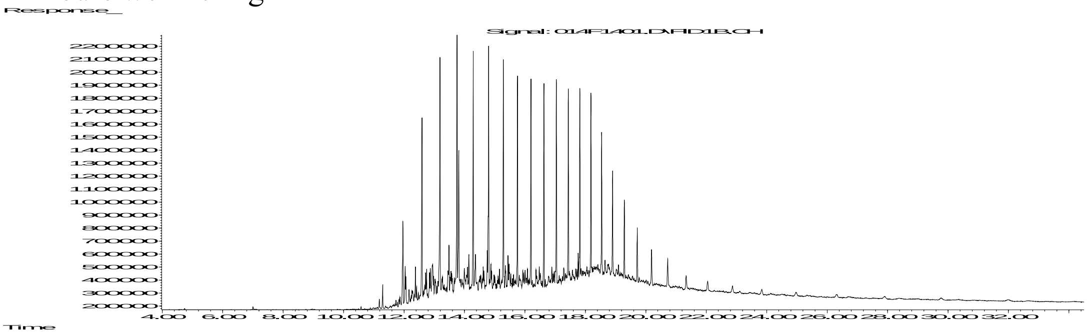
Fresh oil



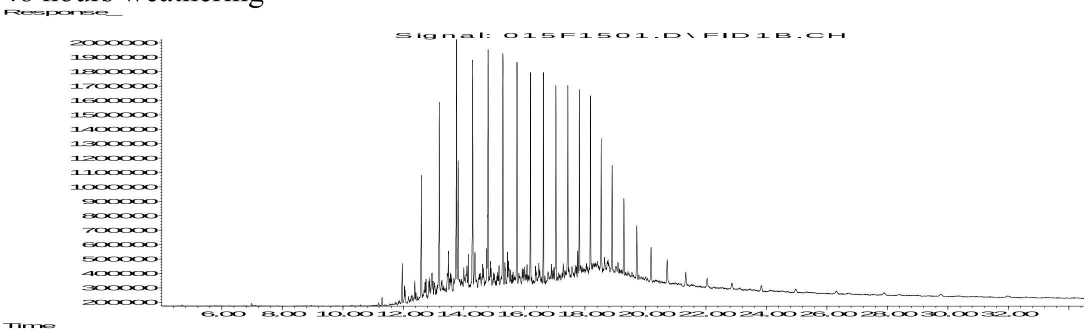
9 hours weathering



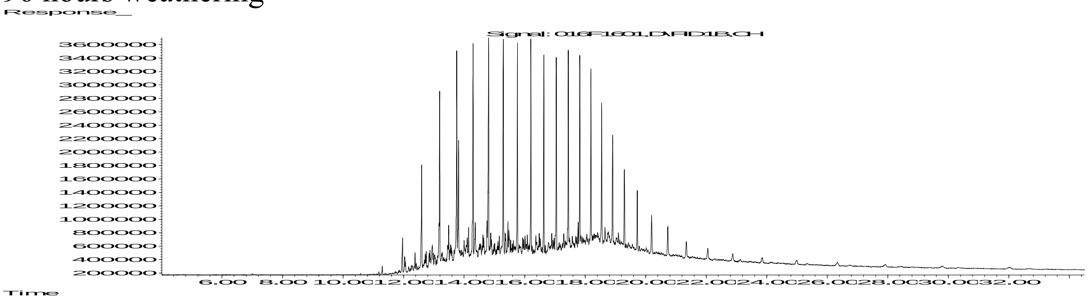
24 hours weathering



48 hours weathering



96 hours weathering

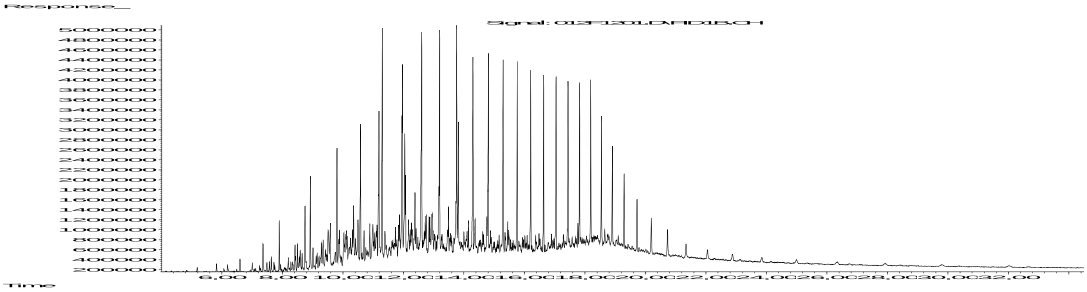


LEEDER CONSULTING

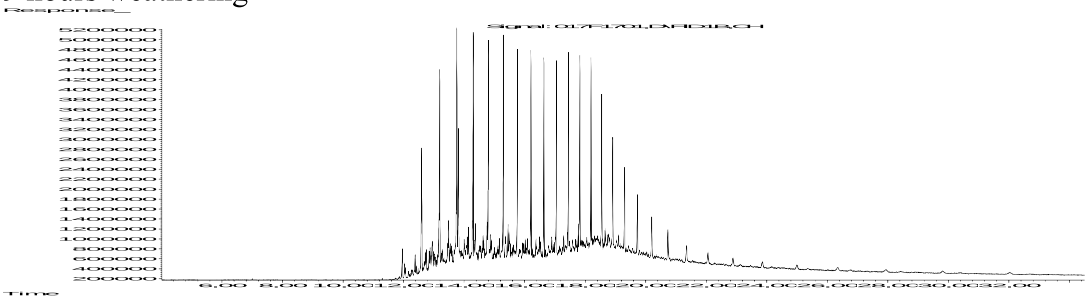
Report No: M240943R1

Fremantle 180cSt, summer

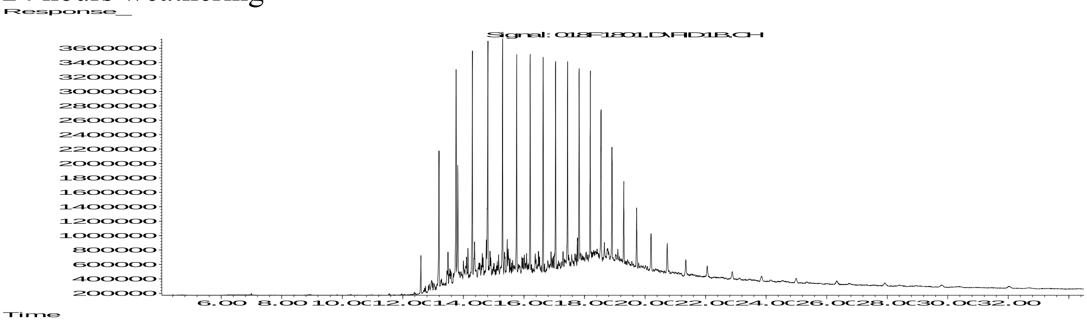
