Using bio-diesel onboard vessels

An overview of fuel handling and emission management considerations

Mærsk Mc-Kinney Møller Center
for Zero Carbon Shipping

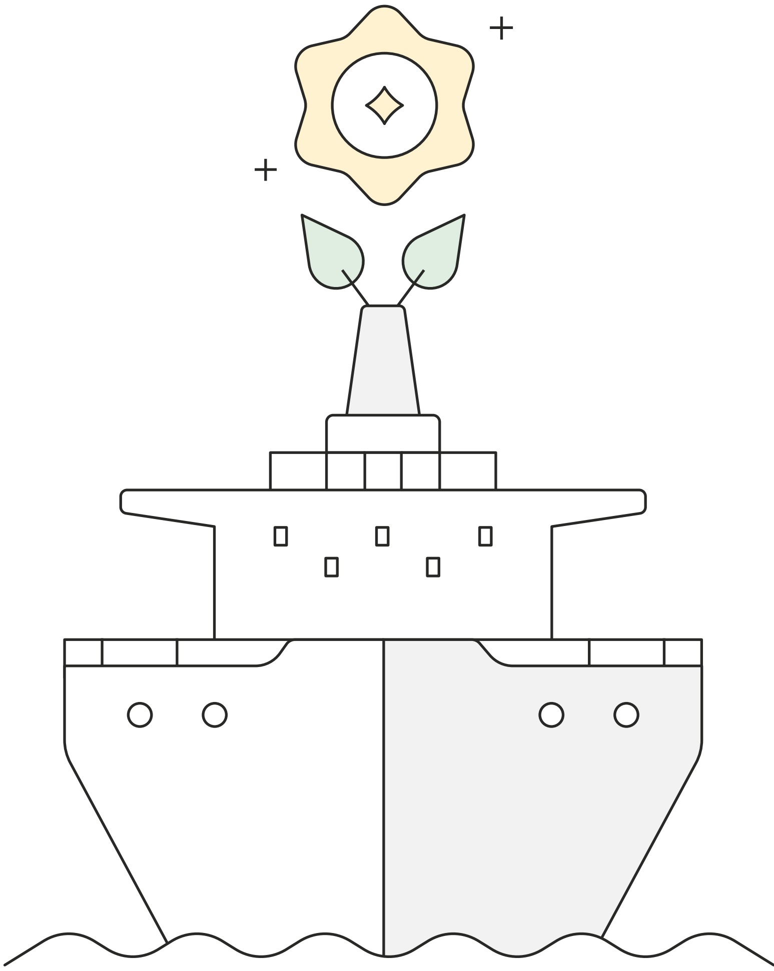
This paper is the fourth in the Onboard Vessel Solutions series:

Vessel Emission Reduction Technologies & Solutions

The paper series covers the impact and role of vessel greenhouse gas and air pollutant emission reduction in maturing alternative fuel pathways. Onboard impact is defined in terms of tank-to-wake global warming potential, with the role of onboard emission reduction either being for regulatory compliance or as an option to reduce emissions. Fuel pathway maturity is an assessment of solution readiness across the entire value chain.

Based on identified vessel emission risks, the paper series deep dives into specific emissions that need to be addressed to increase alternative fuel pathway maturity. The objective of these deep dives is to understand current or potential emission levels, set reduction targets, and identify and map applicable technologies and solutions. Emission reduction potential is then determined, and recommendations given to mature the selected fuel pathways.
Finally, areas or concepts for further research and development are identified, including recommended future project topics.

Papers are based on work completed as part of Center projects and working groups consisting of Center partners and external participants and contributors. Working groups provide a collaborative framework facilitated by the Center to jointly engage partners and external experts and companies on specific topics to deliver clear and impactful results.



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Abbreviations & Definitions

ASTM	ASTM International, a consensus-based standards setting organization
BOD	Bunkers on delivery
BOR	Bunkers on re-delivery
Bio-diesel	A mixture of Fatty Acid Methyl Esters (FAME). A fuel that can be produced from a wide range of vegetable oils or animal fats. May be used as a replacement or as a component of diesel fuel.
Bio-oils	Bio-oil is a category of biofuels that can be obtained from thermochemical conversion of biomass, via pyrolysis and hydrothermal liquefaction. For example, hydrothermal liquefaction crude.
Biofuels	Fuels produced from biomass, including bio-diesel and bio-oil.
C-H	Carbon-hydrogen
EJ	Exajoules
EN	European Standard
FOG	Fat, oil & grease
GHG	Greenhouse gas
HFO	Heavy fuel oil
HVO	Hydrotreated vegetable oil
HTL	Hydrothermal liquefaction
IACS	International Association of Classification Societies
ICE	Internal combustion engine
IMO	International Maritime Organization
ISCC	International Sustainability & Carbon Certification
ISO	International Organization for Standardization
MARPOL	International Convention for The Prevention of Pollution from Ships

MR	Medium range
MEPC	Marine Environment Protection Committee
MGO	Marine gas oil
MMMCZCS	Mærsk Mc-Kinney Møller Center for Zero Carbon Shipping
NO_x	Nitrogen oxides
NTC	NO_x Technical Code
SOLAS	International Convention for the Safety of Life as Sea
SNG	Synthetic natural gas
UI	Unified interpretation
VLSFO	Very low sulfur fuel oil
WAT	Wax appearance temperature
WDT	Wax disappearance temperature

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The bio-diesel handling and emissions working group was led by Sam Nivin (NORDEN). Special thanks to key contributors Georgios Plevrakis (American Bureau of Shipping), Bruno Griffaton (TotalEnergies), Giorgio Guadagna (Stolt Tankers), Kevin Lappage (bp), Dorte Kubel (MAN Energy Solutions), Dorthe Jacobsen (MAN Energy Solutions), Mirko Bugsch (MAN Energy Solutions), Robert McCormick (National Renewable Energy Laboratory), and Thomas McKenney (MMMCZCS). Claus Graugaard (MMMCZCS) was the project supervisor.

Executive Summary

Alternative marine fuels can be delivered from various alternative feedstocks and production processes. Bio-diesels and bio-oils are liquid biofuels made from sustainable biomass and biowaste with lower climate impacts than traditional fossil fuels. They may provide direct, low-emission replacements for conventional marine fuels or within blends. They are also potential pilot fuels for dual-fuel internal combustion engines (ICEs) using other alternative fuels like methane, methanol, and ammonia.

Bio-oils offer greater long-term viability and more potential impact on decarbonization than bio-diesels as they can utilize a larger variety of feedstocks, increasing their potential availability. As a result, the Mærsk Mc-Kinney Møller Center for Zero Carbon Shipping (MMMCZCS) only considers bio-oils as a scalable alternative fuel pathway. However, although bio-diesels are already available and in use in the shipping industry, bio-oils are not yet available in sufficient quantities for onboard use and testing.

While bio-diesels and bio-oils do not have the same chemical composition, performance, or qualities as each other, they present similar challenges for onboard use. As a result, we established a dedicated working group to study the potential challenges of using bio-diesel onboard vessels, which we expect to provide foundational knowledge of the challenges associated with the use of bio-oils onboard.

This paper presents the results from the working group, including an overview of regulatory drivers, onboard vessel bunkering, handling, and storage considerations. We also include experimental results from our investigations of fuel stability and NO_x emissions measurement tests. Furthermore, we provide our recommended step-by-step processes for bunkering and onboard handling.

