- IDEALFUEL -

Lignin as a feedstock for renewable marine fuels

GRANT AGREEMENT No. 883753

HORIZON 2020 PROGRAMME - TOPIC LC-SC3-RES-23-2019
“Development of next generation biofuel and alternative renewable fuel technologies for aviation and shipping”

Deliverable Report

D4.7 – Draft safety data sheet for the most optimum Bio-HFO

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 883753

Deliverable No.	IDEALFUEL D4.7	
Related WP	WP4	
Deliverable Title	Draft safety data sheet for the most optimum Bio-HFO	
Deliverable Date	30-04-2024	
Deliverable Type	REPORT	
Dissemination level	Public	
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Approved by	Roy Hermanns (Project Coordinator)	30-04-2024
Status	FINAL	30-04-2024

Disclaimer/ Acknowledgment

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 883753. The information and views set out in this publication does not necessarily reflect the official opinion of the European Commission. Neither the European Union institutions and bodies nor any person acting on their behalf, may be held responsible for the use which may be made of the information contained therein.

Publishable summary

The overall objective of IDEALFUEL is to enable the utilization of lignocellulosic feedstocks for an ultimate renewable biogenic heavy fuel oil (bio-HFO) with drop-in capability in a sustainable manner for the replacement of the marine fuel. In order to determine the usability of the novel bio-HFO, the fuel properties much comply with the limits for residual marine fuel set by ISO 8217 standard. In general, the produced novel fuels cannot meet all the requirements, so they will be blended with conventional fuels to meet the standards and put on the market.

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1 Introduction

The primary aim of the Horizon 2020 Project IDEALFUEL is to facilitate the utilization of lignin from lignocellulosic biomass as a sustainable maritime fuel. The project seeks to develop an efficient and affordable chemical pathway for converting lignocellulosic biomass into Bio Heavy Fuel Oil (Bio-HFO) with low sulphur content, allowing it to be seamlessly integrated as a drop-in fuel in the existing maritime fleet.

The current deliverable, related to task 4.4 of WP4 addresses the environmental health and safety aspects of utilizing Bio-HFO blends and its blends in marine engines. The crude lignin oil and lignin-based Bio-HFOs differ significantly from traditional marine fuel and require special handling procedures. Currently, there are no established instructions for their use in marine applications. OWI, in conjunction with GOOD and the sounding board, evaluated whether additional measures or precautions are needed when employing these fuels on sea-going vessels. The evaluation covered various aspects, including issues related to safety, transportation from the production plant to a ship, and local storage. The assessment was based on the insights gained in the subtasks T4.1 and T4.3 regarding the fuel properties and fuel-system compatibility.

2 Logistics and handling of conventional Marine fuel

2.1 Identification of the logistics chain

2.1.1 Scope

In Europe, as well as in the marine sector globally, safety codes and labels for Heavy Fuel Oil (HFO) are governed by various regulations and standards to ensure safe handling, storage, transportation, and usage. While HFO typically does not have a low flashpoint, there are several factors and legislation that must be followed to transport and store it safely in these contexts:

European Union (EU) Legislation:

The EU has enacted regulations and directives that apply to the transportation, storage, and handling of hazardous substances, including HFO. These regulations aim to ensure the safety of workers, protect the environment, and prevent accidents and pollution.

Classification, Labeling, and Packaging (CLP) Regulation:

The CLP Regulation is the EU's legal framework for the classification, labeling, and packaging of substances and mixtures, including HFO. It requires manufacturers and importers to classify and label hazardous substances according to specified criteria and provide safety data sheets (SDS) to downstream users.

International Maritime Organization (IMO) Regulations:

The IMO sets forth regulations and guidelines specifically for the maritime sector, including the transport and storage of HFO aboard ships and vessels. These regulations cover aspects such as packaging, labeling, placarding, handling procedures, and emergency response protocols.

A Safety Data Sheet (SDS), formerly known as Material Safety Data Sheet (MSDS), is a comprehensive document that provides detailed information about the properties, hazards, handling, storage, emergency procedures, and disposal considerations for a specific chemical substance or product. SDSs are essential tools for ensuring the safe handling and use of hazardous materials in various industries. The data on the SDS typically includes information covering:

- Hazards Identification
- Composition/Information on Ingredients
- First-Aid Measures
- Fire-Fighting Measures
- Accidental Release Measures
- Handling and Storage
- Exposure Controls/Personal Protection
- Physical and Chemical Properties
- Stability and Reactivity
- Toxicological Information
- Ecological Information
- Disposal Considerations
- Transport Information
- Regulatory Information

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.