Fresh oil



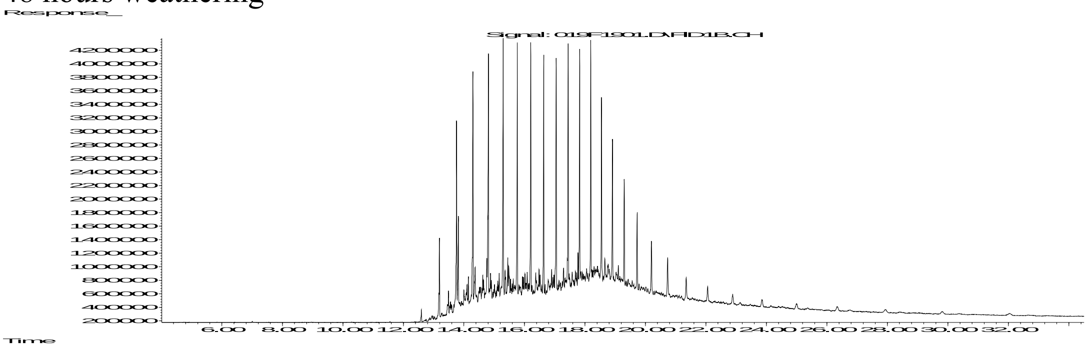
9 hours weathering



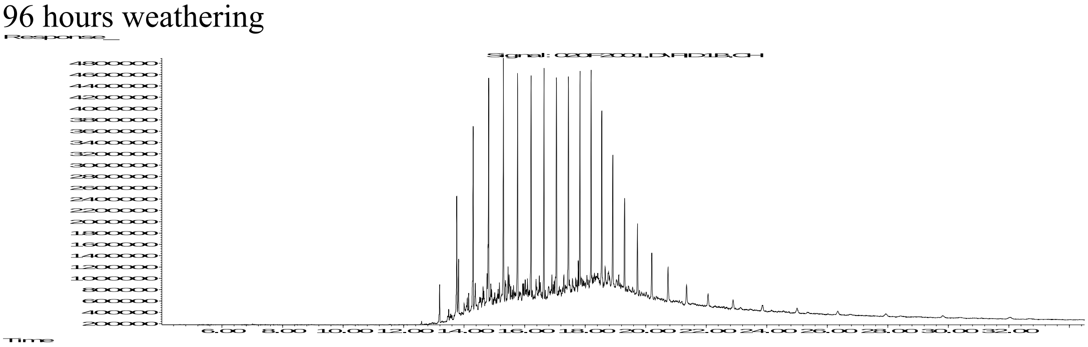
24 hours weathering



48 hours weathering



96 hours weathering

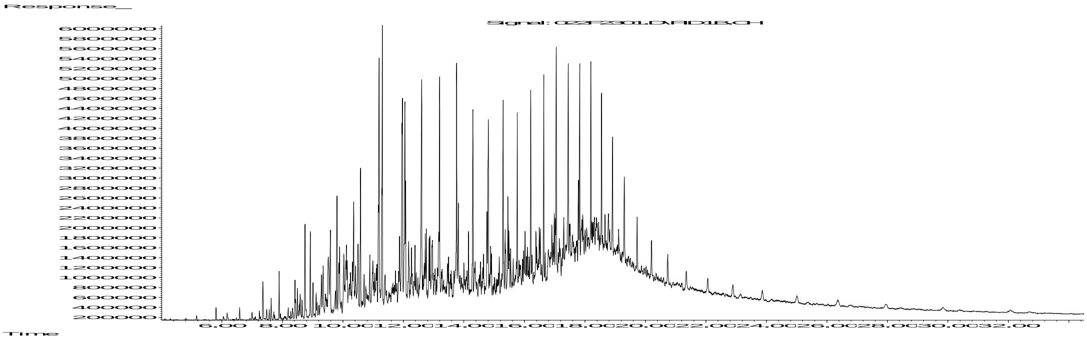


LEEDER CONSULTING

Report No: M240943R1

Fremantle 280cSt, winter

Fresh oil



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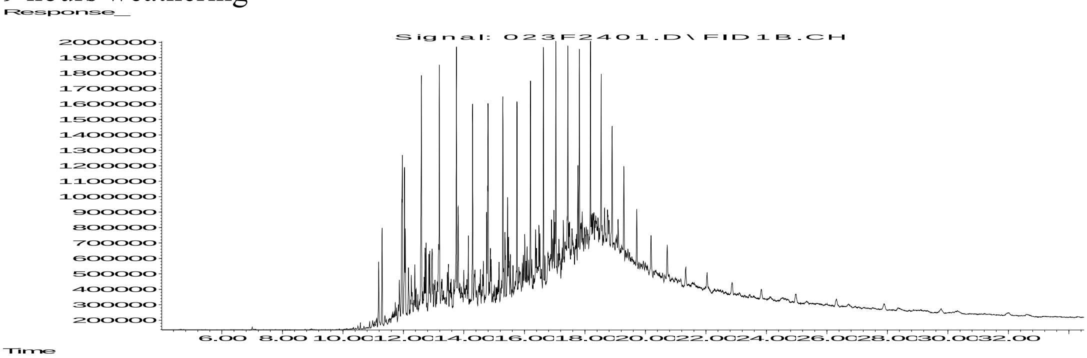