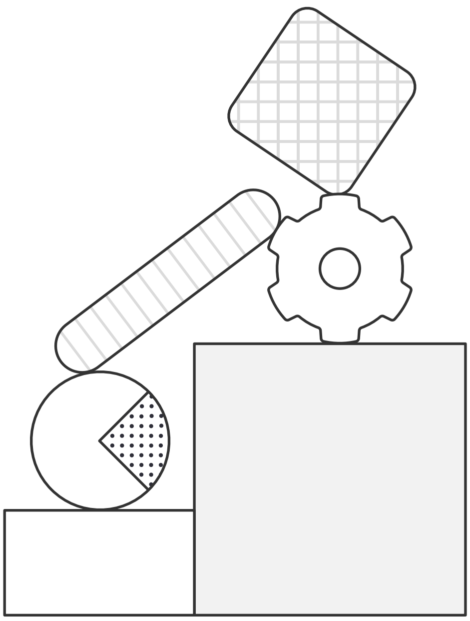
Based on our investigations, the working group made the following conclusions:

- Recent regulatory developments have lowered the barriers to using biofuels onboard vessels. However, work is still needed on fuel standards and sustainability life-cycle certification.
  - The Unified Interpretation (UI) approved at MEPC 78 in June 2022 allows for a more streamlined regulatory scenario for the use of biofuels onboard vessels, especially if flag states adopt the UI and classification societies and engine makers confirm no changes to the engine's NO_x critical components or settings/operating values.
  - With the lack of applicable fuel standards, it is presently up to the individual shipowner or operator to build knowledge and experience about proper fuel parameters and handling.
  - While some sustainability certification schemes exist, they must be standardized and aligned with the current and upcoming global and regional regulations.
- Due to the possibility of varying stability, acidity, and corrosion characteristics of bio-diesels, they must be handled and stored correctly onboard using operational measures with limited technical changes.
  - We recommend pre-bunkering steps including determining the blend composition, laboratory testing, and confirming compliance with International Maritime Organization (IMO) safety regulations and machinery.
  - Onboard handling requires bunker storage tank cleaning (subject to the sludge and sediment content in the bunker tanks) and adjustment of storage and transfer temperatures.
  - Fuel sample analyses can be used to indicate acceptable oxidation stability levels for typical fuel use periods. If required, readditization of antioxidants can prevent fuel oxidation, as seen from studies done in the automotive industry. Such trials are yet to be conducted in the maritime industry onboard vessels.

- Results from three emissions measurement tests showed that NO_x emission levels of bio-diesel and bio-diesel blends combusted in two-stroke slow speed marine engines are comparable with conventional fossil fuels, including heavy fuel oil (HFO), very low sulfur fuel oil (VLSFO), and marine gas oil (MGO).
  - These results also indicate that there is no need for special emission reduction technologies or solutions to reduce NO_x emissions further when using bio-diesels. However, if NO_x emission reduction is necessary, commercially available technologies and solutions exist.

The conclusions presented in this paper are based solely on tests of fatty acid methyl esters (FAME)-based bio-diesel fuels. The NO_x emission levels presented here form a benchmark for comparison with fast pyrolysis and hydrothermal liquefaction bio-oils when their technology matures, and they are available in larger quantities.

To increase the viability of the liquid biofuel pathways, we encourage flag states, classification societies, and engine makers to jointly leverage the approved UI to remove the regulatory barriers for the use of bio-diesels and bio-oils onboard vessels and support the development of fuel standards for blends with higher percentages of bio-diesel and bio-oil.



01 Introduction

Biofuels are low-carbon fuels that could be key in decarbonizing the shipping industry. Our analyses suggest that switching from very low sulfur fuel oil (VLSFO) to biofuels could reduce well-to-wake (WTW) emissions by 90-100%,[1] making them attractive options for decarbonization.

Biofuels are fuels with a biogenic origin. However, to be considered sustainable alternative fuels, they must be produced from sustainable biomass or biowaste. Biofuels include a range of fuels whose chemical and physical properties depend on their feedstock type, conversion process, and upgrading. Table 1 provides a high-level mapping of the biofuels under consideration for the maritime industry and their current technology readiness.

The maritime industry is currently considering three biofuels: bio-methanol, bio-methane (also known as synthetic natural gas), and bio-oils. Liquid biofuels are particularly interesting for the maritime industry as they can be used onboard existing vessels running on HFO, VLSFO, or MGO without major modifications. As a result, they can be used as direct replacements for fuel oils (i.e., they are drop-in fuels). Furthermore, they can be used in blends with conventional fuels or as low-emission pilot fuels in dual-fuel ICEs using other alternative fuels like methane, methanol, and ammonia.

Table 1: Biofuel mapping (Source: MMMCZCS).

<table>
<tr><th rowspan="2">Fossil Fuel Replaced</th><th rowspan="2">Type of Biofuel</th><th colspan="4">Process Pathway and Technology Readiness Level (TRL)</th><th rowspan="2">Feedstock</th></tr>
<tr><th>Process Step 1</th><th>TRL</th><th>Process Step 2</th><th>TRL</th></tr>
<tr><td rowspan="2">Liquified natural gas (LNG)</td><td>Bio-methane</td><td>Anaerobic digestion</td><td>9</td><td>Upgrade</td><td rowspan="2">9</td><td>Agricultural residue, sewage sludge, food waste</td></tr>
<tr><td>Synthetic natural gas (SNG)</td><td>Anaerobic digestion</td><td>9</td><td>Methane synthesis from carbon dioxide (CO_2)</td><td>Agricultural residue, sewage sludge, food waste</td></tr>
<tr><td rowspan="2">Fossil-based methanol</td><td rowspan="2">Bio-methanol</td><td>Anaerobic digestion to methane</td><td>9</td><td rowspan="2">Synthesis</td><td rowspan="2">9</td><td>Agricultural residue, sewage sludge, food waste</td></tr>
<tr><td>Gasification of biomass</td><td>7</td><td>Lignocellulosic biomass</td></tr>
<tr><td rowspan="2">Residuals and distillate (e.g., HFO, VLSFO, MGO)</td><td>Fatty acid methyl esters (FAME) bio-diesel</td><td>Transesterification</td><td>9</td><td>-</td><td>-</td><td rowspan="2">Waste fats, oils, greases (FOG), vegetable oils (palm, soy)</td></tr>
<tr><td>Hydrotreated vegetable oils (HVO) bio-diesel</td><td>Hydroprocessing</td><td>9</td><td>-</td><td>-</td></tr>
<tr><td rowspan="2">Residuals (e.g., HFO, VLSFO)</td><td>Fast pyrolysis (FP) bio-oil</td><td>Pyrolysis</td><td>8-9</td><td>Upgrade</td><td rowspan="2">6</td><td>Lignocellulosic biomass, forestry/agricultural residue</td></tr>
<tr><td>Hydrothermal liquefaction (HTL) bio-oil</td><td>Hydrothermal liquefaction</td><td>6</td><td>Upgrade</td><td>Lignocellulosic biomass, forestry/agricultural residue, wet waste</td></tr>
</table>

1 Maritime Decarbonization Strategy 2022: A decade of change, MMMCZCS, 2022

Liquid biofuels include bio-diesels and bio-oils. Bio-diesel is currently being used in shipping, with FAME bio-diesels being the most common.
To be considered sustainable alternative fuels, FAME must be produced from waste oils and animal fats as viable sustainable alternative fuels that do not lead to competition between fuels and food crops. However, limited supplies of sustainable biomass feedstocks mean bio-diesels are not widely available. As a result, in 2022, the global second-generation FAME production was only around 0.3 EJ of fuel for all sectors.[2] Accounting for the competition from other industries, we estimate only 0.04 EJ of FAME bio-diesel is available for shipping, corresponding to 0.3% of the sector's energy demand.[2] Still, despite its availability challenges, bio-diesel is one of the most relevant and available alternative fuel options for shipping today.

Although sustainable biomass[3] availability and cross-sector competition are also expected to limit bio-oil supply, they can utilize a larger variety of feedstocks than bio-diesel, giving them greater long-term potential as an alternative fuel in the shipping industry. However, bio-oils are not yet commercially available due to low production technology readiness levels. Their scale-up and future commercial availability will depend on hydrothermal liquefaction and fast pyrolysis commercialization.