2.1.2 Logistics chain

Producing Heavy Fuel Oil (HFO) involves several stages, from the extraction of crude oil to its refinement and eventual delivery to ports and terminals. An overview of the different processes in the logistics chain is given below.

- Extraction of Crude Oil:
    - Crude oil is typically extracted from underground reservoirs through drilling wells.
    - Once extracted, the crude oil is transported via pipelines, tanker trucks, or ships to storage facilities or directly to refineries.
- Refining Process:
    - Upon arrival at the refinery, crude oil undergoes a series of refining processes to separate it into various components based on their boiling points.
    - The primary refining process is distillation, where the crude oil is heated in a distillation tower. Different fractions of the crude oil vaporize at different temperatures and are collected at different levels of the tower.
    - The heavier fractions, which include the components used to produce HFO, remain at the bottom of the distillation tower and are collected as residual fuel oil.
- Production of Heavy Fuel Oil:
    - The residual fuel oil obtained from the distillation process undergoes further treatment to remove impurities and adjust its properties.
    - Additional refining processes such as vacuum distillation, thermal cracking, and visbreaking may be employed to improve the quality and adjust the specifications of the HFO.
    - The resulting product is Heavy Fuel Oil, which typically has a higher viscosity and sulfur content compared to lighter refined products like gasoline or diesel.
- Delivery to Ports/Terminals:
    - Once produced, Heavy Fuel Oil is transported from the refinery to ports and terminals for distribution.
    - Transportation methods may include pipelines, tanker trucks, or dedicated HFO tankers.
    - At ports and terminals, HFO is stored in tanks or bunkers awaiting further distribution or use.
    - Shipping companies, power plants, and industrial facilities are among the primary consumers of HFO, using it as a fuel for propulsion or power generation.
    - Overall, the production of Heavy Fuel Oil involves extracting crude oil, refining it into various fractions, and further processing those fractions to produce the desired specifications for HFO. The final product is then transported to ports and terminals for distribution to end-users.

In Figure 1 below, an overview of the standard logistics chain for Heavy Fuel Oil is shown. Looking at conventional fossil fuels, crude oil is extracted and sent to a refinery [1].

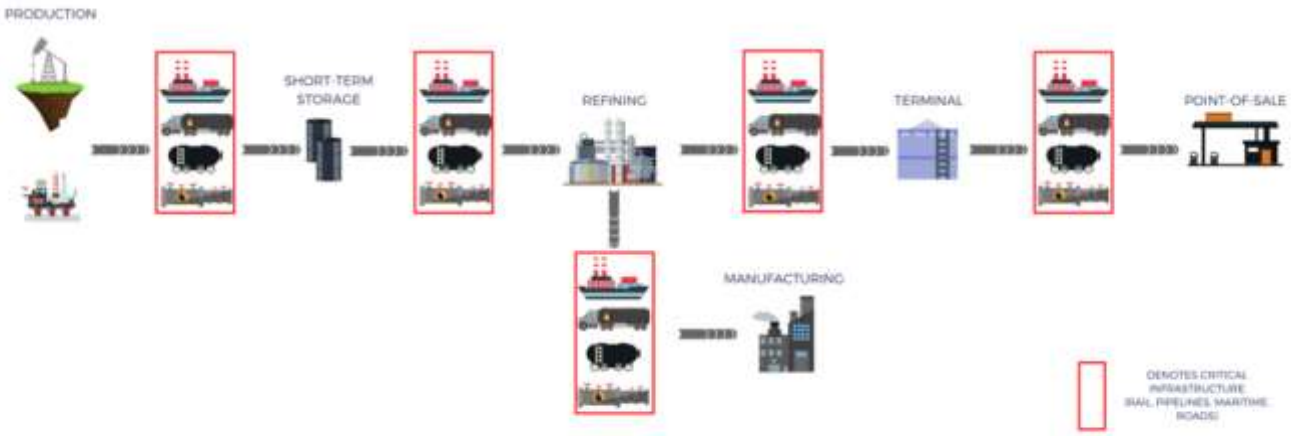

Figure 1: Overview of the standard logistics chain

Considering any biofuel HFO product – due to the general specifications, most of the legislation and procedures required for transporting HFO will apply for any BioHFO type product. The primary difference lies in the collection and pre-processing of various feedstocks before they are sent to a refinery for refinement to HFO.