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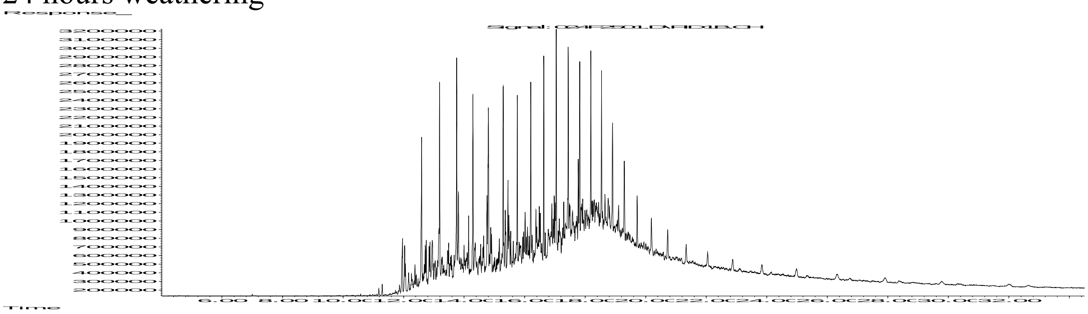

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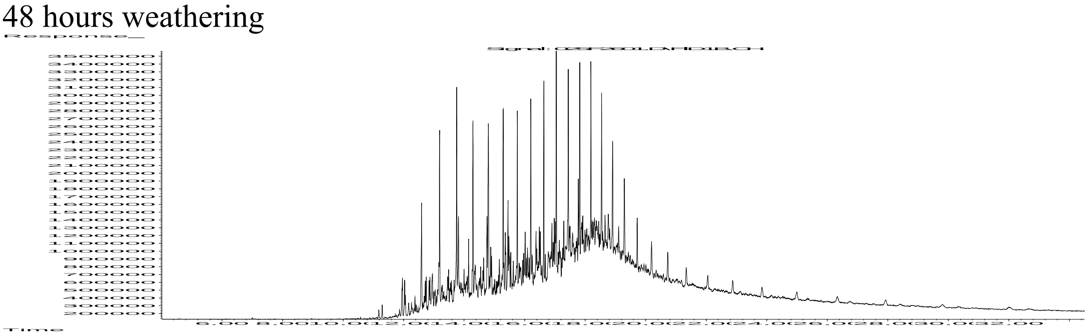

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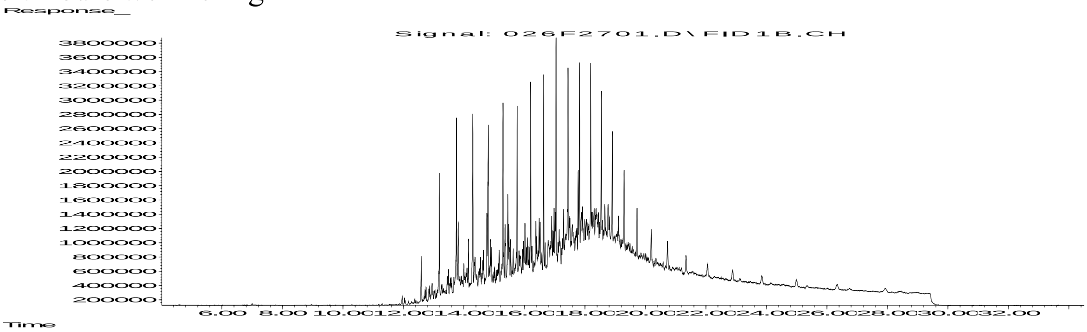
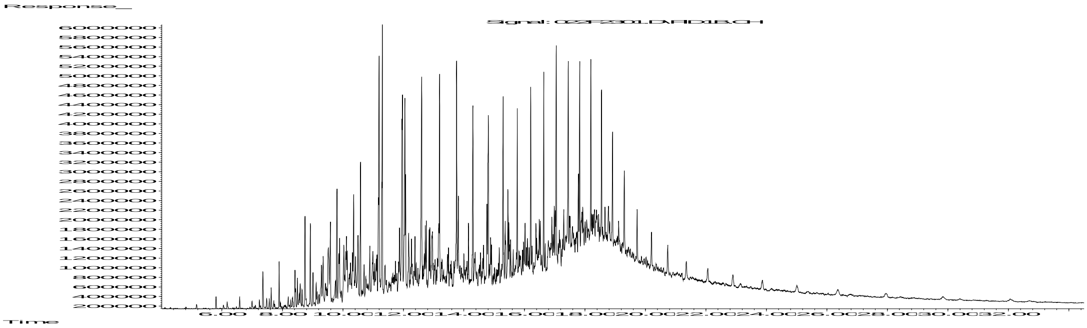