An MMMCZCS assessment of fuel pathway maturities[4] found that using bio-oils onboard will also present challenges related to onboard storage, fuel conversion, and vessel emissions (Figure 1). The assessment stated that combusting bio-oils in existing engines appears feasible. Still, the impact of varying fuel properties relative to conventional fossil fuels requires attention, including a better understanding of onboard handling and storage. The properties of bio-oils, including their stability, acidity, and corrosion characteristics, vary depending on the fuel's feedstock and production processes. As a result, measures must be taken during bunkering to confirm the fuel's composition, compatibility with machinery, and onboard handling procedures such as tank cleaning, temperature control, and storing to ensure long-term stability.
Nitrogen oxides (NO_X) emissions from ICEs using bio-

Figure 1: Fuel Pathway Maturity Map (Source: MMMCZCS).

	Feedstock availability	Fuel production	Fuel storage, logistics & bunkering	Onboard energy storage & fuel conversion	Onboard safety & fuel management	Vessel emissions	Regulation & certification
e-ammonia	Mature	Solutions identified	Major challenges	Major challenges	Major challenges	Major challenges	Major challenges
Blue ammonia	Solutions identified	Solutions identified	Major challenges	Major challenges	Major challenges	Major challenges	Major challenges
e-methanol	Solutions identified	Solutions identified	Solutions identified	Mature	Mature	Mature	Solutions identified
Bio-methanol	Solutions identified	Solutions identified	Solutions identified	Mature	Mature	Mature	Solutions identified
e-methane	Solutions identified	Solutions identified	Mature	Mature	Mature	Solutions identified	Solutions identified
Bio-methane	Solutions identified	Solutions identified	Mature	Mature	Mature	Solutions identified	Solutions identified
Bio-oils	Solutions identified	Major challenges	Solutions identified	Solutions identified	Mature	Solutions identified	Solutions identified

Mature
Solutions are available, none or marginal barriers identified

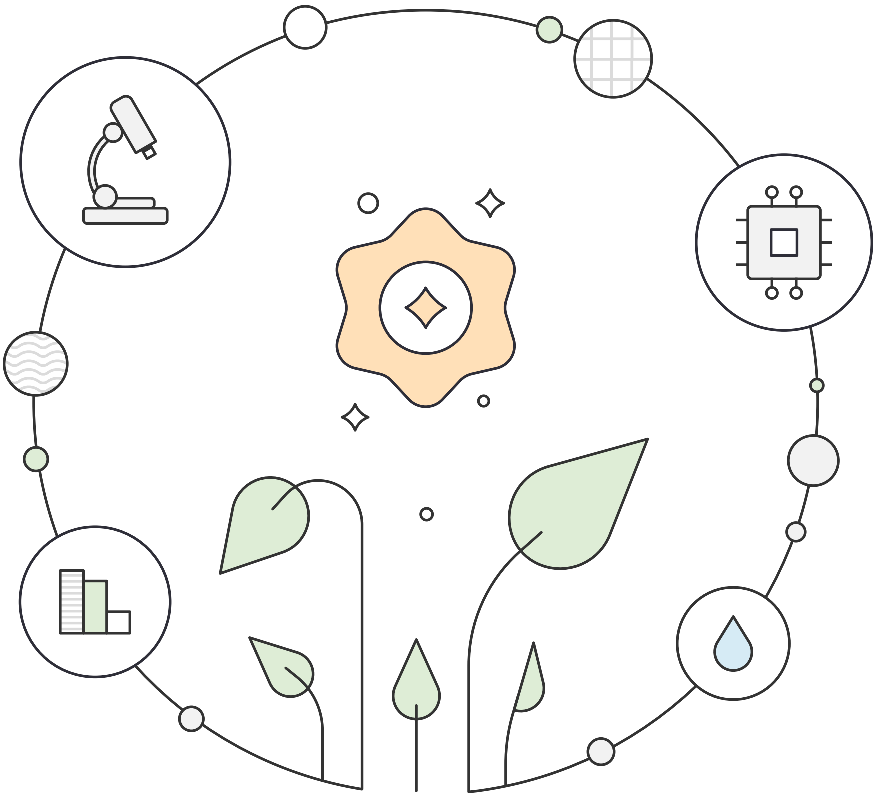
Solutions identified
Solutions exist, but some challenges on e.g., maturity and availability

Major challenges
Solutions are not developed or lack specification

2 Bio-oils as marine fuel, prospects for the shipping industry, documentation of assumptions for NavigaTE 1.0, MMMCZCS, 2021.
3 Defined as biomass that has been cultivated and/or sourced from a system of agricultural practices aimed at fulfilling the relevant ecological, economic, and social functions of the land used to cultivate the biomass.
4 Detailed in the first paper in the Vessel Emission Reduction Technologies & Solutions paper series entitled 'Determining the impact and role of onboard vessel emission reduction'.

oils could also present a regulatory compliance risk for shipowners and operators wishing to use this type of marine fuel. While knowledge of emissions from next-generation bio-oils is limited, we expect that bio-oils from different feedstocks and with varying quality levels may lead to different emission profiles. Compared with fossil-based fuels, we expect bio-oil combustion to result in reduced local air pollutants, including sulfur oxides (SO_x) and particulate matter (PM), due to the fuel's low sulfur content and high oxygenation.

However, NO_x emissions may be higher as they increase approximately linearly with the fuel's oxygen content in some cases, and bio-oils contain more oxygen than fossil-based fuels. Solutions to manage vessel emissions from bio-oils exist, and these solutions can be implemented if needed when there is more knowledge on the emissions levels of these fuels. While bio-diesels and bio-oils do not have the same chemical composition, performance, or qualities, they present similar challenges for onboard use. To support the short-term usage of bio-diesels and build transferable knowledge for introducing bio-oils, we established a dedicated working group to perform a deep dive into the onboard handling and storage of bio-diesel and the emission risks from its combustion. This paper presents the results from the working group, including an overview of regulatory drivers, onboard vessel bunkering, handling, storage considerations, and results from NO_x emission measurements. As bio-oil products become more readily available, onboard handling, storage, and combustion testing will determine their vessel compatibility and similarities to bio-diesels.



02 Regulatory Considerations

There are two main regulatory considerations related to using bio-diesels and bio-oils: 1) emission regulations, and 2) fuel standards and certification. The central emission regulation for bio-diesels and bio-oils is the NO_x emission limits set within Regulation 13 of MARPOL Annex VI (limits for NO_x emissions from diesel engines). Fuel standards and certification are also important regulatory considerations for ensuring that a fuel is truly sustainable and that its properties, including how it should be managed and used onboard the vessel, are understood. This section provides more details on each regulatory consideration.

2.1 NO_x emission regulations

Bio-diesels tend to have higher oxygen content in the fuel when compared to fossil-based marine fuels. Therefore, their combustion can lead to higher NO_x. NO_x formation in diesel engines is dominated by thermal nitric oxide (NO) formation. Combustion in diesel engines happens at locally stoichiometric fuel-air ratio conditions, which result in high combustion temperatures. Thus, due to the high temperature (above 1300°C) during combustion in the engine's cylinders, oxidation of some of the nitrogen in the air to NO_x gases occurs, leading to NO_x emissions[5]. The potential increase in NO_x emissions is related to the higher oxygen content, which presents a risk in complying with Regulation 13 of MARPOL Annex VI.

Before June 2022, shipowners or operators who wished to test bio-diesel onboard vessels required an exemption from their flag state. This was because the Regulation 18.3 of MARPOL Annex VI requires that bio-diesels shall not cause the engine to exceed the applicable NO_x emissions limits. Meeting this requirement was a challenge, because the NO_x Technical Files of the engines are certified using a distillate grade (DM grade) marine fuel in accordance with ISO 8217. To demonstrate the NO_x emissions levels or trial the bio-diesel onboard a vessel, it was required to apply for an exemption from the flag state. The exemption from a flag state to use bio-diesel onboard was applied under Regulation 3: 'Trials for Ship Emission Reduction and Control Technology Research', which falls under MARPOL Annex VI.