Figure 2: NREL Biodiesel Handling and Use Guide [2]

2.1.3 Storage & handling of Marine fuel

Fuel specifications are defined in line with wishes and capabilities of engine OEMs in which these fuels will be burned. As such, OEMs often deliver their own fuel handling guidelines which specify the spec of fuel to be used. The International Council on Combustion Engines (CIMAC) has published a comprehensive guide in 2019 on “Marine fuel handling in connection to stability and compatibility” which describes general handling practices. Service letters from OEMs, such as MAN Energy Solutions, also provide fuel handling guidelines.

Due to differences in various parameters such as pour point, flashpoint, cloud point, viscosity etc. Different fuels are subject to different handling guidelines to ensure they remain fit for use in engines. Certain qualities of FAME (coming from different feedstocks and production pathways) for example, have been shown to crystallize at lower temperatures. This crystallization of the fuel can harm the engine and fuel system, hence the need for strict guidelines and procedures.

In traditional practices, blending of residual fuels primarily focused on viscosity control. However, with the expanded availability of high-density refinery products, density emerged as an additional consideration in blending processes. The evolving regulatory landscape, particularly with the implementation of MARPOL Annex VI Regulation 14.1.3, which imposes stringent restrictions on marine fuel sulfur content, has shifted the primary blend target from viscosity and density to sulfur content.

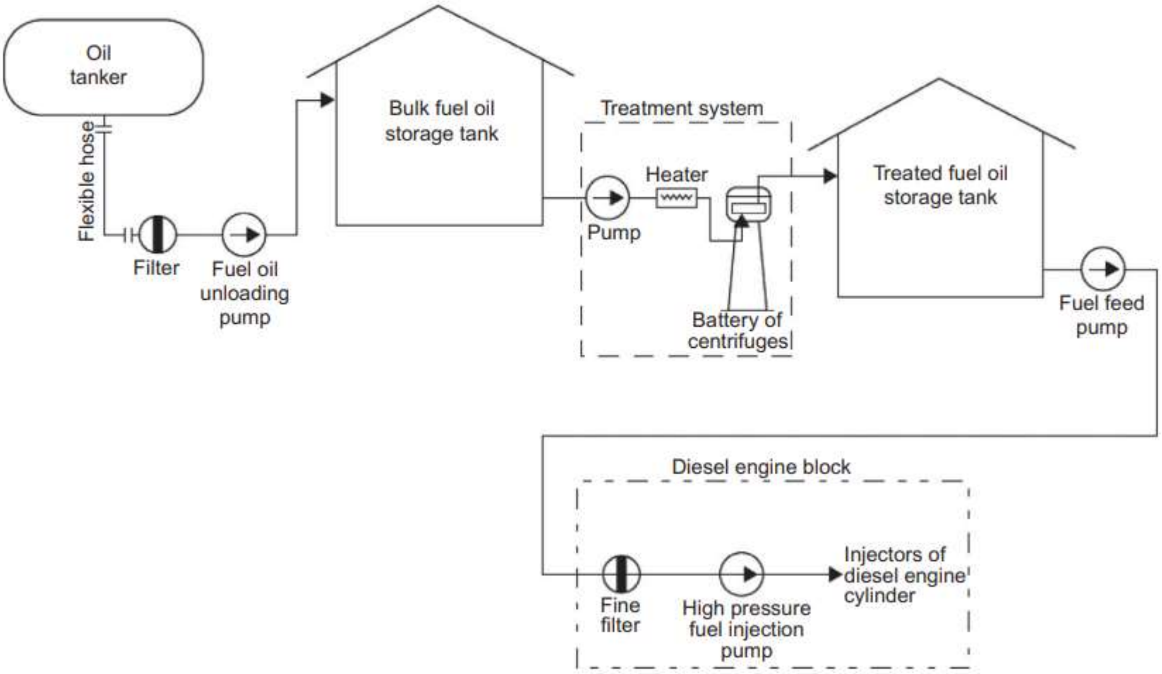

Figure 3: Process chain of fuel from oil tanker to engine [3]

2.1.4 Instructions for handling Marine fuel

2.1.4.1 Handling of Heavy fuel oil

Due to the high viscosity of heavy fuel oils (residual fuels), vessels utilizing HFO are equipped with fuel treatment systems to heat the fuel and lower the viscosity for better combustion performance.