LEEDER CONSULTING

Report No: M240943R1

Fremantle 280cSt, summer

Fresh oil



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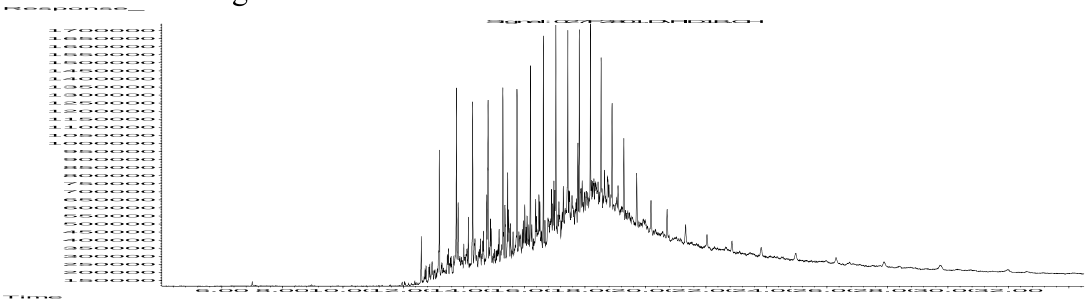

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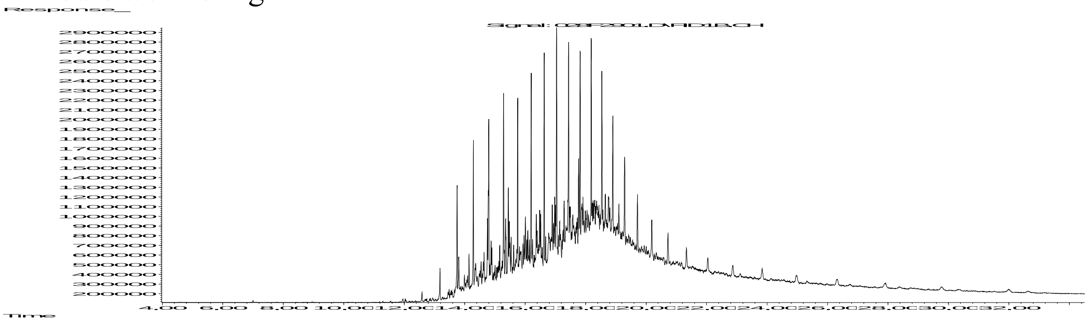

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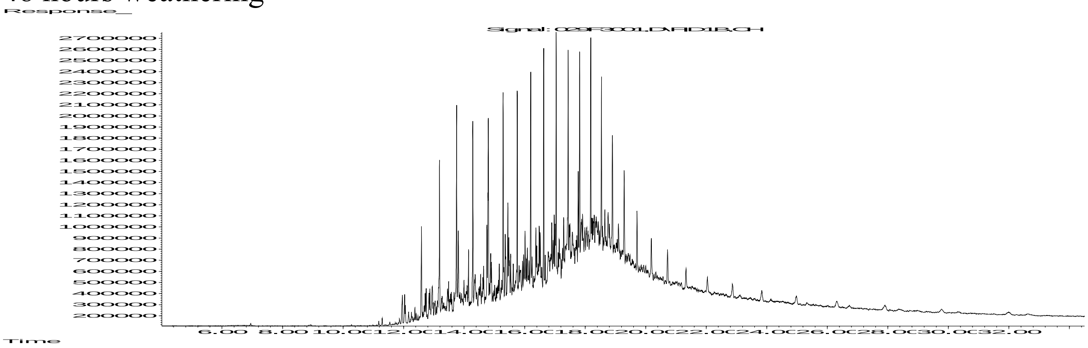
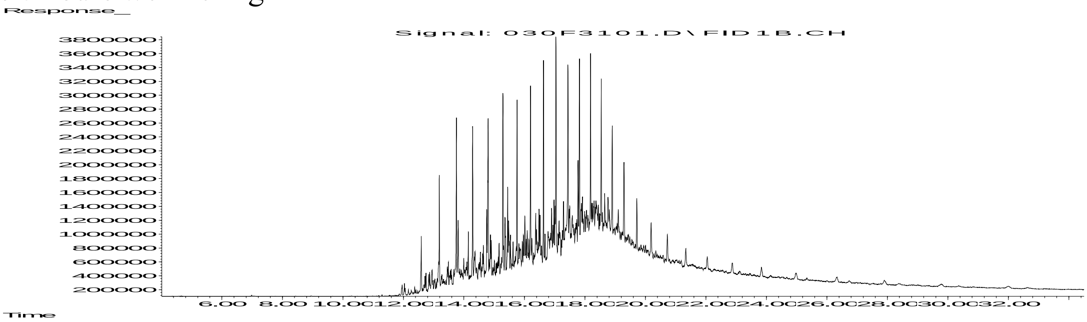