When an exemption for a bio-diesel trial was granted, some flag states also required emissions measurements or detailed reporting on the issues faced during fuel usage as a part of the exemption. They required proper documentation of the fuel's compatibility with equipment onboard, and that appropriate fuel-handling steps are taken, including involvement of the relevant classification society and engine maker. Typical recommendations provided to flag states included the observation of the following factors during bio-diesel usage onboard the vessel:

- In the short term, the condition of various seals and fuel filters and the state of cylinder lubrication.
- In the long term, testing for fuel storage effects (e.g., sludge accumulation), fuel stability/durability, and the operational impacts on the vessel due to the new type of fuel being used.

In June 2022, MEPC 78 approved a UI regarding the exemption and testing procedures needed to use biofuels and blends onboard vessels[6]. This was done to establish that marine engines running on biofuels operating within the parameters dictated in their Technical File do not necessarily lead to excess NO_x emissions.

The UI was submitted to the IMO by the International Associations of Classification Societies (IACS)[7] to address the requirement of an exemption to use biofuel on ships. It is, however, important to note that the conditions stated by the UI are only applicable if a vessel's flag state adopts the UI. The UI states that, for biofuel blends up to 30%, there is no exemption required from the flag state to use these fuels in the vessel's engine. Thus, if a flag state has adopted the UI, the regulatory scenario is expected to be more relaxed, as the only requirement to use the biofuel blend (up

5 Monica Johansson, Junfeng Yang, Raúl Ochoterena, Savo Gjirja, Ingemar Denbratt, 'NOx and soot emissions trends for RME, SME and PME fuels using engine and spray experiments in combination with simulations', 2013, pp. 293-302.
6 Report of the Marine Environment Protection Committee of its 78th session, Maritime Environment Protection Committee, IMO, 24 June 2022.
7 MEPC.1/Circ.795/Rev.7 Annex – 'UNIFIED INTERPRETATIONS TO MARPOL ANNEX VI'.

to 30%) in the vessel's engine is providing a bunker delivery note (BDN) that explicitly states the type and volume of biofuel blended into the fuel.

For the use of bio-diesel blends of 30-100% (B30 to B100), the engine that is already certified according to Regulation 13 (NO_X Regulations) is permitted to use bio-diesel or a bio-diesel blend if there are no changes to its NO_X critical components or settings/operating values outside those as given by that engine's approved Technical File.

Figure 2: Types of "biofuels" covered under the UI on Regulation 18.3 MARPOL Annex (Source: IMO MEPC 78).[8]

"a fuel oil which is a blend of not more than [30%] by volume of biofuel should meet the requirements of regulation 18.3.1 of MARPOL Annex VI. A fuel oil which is a blend of more than [30%] by volume of biofuel should meet the requirements of regulation 18.3.2 of MARPOL Annex VI. For the purposes of this interpretation, a biofuel is a fuel oil which is derived from biomass and hence includes, but is not limited to, processed used cooking oils, fatty-acid methyl-esters (FAME) or fatty-acid-ethyl-esters (FAEE), straight vegetable oils (SVO), hydrotreated vegetable oils (HVO), glycerol or other biomass to liquid (BTL) type products. The Product Name, as entered onto the bunker delivery note, should be of sufficient detail to identify whether, and to what extent, a biofuel is blended into the product as supplied."

Under the approved UI, shipowners are expected not to undertake the NO_X emissions assessments required by Regulation 18.3.2.2 of MARPOL Annex VI. As a result, it is expected to be easier to comply with NO_X limit requirements when using bio-diesels. To prove to the flag state and classification society that no NO_X critical components have been modified, shipowners are expected to provide a supporting statement from the engine maker.

2.2 Fuel standards certification

One of the major challenges of using bio-diesels and bio-oils in the maritime industry is the lack of applicable fuel standards. This poses a challenge, as there is no standard reference to compare fuel properties to, thus creating uncertainty around the proper handling, usage, and safety of the fuel onboard a vessel. ISO 8217 only deals with marine fuels that are of fossil fuel origin with up to a maximum of 7% FAME content. Thus, using this fuel standard as the reference for bio-diesels and bio-oils is difficult. As no fuel standard is available for bio-diesels in a marine context, it is up to the individual shipowner or operator to build knowledge and experience on proper fuel parameters and handling. This also poses an obstacle to the quick uptake of bio-diesel in the maritime industry.

In addition to ensuring proper fuel parameters, shipowners and operators must ensure their biofuels are sustainable. Sustainability certification is an effective means to ensure that the fuel complies with sustainability criteria and guarantees that the environmental benefits of the fuel provided are valid. Certifications such as the International Sustainability & Carbon Certification (ISCC) focus on greenhouse gas (GHG) reductions throughout value chains, sustainable land use, protection of natural habitats, and social sustainability for feedstock production.

8 Reduction of GHG emissions from ships, Interpretation of regulation 18.3 of MARPOL Annex VI, related to biofuels, Submitted by IACS, Maritime Environment Protection Committee, IMO, 16 September 2021.

03 Onboard handling and storage

The properties of bio-diesels, including their stability, acidity, and corrosion characteristics, vary depending on the fuel's feedstock and production processes. As a result, how they are handled and stored onboard vessels must be carefully considered. This section provides our recommendations for properly preparing a vessel for bio-diesel bunkering, onboard handling after bunkering the fuel, and storage stability over time. It has been noted that if the FAME bio-diesel is delivered as according to EN 14214 or ASTM D6751, issues faced should be very limited. The following recommendations on handling and storage are specific to FAME-based bio-diesels.

3.1 Bunkering

Before considering how the bio-diesel should be handled and stored onboard, the fuel properties must be determined, tested, and confirmed to follow IMO safety regulations and be compatible with onboard machinery and systems. Below, we outline a step-by-step process that we recommend for determining the fuel properties.

Step 1: Determining the blend composition

Identify the blend percentage of the bio-diesel and the fossil fuel it is blended with. The most common blends are B20, B30, and B50. Based on the blend percentage, determine if the flag state needs to be involved in providing an exemption based on the UI. We recommend involving the relevant classification society and engine maker before using a new fuel type.

Step 2: Perform labolatory testing

Bio-diesel must be tested to determine best practices for onboard handling. The most common parameters that bio-diesel is tested for are those specified in ISO 8217. In addition to those parameters, additional tests are advisable, such as the wax appearance temperature (WAT) and wax disappearance temperature (WDT), fuel transfer temperatures, and fuel injection temperatures. Conducting a temperature-viscosity relationship analysis to determine the fuel injection temperature to achieve a required fuel viscosity is critical. Generally, we recommend storing bio-diesel above the WAT.

When possible, getting the fuel sample analysis before bunkering and using the bio-diesel or blend on the vessel is suggested. When performing back-to-back testing, we recommend testing the bio-diesel and the reference fossil fuels using the same parameters. This will aid understanding of the differences in their physical and chemical characteristics. Testing the fuels using the same parameters will also allow for back-to-back emissions measurements under the same operational conditions, enabling easy comparison. Table 2 provides a general indication of the common characteristics of bio-diesels relative to diesel.

Table 2: Properties of FAME and HVO (Source: ABS "Setting the Course to Low Carbon Shipping - Pathways to Sustainable Shipping).