Handling guidelines for Heavy Fuel Oil (HFO) in marine and bunkering operations typically include:

I. Storage and Transfer: HFO should be stored in designated tanks that are equipped with heating systems to maintain the desired temperature. When transferring HFO between storage tanks and bunkering facilities or vessels, proper procedures should be followed to prevent spills and ensure safety.

II. Temperature Control: Continuous monitoring of HFO temperature is essential to ensure it remains within the optimal range for handling and combustion. Heating systems should be maintained and operated according to manufacturer guidelines.

III. Safety Measures: Adequate ventilation and personal protective equipment (PPE) should be provided to personnel involved in handling HFO to minimize exposure to vapors and fumes. Additionally, spill containment measures and emergency response protocols should be in place to mitigate environmental and safety risks.

IV. Quality Control: Regular testing and analysis of HFO quality, including viscosity, density, sulfur content, and other parameters, are necessary to ensure compliance with regulatory standards and optimal engine performance.

As opposed to methanol and hydrogen, which are low-flashpoint fuels, HFO and diesel-like fuels are relatively straightforward and these guidelines have been in place for decades already, simplifying the adoption of drop-in fuels like Bio-HFO which are predominantly suited to existing infrastructure and practices.

General Guidelines

Ensure all potential sources of ignition are removed. Take preventive measures to mitigate static discharges. During gas unloading, avoid inhaling vapors, including hydrogen sulphide (H2S) and hydrocarbons. Provide sufficient ventilation. For oil mist, prevent inhalation and skin or eye contact. Wear appropriate personal protective equipment (PPE) and use local ventilation as necessary. Wash hands and any contaminated areas with soap and water before leaving the work area.

The product is typically handled at elevated temperatures. Storage and handling temperatures should not surpass the flash point. If there's a risk of contact with hot product, ensure all protective gear is suitable for high-temperature use.

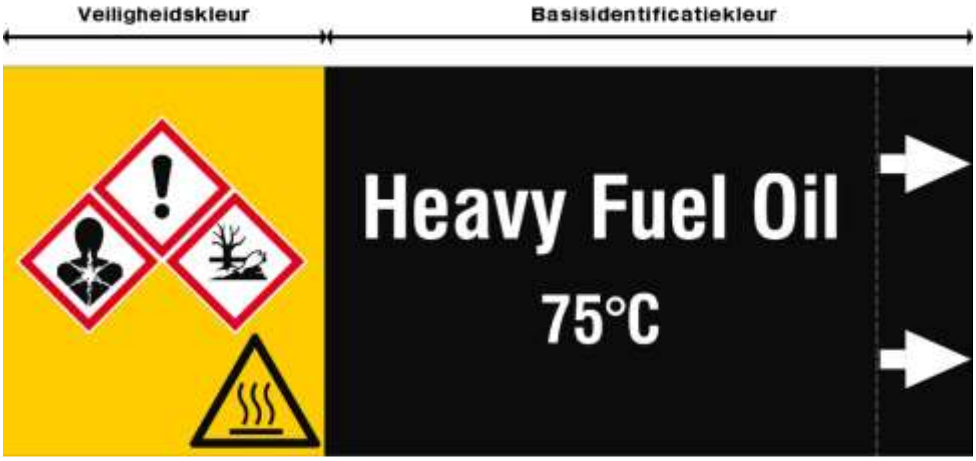

Figure 4: HFO safety guidelines [4]

Residual Fuel Handling Guidelines

Understanding the chemical composition of residual marine fuel poses a challenge due to its variability depending on the source of crude oil and manufacturing processes. Nonetheless, key constituents of residual fuel include asphaltenes, resins, and liquid hydrocarbons. The term "asphaltenes" encompasses a broad spectrum of heavier hydrocarbon structures with high molecular weight and carbon/hydrogen ratios, the precise composition of which is contingent upon the crude source and blend stocks chosen.

The nature of liquid hydrocarbons influences the fuel's ability to suspend asphaltenes effectively, thereby maintaining stability crucial for efficient combustion. Failure to sustain asphaltenes in suspension leads to their precipitation as sludge, rendering the fuel unstable. Any disruption to this suspension results in an irreversible unstable state, carrying potentially significant operational implications.

The stability of a residual fuel is defined by its resistance to precipitate asphaltenic sludge despite being subjected to forces, such as thermal and ageing stresses, while handled and stored under normal operating conditions. ISO 8217:2017 specifies that fuels must be stable. Fuels which are unstable are essentially unusable since the precipitated asphaltenes, together with the entrained fuel, forms excessive sludge concentration in tanks and can readily choke purifiers, filters, fuel injection equipment and even fuel lines themselves. Under such conditions fuel treatment is often impossible and even transfer becomes problematic. In the case of thermal instability, problems will normally be encountered in the purifier or service system fuel oil heaters. In either case, even if great care and focus are taken in using the onboard cleaning system, the precipitated material can form a hard adhering, coke like material which is not easily removed other than by manual means [5].