LEEDER CONSULTING

Report No: M240943R1

96 hours weathering

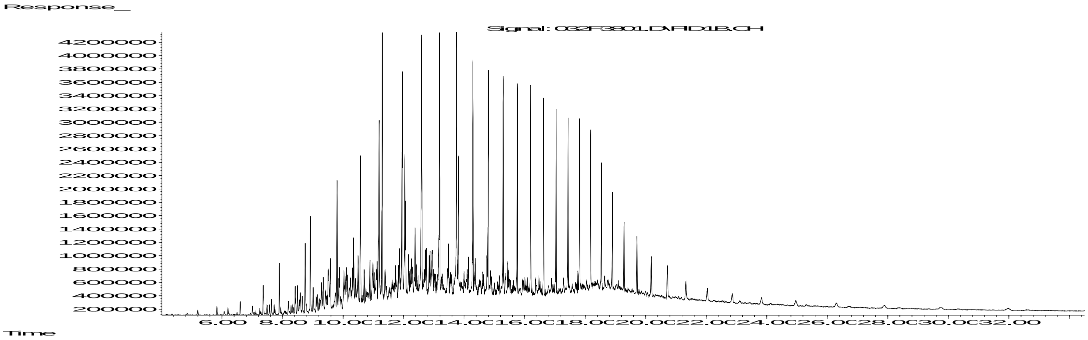


LEEDER CONSULTING

Report No: M240943R1

Fremantle 380cSt, winter

Fresh oil



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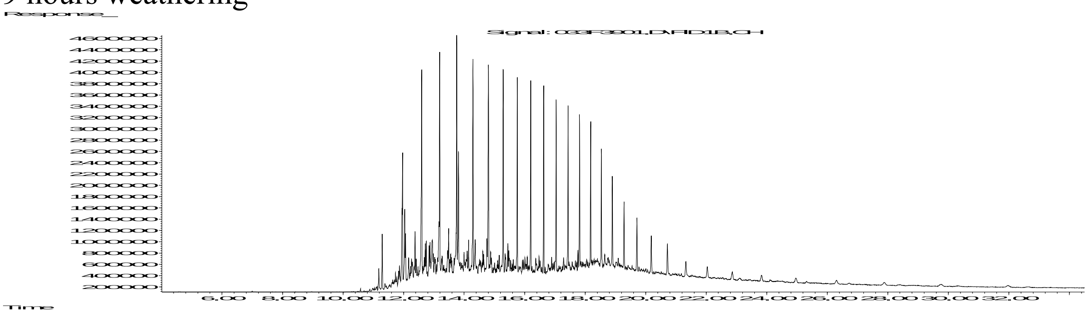

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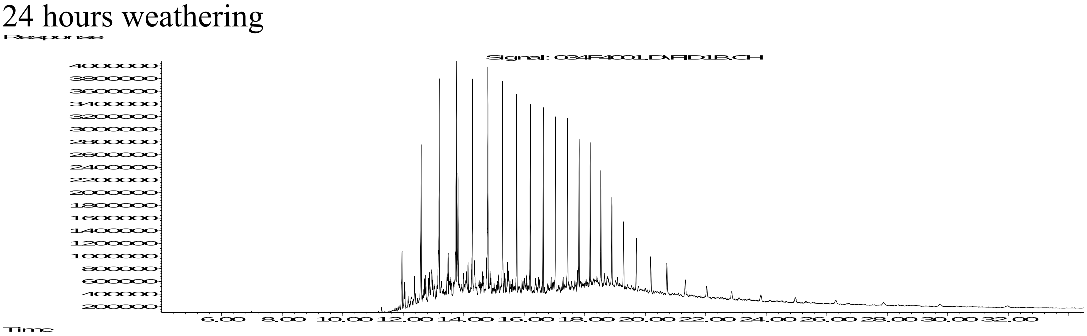

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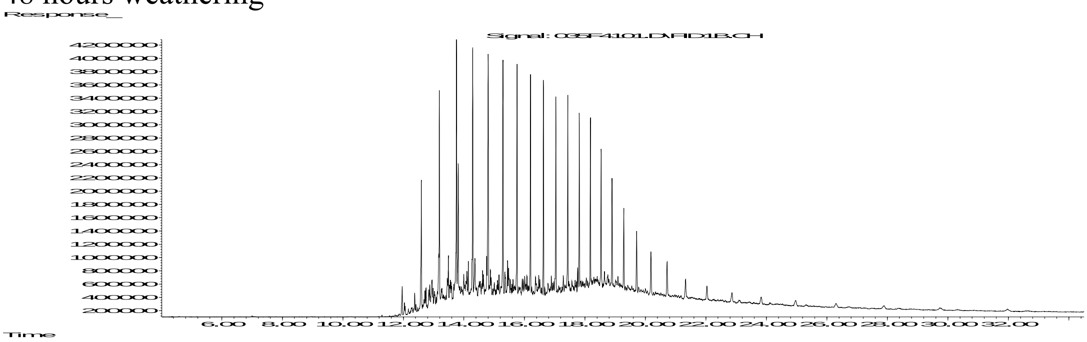
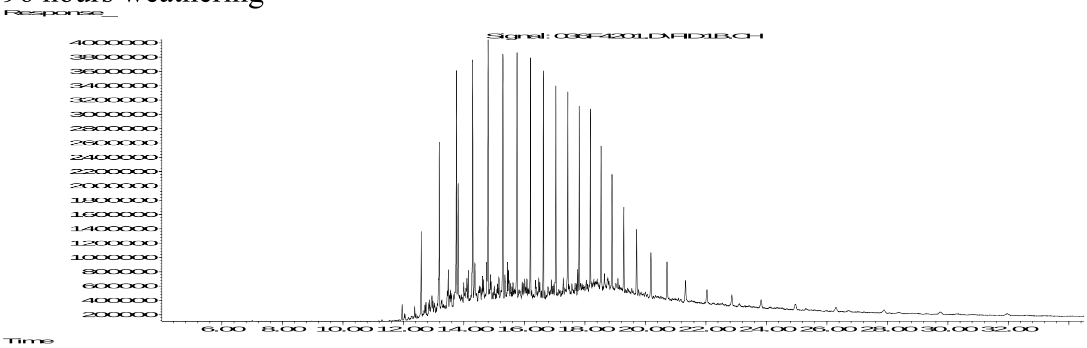