Chemical composition	FAME	HVO	Diesel
Density at 20°C (kg/m^3)	885	780	825
Lower Heating Value (LHV) (MJ/kg)	37.1	44.1	43.1
Viscosity at 20°C (mm^2/s)	7.5	3.0 (at 40 °C)	5.0
Surface Tension (N/m)	0.026	-	0.028
Cetane Number (CN)	56	80-99	40-50
Stoichiometric Air/Fuel Ratio	12.5	-	15
Oxygen Content (% vol.)	~ 11	0	0
Aromatics Content (% vol.)	-	0	~ 30
Sulfur Content (ppm)	-	0	<3.5

Step 3: Confirm compliance with IMO safety regulations and machinery

The International Convention for the Safety of Life at Sea (SOLAS) mandates a flashpoint for fuel oil to be no less than 60°C under II-2 Regulation 4.2.1.1. This is ensured with the help of the fuel provider and documented on the BDN and contractual specifications. It is also critical to check the compatibility between the bio-diesel and the vessel's machinery. This can be done in coordination with the fuel provider, classification society, shipowner, and engine maker. The physical and chemical properties of the bio-diesel might be like those of petroleum fuels; however, certain species present in bio-diesel may create compatibility issues with a vessel's machinery.

3.2 Onboard handling

Once the bio-diesel fuel properties are known and confirmed to comply with regulations and be compatible with onboard vessel machinery, onboard handling, including transfer and storage, must be considered. Below, we outline our recommended process for handling bio-diesels onboard vessels.

Step 1: Bunker storage tank cleaning

Before bunkering bio-diesel into onboard storage tanks, we recommend cleaning, and clearing sludge (to the maximum possible level) from the tanks. This ensures that sludge and water content in the bunker storage tanks do not contaminate the bio-diesel. The level of cleaning required is, of course, subject to the condition of the tanks and the level of sludge/sediment content within the tanks.

Step 2: Storage and transfer temperatures

Adjust the temperature in the bunker storage tank and fuel system to a suitable temperature for the fuel. This will be determined based on the WAT and WDT of the bio-diesel. Check the viscosity and cold flow properties and adjust accordingly in the system. A fuel temperature-viscosity graph can inform the required fuel temperature to ensure the needed fuel injection viscosity.

In addition to the required storage and transfer temperatures that must be maintained in the fuel system, it is also essential to ensure that excess water in the tanks can be drained and removed when needed. Removing water decreases the risk of microbial growth and, thus, lowers the instability risks of the bio-diesel. It is also important to monitor the flow and clogging levels of the filters. This will help advise the frequency of cleaning required to keep the fuel filters functioning at optimal levels.

3.3 Storage ability

One of the concerns of having bio-diesel stored onboard a vessel is its storage stability, which is the potential for the fuel to change when stored under certain conditions. This section focuses on the main parameters investigated to understand bio-diesel's storage stability driven by the fuel's oxidation. To find out more about the storage stability of bio-diesel, working group member BP Shipping conducted two case studies. The case studies included fuel sample analyses of bio-diesel blends at different time periods after bunkering: B30 and B50 fuel blended with VLSFO was tested once loaded, after six months, and after 12 months of storage on a medium range (MR) tanker. This section includes the results of their investigations.

This section also provides insights from readditization studies performed by working group member National Renewable Energy Laboratory (NREL) in the automotive context. Readditization, introducing an additive to the fuel after bunkering, can bring an off-specification bio-diesel back to an acceptable quality level.

Oxidation stability

The presence of unsaturated compounds in bio-diesels lends to their potential for oxidative degradation. Unsaturated compounds have weak carbon-hydrogen (C-H) bonds that can break, creating sites that easily react with dissolved oxygen to form peroxides that initiate the oxidation process. As oxidation proceeds, peroxides decompose to form acids and compounds that can polymerize to form insoluble gums. Too much acid can cause problems such as corrosion of the fuel handling and injection system, while insoluble gums can lead to deposits that constrict flow or even clog fuel handling and injection equipment onboard the vessel. These unsaturated compounds in bio-diesels are inherent in the vegetable oils and the animal fats from which they are derived. This oxidative nature is beneficial from a biodegradability perspective; however, this is an undesirable characteristic from a fuel-quality standpoint.

The oxidation mechanism of fatty acid esters has three main phases:

Phase 1 – Induction period or lag phase: In this phase, oxygen consumption occurs slowly, and the antioxidant compounds already present in the bio-diesel are depleted, but the chemical composition of the fuel is not yet significantly impacted. The goal of managing oxidation stability in the fuel storage system, or onboard a vessel, is maintaining the fuel in phase 1 until it is combusted.

Phase 2 – Exponential phase: Oxygen consumption and peroxide formation increase rapidly in this phase. The antioxidant compounds have been consumed by this point, and oxygen reacts with the fuel base.

Phase 3 - During this phase, there is an exponential increase in the production of acids and other degradation products, thereby heavily impacting the bio-diesel quality.

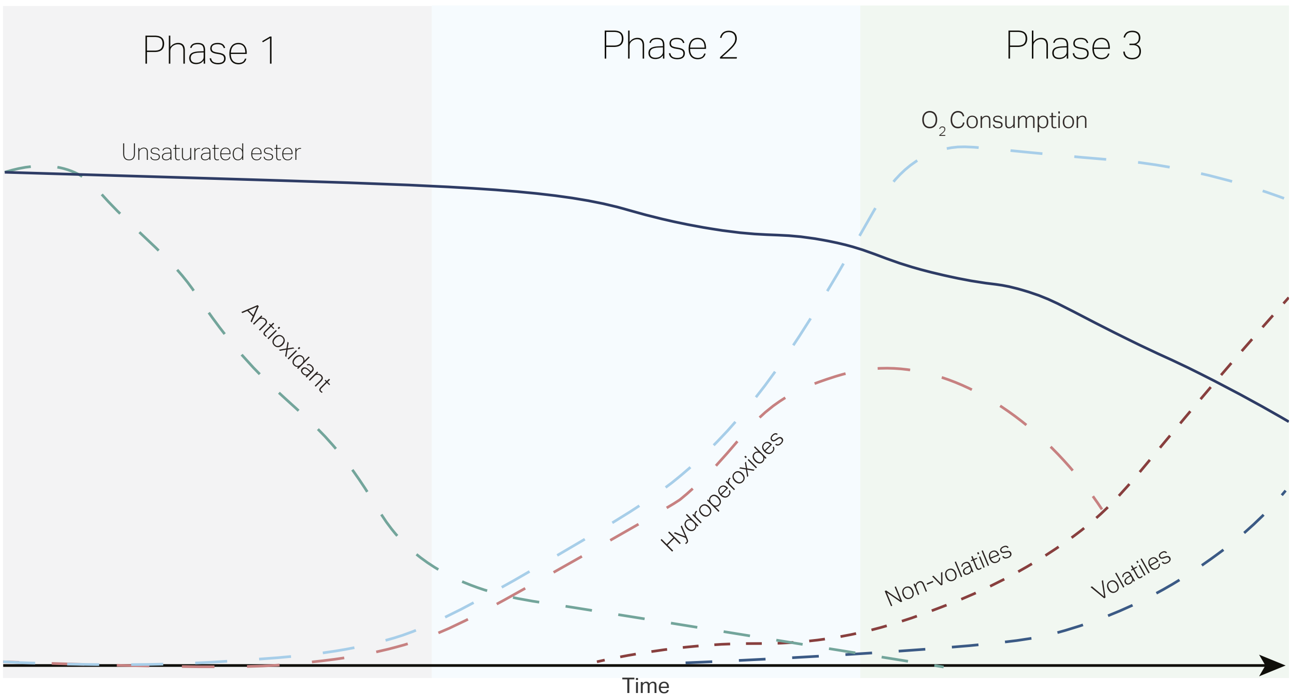
The various phases of oxidation are illustrated in Figure 3.

The case studies conducted by BP Shipping focused on three main parameters indicating the fuel's oxidation formation, and acidity. Table 3 details the full fuel sample analysis results for the B30 and B50 bio-diesel blends analyzed in the case studies.

As shown in Table 3, the viscosity of the bio-diesels increased slightly over time, suggesting that the fuel oxidized over time. Higher viscosity due to oxidation can lead to heavy loading on purifiers, filters, and deposition in tanks, which should be monitored, and operational adjustments made, as necessary.