If stored long enough the biofuel will start to oxidize, which causes an increase in acid number, viscosity and peroxides. This doesn’t happen linear, at first the biofuel remains relatively stable, until the induction point is reached where the biofuel typically starts to degrade rapidly.

Blending of Fuels with Different Viscosities

Blending fuels with significantly different viscosities, such as RMD380 (a lower viscosity heavy fuel oil) with RMK700 (a higher viscosity heavy fuel oil), can indeed present challenges related to homogeneity. Homogeneity refers to the uniform distribution of fuel components throughout the blended mixture. When blending fuels with different viscosities, achieving and maintaining homogeneity becomes crucial to ensure consistent fuel quality and performance.

There are several potential issues associated with blending low viscosity fuels like RMD380 with higher viscosity fuels like RMK700:

- Separation: Due to the difference in viscosity, there is a risk of incomplete blending and stratification of the fuel components within the blend. If not properly mixed, the heavier components may settle at the bottom of storage tanks or fuel lines, leading to fuel quality issues and inconsistent combustion performance.
- Pumpability: Blending low viscosity fuels with higher viscosity fuels can affect the overall viscosity of the blend, potentially impacting its pumpability and flow characteristics. If the blend viscosity exceeds the capabilities of fuel transfer systems and engines' fuel injection systems, it may lead to fuel delivery issues, clogging, and reduced engine performance.
- Combustion Performance: Inconsistent blending can result in variations in fuel properties, such as viscosity, density, and sulfur content, which can affect combustion performance and engine operation. Non-homogeneous blends may lead to uneven fuel distribution in combustion chambers, incomplete combustion, increased emissions, and reduced engine efficiency.

To address these challenges and ensure homogeneity when blending fuels with different viscosities, various strategies can be employed:

- Mechanical Mixing: Utilizing mechanical mixing equipment, such as agitators or recirculation systems, can help achieve thorough blending and ensure uniform distribution of fuel components throughout the mixture.
- Temperature Control: Maintaining appropriate temperatures during blending and storage can enhance the blending process and promote homogeneity. Heating the blend can reduce viscosity differences and facilitate mixing.
- Sampling and Testing: Regular sampling and analysis of blended fuels are essential to monitor fuel quality, verify homogeneity, and detect any separation or stratification issues. Adjustments to blending procedures can be made based on test results to ensure consistent fuel performance.

Overall, while blending low viscosity fuels like RMD380 with higher viscosity fuels like RMK700 can present challenges related to homogeneity, careful attention to blending processes, temperature control, and quality assurance measures can help mitigate these issues and ensure consistent fuel quality and performance.

2.1.4.2 Handling of Diesel (MGO)

Diesel, a petroleum derivative with high flammability, serves as fuel for diesel engines. It's crucial to store, handle, and transport it with care to mitigate health risks, environmental harm, and the potential for ignition by flames or sparks.

The utilization of diesel fuel carries numerous adverse impacts on the environment, both during its use and afterward. When diesel spills or leaks outdoors, its liquid form poses a toxicity risk, endangering various animal and plant species and contaminating ground and drinking water sources [6]. Additionally, direct contact with diesel fuel can lead to skin and eye irritation, resulting in rashes and other reactions. Prolonged exposure to diesel exhaust has been associated with cancer and disorders of the central nervous system. Moreover, inhaling diesel fumes, which contain microscopic toxic particles, can induce dizziness and drowsiness by infiltrating the lungs [7]. Consequently, stringent safety measures must be implemented when handling diesel fuel to avert accidents or environmental harm, as shown in Figure 5.

Safety Tips
In Fuel (Diesel) Handling

Improper fuel handling and storage can lead to serious health issues, enviornment contamination and damage to property. The following safety tips should be practiced to avoid accidents and damages due to improper fuel handling and storage practices:

Figure 5. Safety instructions for handling of Diesel Error! Reference source not found.