LEEDER CONSULTING

Report No: M240943R1

96 hours weathering

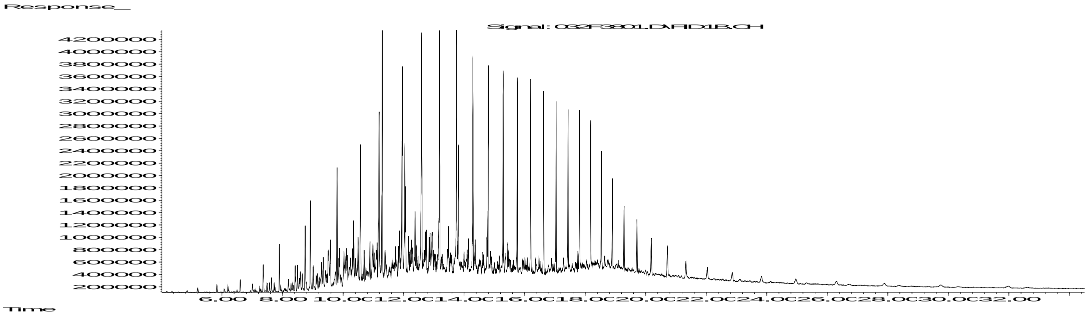


LEEDER CONSULTING

Report No: M240943R1

Fremantle 380cSt, summer

Fresh oil



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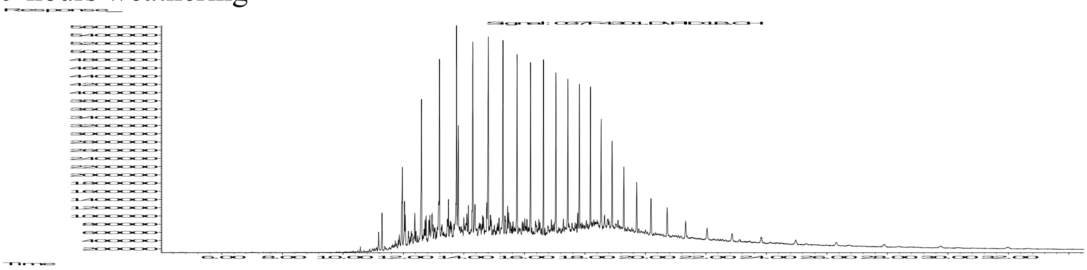

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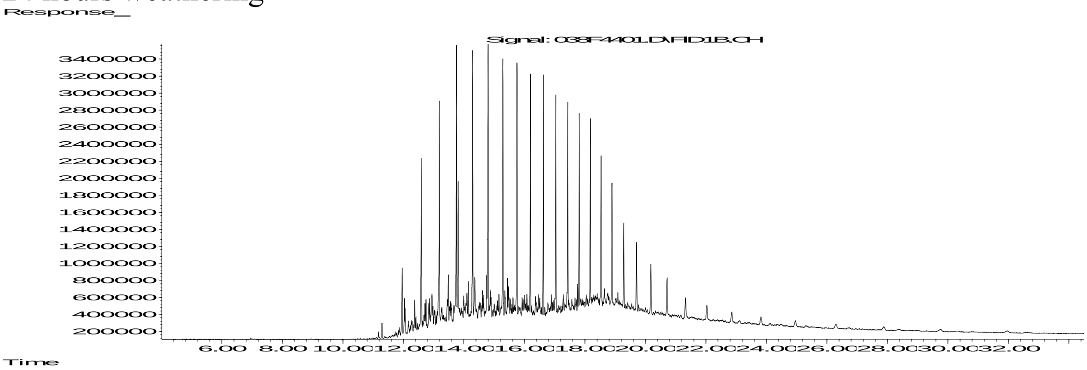

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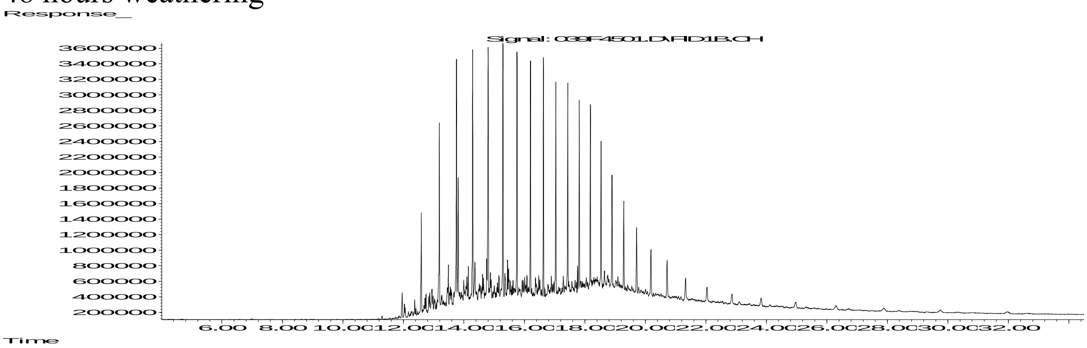
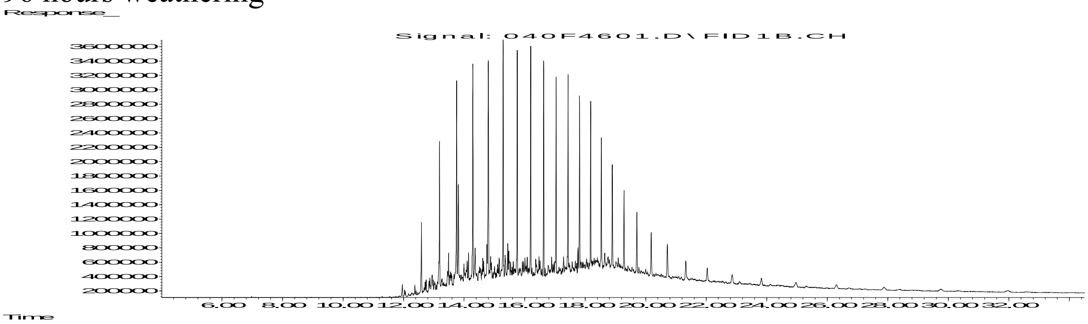