The sediment amount after thermal aging was measured using the total sediment potential (TSP). The test results showed that the TSP of the B30 (30% bio-diesel & 70% VLSFO) blend exceeded the limit of 0.10% m/m as specified in ISO 8217 for an ISO-F-RMD80. After six months, the TSP was 0.23%, and after 12 months it was 0.36%. An extended analysis of the total sediment existent (TSE) indicated that the high sediment result was primarily due to extraneous dirt and, therefore, not caused by fuel oxidation. Similar observations were made regarding the TSP and TSE for the B50 (50% bio-diesel & 50% VLSFO) blend. High quantities of sediments can lead to issues with

Figure 3: Phases of oxidation mechanism of fatty acid esters (Source: NREL, McCormick).



combustion in engines, so sedimentation must be carefully monitored.

The formation of acids due to oxidation was measured using the total acid number (TAN). The TAN for the VLSFO/B30 blend was at a satisfactorily low level for a marine fuel (below 2.5 mgKOH/g) and would not be expected to give rise to problems during use. A maximum TAN was recorded to be 0.35 mgKOH/g after six months and 0.37 mgKOH/g after 12 months. The TAN for the VLSFO/B50 blend was found to be above average at 0.43 mgKOH/g after six months and 0.63 mgKOH/g after 12 months. These observations are under the maximum limit of 2.5 mgKOH/g. Acids in bio-diesels can lead to corrosion in the fuel system. Although the use of the fuel may not cause problems at this TAN level, the vessel operator should closely monitor the fuel pumps with respect to the fuel pump index, which indicates the condition of the fuel pumps.

The results of the two fuel sample analyses indicated an acceptable level of oxidation stability; however, further investigation is needed to understand the long-term stability of pure B100 bio-diesels stored onboard vessels. The oxidation stability of bio-diesels onboard vessels also depends on proper handling and onboard conditions experienced by the fuel.

Table 3: Fuel sample analysis results of VLSFO and B30/B50 bio-diesel blends (Source: BP Shipping).

			VLSFO		**B30**			**B50**		
ISO-F Grade (2010/12)	**Test Method**	**UoM**	RMD-80VLS	VLSFO (As Loaded)	B30 (As Loaded)	B30 (Aged 6 Months)	B30 (Aged 12 Months)	B50 (As Loaded)	B50 (Aged 6 Months)	B50 (Aged 12 Months)
Density @ 15°C	ISO 12185	kg/l	0.9750 Max	0.9691	0.9445	0.9474	0.9498	0.9314	0.934	0.9364
K Viscosity at 50°C	ISO 3104	cSt	80 Max	72	20.4	24.9	30	12.8	14.4	16.2
K Viscosity at 100°C calc	Calc	cSt		12	5.5	6	7	4	4	4.5
Total Sediment	ISO 10307-2A	% m/m	0.10 Max	<0.01	0.01	0.23	0.36	<0.01	0.11	0.17
Totall Sediment Existent	ISO 10307-1	% m/m	0.10 Max			0.26	0.35		0.07	0.16
Total Acid Number	ASTM D664	mg-KOH/g	2.5 Max	0.27	0.28	0.35	0.37	0.32	0.43	0.63
Asphaltenes		% m/m		2.1	1.5			1.3		

Readditization to extend bio-diesel storage life

In the case studies outlined in the previous section, although we did not see a direct need to reduce oxidation to maintain storage stability, this may not always be true, especially with higher bio-diesel blends. Readditization can reduce oxidation and extend the storage life of bio-diesel fuels. It is also to be noted that readditization of antioxidant to the fuel has not yet been trialed in the maritime sector onboard vessels.

The automotive industry has gathered extensive knowledge and experience about using readditization to maintain storage stability. This knowledge can be adapted to maritime bio-diesel usage. An accelerated test[9] using a Rancimat™ setup to measure the oil stability index can be used to determine if a fuel is still in the induction period or lag phase (phase 1) by calculating an induction time and to give a rough indication of how long a fuel can maintain being in phase 1.[10] An induction time of less than one hour indicates that a fuel is no longer in phase 1, while longer induction times suggest that the fuel has some oxidation reserve. Tests conducted by NREL on B100 bio-diesel using the ASTM D4625 protocol of storage open to air at 43°C[11] confirmed that induction time decreases over aging time, and that if an additional antioxidant is added before the onset of phase 2 (readditized B100), the time in phase 1 can be extended. However, readditization must occur before induction time drops to one hour.

9 In this test, the bio-diesel or blend is heated to 110°C while air is bubbled though the liquid. After some time (referred to as the induction time), the antioxidants in the fuel are consumed and rapid oxidation begins. Under these relatively hot and oxygen-rich conditions, oxidation produces volatile acids that are carried out of the fuel by the air and into a water bath. The conductivity of the water bath is monitored, and rapidly increases when the volatile acids appear. This induction time can be thought of as the ratio of antioxidant in the fuel to pro-oxidants (e.g., double bonds or dissolved metals such as copper).

10 L.M. Du Plessis, J.B.M. De Villiers, W.H. Van Der Walt, 'Stability studies on methyl and ethyl fatty acid esters of sunflower seed oil', Journal of the American Oil Chemists Society, 62 (4) (1985), pp. 748-752.

11 Christensen, E., McCormick, R.L. 'Long-Term Storage Stability of Biodiesel and Biodiesel Blends', Fuel Processing Technology, 128 339–348 (2014).

04 Emission measurement results

While the UI approved by IMO now makes it easier to comply with NO_x limit requirements when using bio-diesels, it is still relevant to understand their NO_x emissions. Publicly available documentation of testing methodologies and emission measurements can support owners when approaching flag states who have not adopted the UI or still require an assessment. In addition, onboard vessel emission measurement experience can be used as a basis for further evaluation and understanding of other onboard vessel emissions, including carbon dioxide (CO_2) and methane.

In this section, we outline the results of three emissions measurement tests conducted onboard vessels to quantify the NO_x emissions from bio-diesel use:

I. Test on B100 – DS NORDEN
II. Test on B30 (bio-diesel blend with VLSFO) and B50 (bio-diesel blend with VLSFO) – BP Shipping
III. Test on B30 (bio-diesel blend with MGO) – Oldendorff Carriers

DS NORDEN and BP Shipping are working group members, whereas the testing data from Oldendorff Carriers are available in a public report.[12]

4.1 Testing methodology

The bio-diesel emissions measurement tests were conducted onboard ocean-going vessels under real operating conditions. The tests followed a similar testing methodology to the one outlined in the NO_x Technical Code 2008 (NTC).

Direct measurement and monitoring (DMM), including testing following NTC Chapter 6.4, was selected to quantify the level of NO_x emissions. This method is used for onboard NO_x measurements that demonstrate a vessel's compliance with the NTC-specified NO_x limits. The other option, testing following NTC Chapter 5, is better suited for emission measurement using an engine test bed.

DMM Testing Methodology

The NO_x emissions from an engine are controlled based on the emission values determined using an applicable test cycle. The DMM method is derived from the NTC, which specifies the E3 test cycle for a propeller-law-operated main engine. Details of the E3 cycle with respect to the engine's name plate maximum continuous rating (MCR) load and engine crankshaft speed are given in Table 4. The engine loads and speeds are used as the setpoints at which the NO_x emissions are measured in an engine running on bio-diesel.

Table 4: E3 specific engine load and engine speed set points.

Load	Speed
100%	100%
75%	91%
50%	80%
25%	63%

Test cycles such as E3 are primarily intended to be used under test bed conditions, in which the engine load and speed at each set point can be adjusted as required to match the given values. However, the DMM methodology is used on a vessel operating under routine trading conditions. Hence, it is not possible to achieve the same level of accuracy in the above-defined set points at which emissions measurement is to be performed. Thus, the required engine load was set (in kW), and the resulting engine speed resulted from various influencing factors: propeller design, ship's loading, and prevailing weather conditions. The NO_x emissions level measured at each set point was then weighted with the E3 weighting factors outlined in Table 5, to obtain an E3 weighted average value for each measured emissions species.