Due to its susceptibility to heat, fire, and static discharge, diesel must be kept away from flames, sparks, and excessive temperatures. Smoking is strictly prohibited, and fire extinguishers should be readily available in areas where the fuel is handled. Protective gear such as gloves, clothing, and safety glasses must always be worn when working with diesel. Adequate ventilation is essential, and prolonged exposure to fuel vapors should be avoided. Furthermore, fuel tanks and containers should be tightly sealed and not overfilled, with any leaks promptly cleaned. Providing training to all personnel working with diesel fuel is crucial to minimize risks and potential damages from mishandling.

To store diesel for extended periods, proper measures must be taken to ensure its safety and prevent contamination. Various-sized tanks can be utilized for this purpose. Selecting the appropriate size, material, and location of storage tanks is paramount for the safety and longevity of the fuel. The choice of tank size depends on individual needs and purposes, as depicted in the Figure 6.

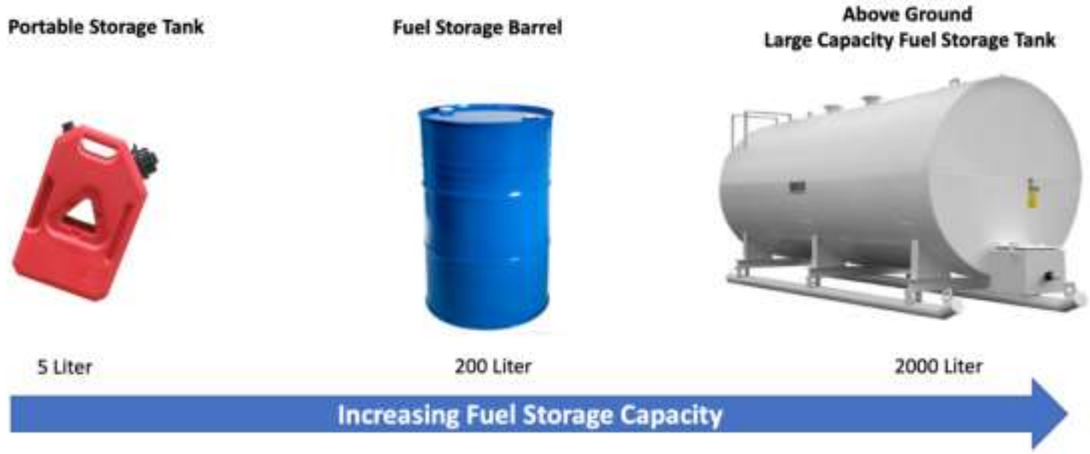

Figure 6. Fuel storage tanks with various storage capacity

Additionally, specific handling procedures are essential for storing diesel to prevent accidents like fuel spills and leaks, which could result in pollution and hazardous workplace incidents. Adhering to the following safety guidelines (Figure 5) is imperative to mitigate these risks.

Figure 7 Safety instructions for diesel storage [9]

3 Analysis methods

To identify the potential bottlenecks in the logistics chain, it is essential to determine the differences in physical-chemical properties between conventional liquid fuels and the bio-HFO. For example, the difference of flash point must be paid attention to since it is a security related property. Based on these differences between conventional liquid fuels (e.g., HFO, MGO) and bio-HFO, an assessment can be performed to identify the compatibility between fuels and infrastructure.

3.1 ISO 8271 norm and test parameters

The international Maritime Organization (IMO) has introduced the ISO 8217 standard, defining the basic requirements for marine fuels. According to the ISO 8217 standard, the parameters subject to testing can be divided into 3 different categories:

- Parameters indicating combustion performance of fuels, including viscosity, cetane number for distillate marine fuel or the calculated carbon aromaticity index (CCAI) for residual marine fuel.
- Parameters indicating the composition of combustion products, such as sulphur content, ash content, carbon residue value, etc.
- Parameters indicating fuel management, such as regulations for transport and storage, composed of flash point, hydrogen sulphide, density, cloud point for distillate marine fuel and water content.

The table 1 lists the most critical parameters along with the corresponding test methods and references for residual marine fuels suitable for Bio-HFO.