LEEDER CONSULTING

Report No: M240943R1

96 hours weathering

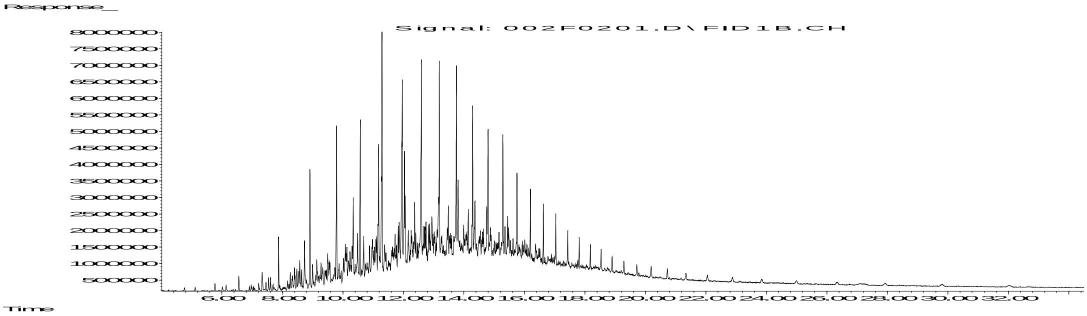


LEEDER CONSULTING

Report No: M240943R1

Singapore 280cSt, winter

Fresh oil



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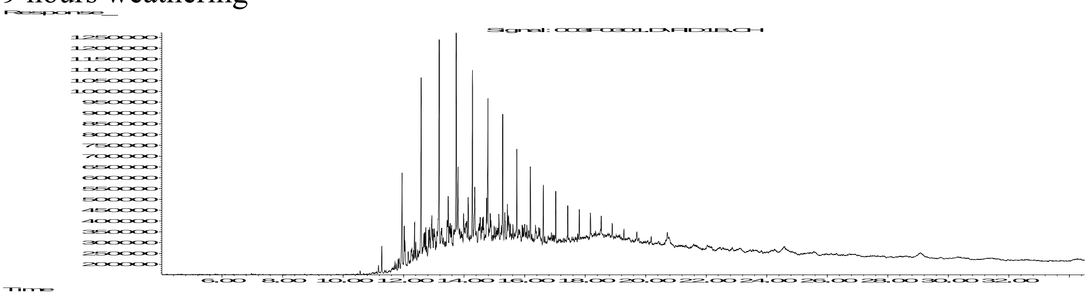

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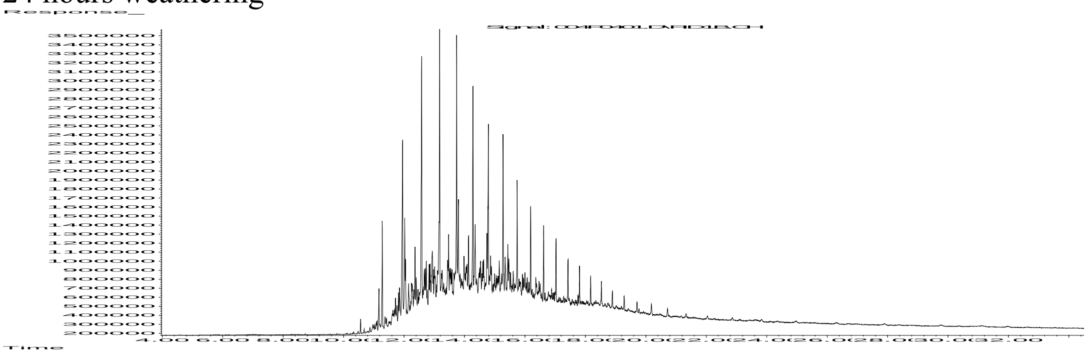

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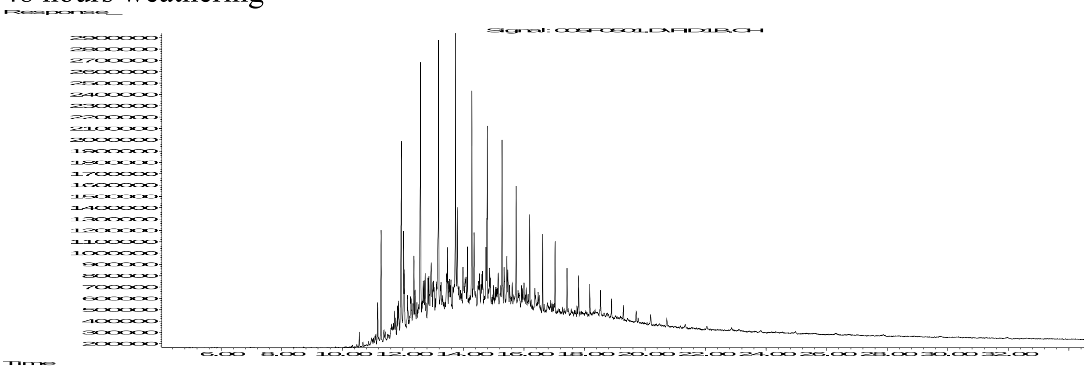
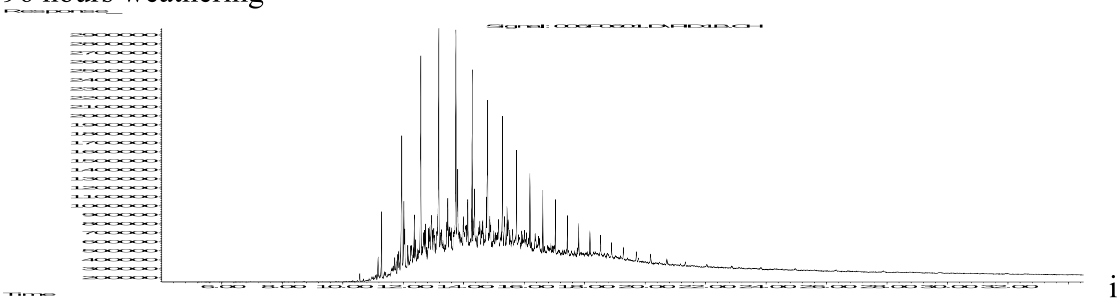