12 Patritsia Maria Stathatou, Scott Bergeron, Christopher Fee, Paul Jeffrey, Michael Triantafyllouc and Neil Gershenfelda, 'Towards decarbonization of shipping: direct emissions & life cycle impacts from a biofuel trial aboard an ocean-going dry bulk vessel', 2022, Sustainable Energy & Fuels.

Table 5: E3 specified weighting factors at the set points.

Load	E3 Cycle Weight Factors
100%	0.2
75%	0.5
50%	0.15
25%	0.15

Table 6: NTC specified NO_X emissions limits under different regulations.

	NO_x Limit Value (g/kWh)
Reg 13.4	14.4
DMM Onboard	15.8
DMM Onboard + Residual Fuel	16.6

DMM requires the use of emission analyzer equipment. Ideally, this equipment should be rated for DMM use and can be portable, so specialist expertise is not required to operate it. The Testo 350 Maritime V2 rated for onboard testing in marine applications was used in the tests presented in this section. This device measures the concentration of NO_X emission components separately as nitric oxide (NO) and nitrogen dioxide (NO_2) using species-specific electrochemical sensor cells. The same approach is used to measure the concentrations of oxygen (O_2), carbon monoxide (CO), and sulfur dioxide (SO_2), whereas an infrared analyzer is used to measure the concentration of CO_2.

NTC-specified NOX limits for measured emissions

The NO_X emission levels specified by the NTC are listed in Table 6. An allowance of 10% was given to the DMM onboard measurement methodology on top of the NTC-specified limit, thus bringing the limit to 15.8 g/kWh. If the fuel tested using the DMM method is of a residual nature, an allowance of 15% is permitted, bringing the limit to 16.6 g/kWh.

4.2 Bio-diesel emission testing results

The three bio-diesel emissions measurement tests conducted onboard vessels are summarized in Table 7. For comparative purposes, each test also measured the NO_X emission levels for standard fossil-based fuels, including HFO, VLSFO, and MGO. All three tests used a MAN engine, but of different sizes.

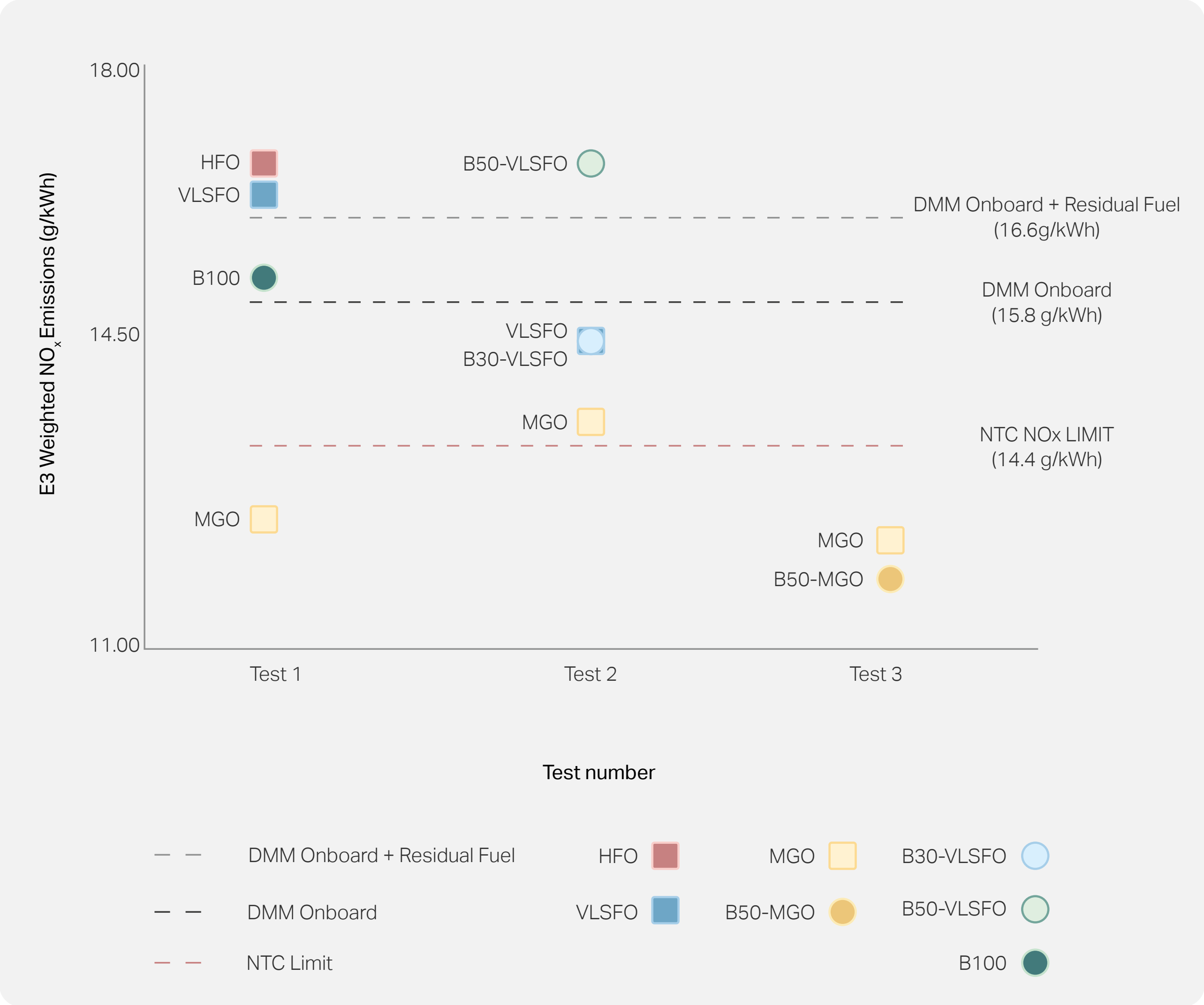
Table 7: Summary of emission measurement tests.

Test	Performed By:	Vessel Type	Biodiesel Type	Main Engine Type
1	DS NORDEN	Dry Bulk, SUPRAMAX	B100	MAN B&W 6S50ME B9.5
2	BP Shipping	Oil Tanker, MR	B30 & B50 (bio-diesel blend with VLSFO)	MAN B&W 6G50ME-B9.3
3	Oldendorff Carriers	Dry Bulk, KAMSARMAX	B50 (bio-diesel blend with MGO)	MAN B&W 6S60MEC8.5

Emission measurement results from the three tests are summarized in Figure 4. In addition to the bio-diesel blends tested, the NO_x emission levels for the other fossil-based fuels tested are also shown. The NTC NO_x limit line is also shown for reference. While Test 2 and Test 3 tested a B50 blend, the blending was not done with the same fossil fuel. Test 2 was with VLSFO, and Test 3 was with MGO. Therefore, it is not possible to directly compare the different test results. The main takeaways are considered based on relative emission levels within each test.

Test 1 was performed with 100% bio-diesel (B100) and compared with fossil fuels HFO, VLSFO, and MGO in back-to-back testing. The E3 weighted NO_x emissions of bio-diesel tended to be comparable with or slightly lower than those observed from HFO and VLSFO fuels (about 5% and 6% lower than VLSFO and HFO, respectively). This establishes that, although the NO_x emission level of B100 is higher than the NTC-allowed NO_x limit, it is on the same level as that of fuels already used today. It is a common observation amongst the other tests that under real operating conditions, the weighted average NO_x emissions of residual fossil bunkers are above the NTC-specified NO_x limit.

Figure 4: Summary of NO_x emissions levels measured by various tests (Source: DS NORDEN, BP Shipping and Oldendorff Carriers).



The NO_x emissions of the fossil bunkers are seen to be higher than that of the NTC-specified limits because of the inability to reproduce the test bed conditions while performing testing and measurement under the real operating conditions. On tests performed in operating conditions of the vessel it is possible to constantly maintain the needed engine load set point, but the engine's RPM cannot be set constant as can be done while testing in test bed conditions This highlights the need to consider a range of values close to the NO_x emissions specified in the NO_x Technical File for a particular engine, as opposed to the hard limit defined by the NTC. MGO, a distillate fuel, exhibited lower NO_x emissions than the residual fuel oils, with 25% less NO_x emissions than B100.

Test 2 was performed with bio-diesel blends compared with the fossil fuel bunker VLSFO and MGO in back-to-back testing. In this case, the bio-diesel was blended (B30 and B50) with VLSFO. As observed previously with the B100 fuel, the E3 weighted NO_x emissions of bio-diesel blends are similar to those observed from VLSFO fuel. Once again, liquid bio-diesels had similar NO_x emission levels as residual fuels. The B50 fuel exhibits slightly higher NO_x emission levels than B30 and VLSFO, but the NO_x emission level is within 10% of the VLSFO level. The variability of DMM onboard is around 15%. Thus, the NOX emissions from B50 were not significantly different from VLSFO. Again, MGO had lower NO_x emissions as it is a distillate fuel, at 6% and 18% lower than B30 and B50, respectively.

Test 3 was performed with a B50 bio-diesel blended with MGO. It was tested back-to-back with a distillate fuel MGO. The NOX emissions of both fuels were similar, though B50 had 3% lower NO_x emissions than MGO, and were below the NTC limit. This is once again attributed to the distillate grade of the fuel.

All three tests showed that NO_x emission levels of bio-diesel and bio-diesel blends are similar to or lower than conventional fossil fuels, including HFO, VLSFO, and MGO. The results also show that measured NO_x emission levels of conventional fossil fuels like HFO and VLSFO and bio-diesel are typically higher than the NTC NO_x limit. The reasons for NO_x emission levels being higher than the NTC limit for most fuels include engine performance degradation over time in operation, the inability to accurately reproduce test bed conditions for NO_x measurement, and lower accuracy of onboard measurement devices relative to test bed results. From a relative standpoint, it is clear from the three tests that bio-diesel and bio-diesel blends do not significantly increase NO_x emission levels relative to the NTC limit and comparable fossil-based fuels used today.

In addition to NO_x emissions levels, the SO_x and carbon monoxide (CO) emissions were also measured for the B100 fuel from Test 1. The SO_x emissions were found to be much lower than the fossil fuels, which is attributed to the sulfur content in the fuel, which is lower than 0.02% by composition. The CO emissions were 65% lower than the fossil fuels, indicating complete combustion of the fuel. This is due to the uniform nature of the bio-diesel, where the molecules are all FAME, which are more homogenous than fossil fuels.

4.3 NO_x emission reduction technologies and solutions

Before investigating measures to reduce NO_x emissions from bio-diesel operations, it is vital to quantify the NO_x emissions levels and establish a baseline for different blends/compositions. As seen in Section 4.2, available bio-diesel test results do not warrant special emission reduction technologies or solutions to reduce NO_x emissions. However, if NO_x emission reduction was necessary for other fuels, such as new bio-oils and blends, there are commercially available technologies and solutions to do so.

The most common methods for reducing NO_x formation in diesel engines are injection timing delay, the use of cooled exhaust gas recirculation (EGR), fuel-water emulsion, and reducing air charge temperature (e.g., via advanced intake closing such as Miller cycle). After-treatment technologies such as selective catalytic reduction (SCR) are also commonly used to reduce NO_x emissions to comply with the NTC. While slightly changing the engine tuning or system dimensioning to handle increased NO_x levels is straightforward for a newbuild vessel, conversion options are more challenging, depending on the solutions available. In addition, any change to engine parameters could negatively impact fuel consumption, resulting in other emission increases, including CO_2.

05 Conclusions

As bio-oils are not available in sufficient quantities for onboard use and testing, studying the bio-diesels currently used in the maritime industry can provide foundational knowledge and a better understanding of key onboard vessel considerations for liquid bio-diesels and bio-oils. The UI approved at MEPC 78 in June 2022 simplifies the regulatory considerations for using biofuels onboard vessels, especially if the flag state has adopted the UI, and the classification society and engine maker can confirm no changes to the engine's NO_x critical components or settings/operating values. We encourage flag states, classification societies, and engine makers to jointly leverage the approved UI to remove the regulatory barriers to using bio-diesels and bio-oils onboard vessels.

While some regulatory barriers have been removed, the challenges of not having applicable fuel standards and the need for sustainability certifications remain. With the lack of applicable fuel standards, it is up to the individual shipowner or operator to build knowledge and experience on proper fuel parameters and handling. We support the development of fuel standards for higher percentages of bio-diesel and bio-oil blends. While some sustainability certification schemes exist, they must be standardized and aligned with the current and upcoming global and regional regulations.

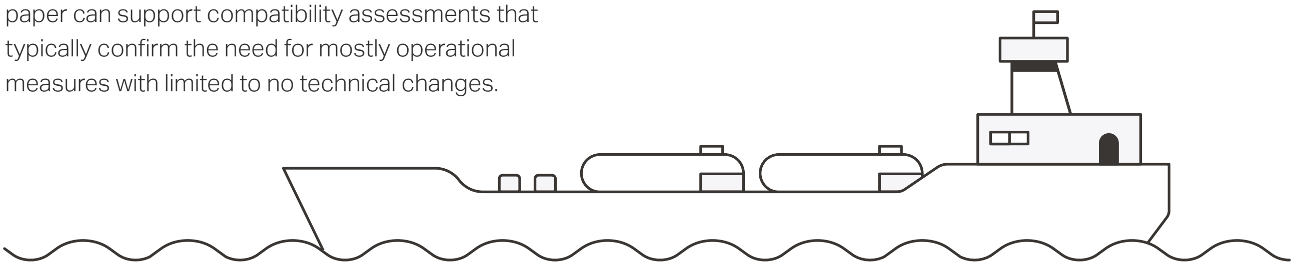
The properties of bio-diesels, including their stability, acidity, and corrosion characteristics, vary depending on the fuel's feedstock and production processes. As a result, how they are handled and stored onboard vessels must be carefully considered; however, following the step-by-step process presented in this paper can support compatibility assessments that typically confirm the need for mostly operational measures with limited to no technical changes.

Fuel storage sample analyses indicate acceptable oxidation stability levels for typical fuel use periods. If required, readditization of antioxidants can prevent fuel oxidation. Further investigation is needed to understand the long-term stability of pure B100 bio-diesels stored onboard vessels.

All three emissions measurement tests presented here showed that NO_x emission levels of bio-diesel and bio-diesel blends are similar to, or lower than, conventional fossil fuels, including HFO, VLSFO, and MGO. These results also indicate that there is no need for special emission reduction technologies or solutions to reduce NO_x emissions further when using bio-diesels. However, if NO_x emission reduction becomes necessary for other fuels, such as new bio-oils and blends, there are commercially available technologies and solutions.

The conclusions presented in this paper are based solely on tests of FAME-based bio-diesel fuels. The NO_x emission levels established by these fuels form a benchmark against which fast pyrolysis and hydrothermal liquefaction bio-oils will be compared with when technology maturation is improved, and they are available in larger quantities. Future work at MMMCZCS will include reviews of bio-oil technology availability and product quality specifications for application in marine ICEs.

In addition to assessing onboard emissions from bio-diesel usage onboard vessels, the MMMCZCS is actively engaged in other areas related to bio-diesels. This includes working to understand the well-to-tank emissions, addressing feedstock availability, developing a fuel life-cycle methodology and fuel standards.



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