LEEDER CONSULTING

Report No: M240943R1

96 hours weathering

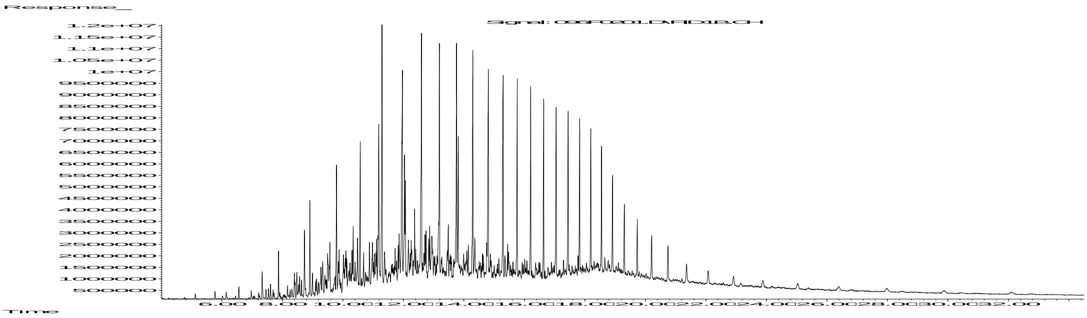


LEEDER CONSULTING

Report No: M240943R1

Singapore 280cSt, summer

Fresh oil



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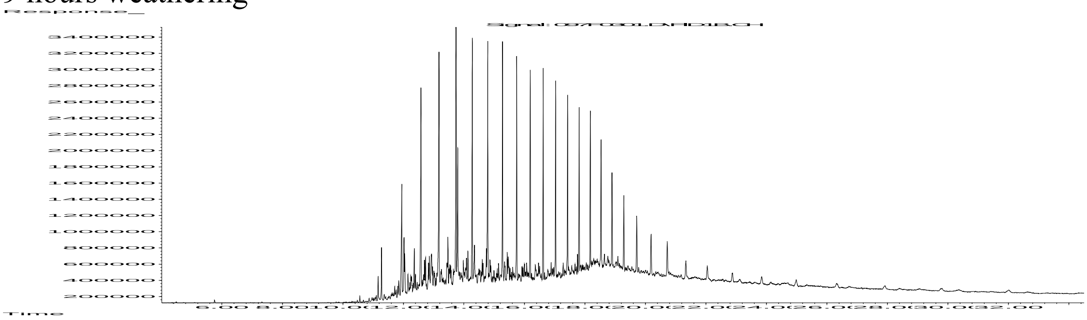

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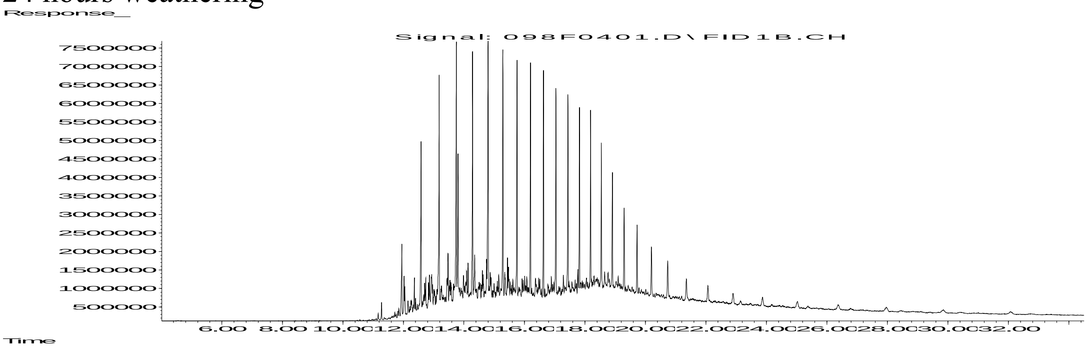

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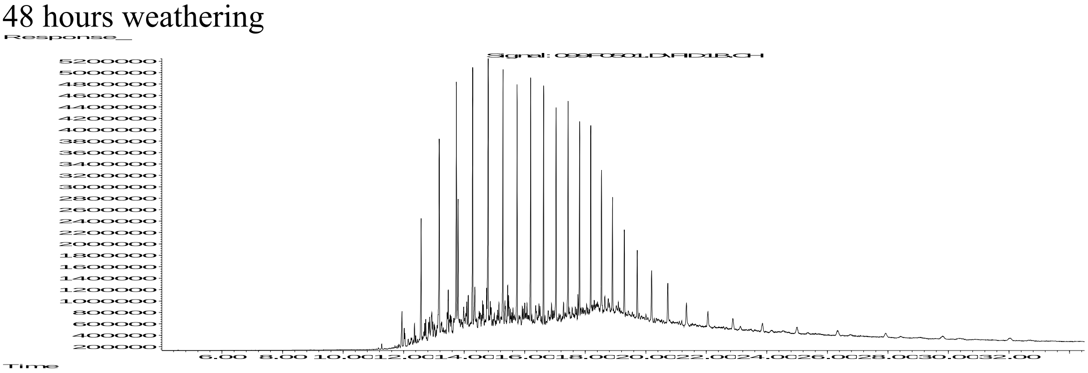

96 hours weathering