Table 1. Most crucial parameters of residual marine fuels

Parameter	Unit	Limit	RMD 80	RMG 380	Test methods(s) and references
Density at 15°C	kg/m³	Max	975	991	ISO 3675 or ISO 12185
Kinematic Viscosity at 50°C	mm²/s	Max	80	380	ISO 3104
Sulphur Content	mass %	Max	statutory requirements		ISO 8754 or ISO 14596 or ASTM D4294
Flash Point	°C	Min	60	60	ISO 2719
Acid Number	mg KOH/g	Max	2.5	2.5	ASTM D 664
Total Sediment (TSE)	mass %	Max	0.1	0.1	ISO 10307-2
Carbon Residue	mass %	Max	14	18	ISO 10370
Pour Point	°C	Max	30	30	ISO 3016
Water Content	vol %	Max	0.5	0.5	ISO 3733
Ash	mass %	Max	150	150	ISO 6245

3.2 Storage stability

To study the ageing behaviour of fuels, fresh samples are aged using accelerated ageing methods. The closed system also referred to as the BigOxy ageing test bench enables thermo-oxidative rapid ageing of fuels. The Big Oxy test rig is based on the PetroOxy method (Figure 8, left) according to standard DIN EN 16091. The fuel sample is heated together with oxygen in a 500 ml volume reactor (Figure 8, right). This subjects the fuel into higher thermal stress and lead to faster thermos-oxidative ageing, that is displayed by a pressure drop (Oxygen uptake of the fuel) in the system. The pressure within the reactors of the Big Oxy test rig is continuously monitored for a period of 16 to 64 hours at 105 °C to evaluate the stability of the fuels. The aged fuel can then be checked for its properties such as viscosity, oxidation stability, water, and acid content etc to determine the extent of fuel ageing in the process.

Figure 8: Standard test method "PetroOxy" and reactor in "BigOxy" test rig.

3.3 Fuel compatibility to engine components

With the introduction of various renewable fuels, drop-in capability of the renewable fuels is of utmost importance, which implies, the fuel must be usable in the already existing technology without loss of efficiency and power output. In this regard, Tec4fuels will be conducting the hardware in the loop testing of these fuels and its blends in a complete common rail system (CoCoS) – test bench. This involves the testing of interaction of fuel injection system components of a 4-stroke marine engine with this new fuel. The hardware in the loop test bench was successfully adapted to the marine high-pressure pump operation and initial tests with the marine gas oil (MGO) were performed as benchmark.

Complete common rail system (CoCoS) is a hardware in the loop test bench which consists of all the fuel injection system components connected in a closed loop. The main difference to an engine testing is the avoidance of combustion which helps in recollecting the fuel back to the supply tank [1]. The closed loop of the test bench consists of a supply pump, fuel filter, high-pressure pump, rail, and the injector. The injector is then connected to a reactor with the help of heating block. The fuel is injected into the reactor, where the fuel spray is allowed to condense and collected back to the tank. Thus, by recollecting the fuel, it can be reused in the closed loop which helps in applying additional stress and eventually lead to fuel degradation. The testing parameters of the components are flexible to select rail pressures up to 2000 bar, and the injection timing are variable upon requirement. To emulate the real-life conditions of an atmosphere, the injector tip is heated up to higher temperatures such as 230 °C to 280 °C. Finally, the test cycle is flexing depending on the quality of the fuel or the requirement of the stress conditions on the components or the fuel [1, 2]. This flexible testing helps in identifying the compatibility of the fuel with the components which can act as a screening test before the Engine testing. The flexibility of the test to use smaller fuel volumes and quick testing times have the advantage over engine testing to save commissioning time, effort, and infrastructure requirements. Although until current project start, the testing was developed for passenger car technology and in the current project, the test method was adapted to marine 4 - stroke system and a new test bench was built for the dedicated testing in the IDEALFUEL project.

In the current project, the principle of the CoCoS is implemented to the marine engine components to check the drop-in compatibility of the IDEALFUEL. Thus, the CoCoS setup was built for the 4-stroke marine engine components. However, after contacting different suppliers regarding the criticalities of the 4-stroke engine fuel injection systems, it was concluded that most of the problems lie within the high-pressure pump such as cavitation, lubricity, etc. Thus, the CoCoS method will be built as a component specific test bench where the high-pressure pump will be tested under different conditions and an optimised test will be developed. The pump used in the current setup is Liebherr LP1 1.2-22 Gen2.1 (Max. 2 litre/minute). Figure 9 shows the P&ID of the test setup:

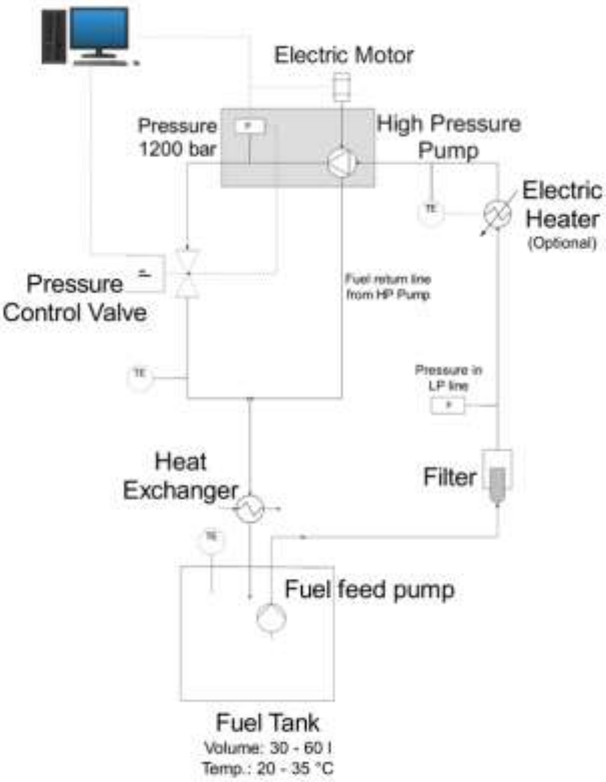

Figure 9: P&ID diagram of the IDEALFUEL test setup.

To adapt for the testing of high-pressure pump, the injector and the rail is replaced by a throttle valve and a pressure sensor. So, the fuel supply pump sends the fuel through the fuel filter to the high-pressure pump. The throttle valve generates the back pressure required for the high-pressure pump and the desired pressure is generated. This fuel is then expanded after the throttle and sent back to the tank along with the fuel return line of the high-pressure pump. The return lines are sent through a heat exchanger to keep the tank temperature below 50 °C. The compression and the expansion of the fuel generates high temperatures, and the influence of constant heat up and cool down of the fuel induces stress which lead to fuel degradation [1, 2]. Thus, the degraded fuel is also used to test the influence of degraded fuel on the components and observe the long-term compatibility of the fuel with the components. The test is also planned to run in cycles with constant ON and OFF phases to allow the cooling of tank to room temperature and, allow the high polymer molecules (formed due to fuel degradation) to sediment in the components. This could influence the functionality of the components. Thus, the method allows the use of as low as 30 litres of fuel sample per test and also helps in accelerating the testing time to nearly 100 h [2, 3]. Although further reduction of sample volumes and test times are possible with changing the experimental conditions upon requirement. Figure 10 shows the setup of the test bench: The grey high-pressure pump is attached to the motor with the help of an adapter. This adapter also helps in lubricating high-pressure pump. This high-pressure pump is then connected to the pressure sensor and then the throttle for the pressure and flow regulations.

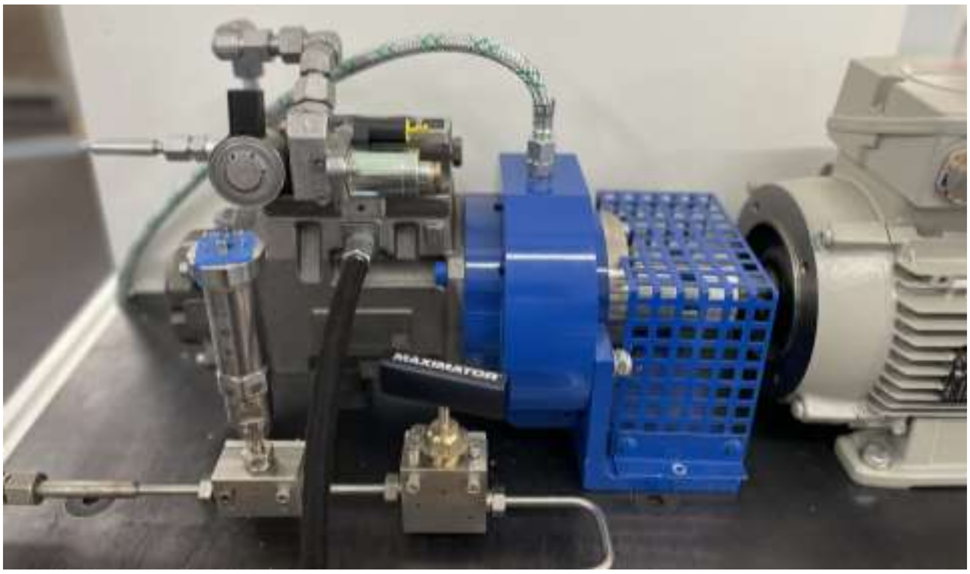

Figure 10: Test bench set-up with high-pressure pump connected to the throttle and a pressure sensor.

4 Handling relevant properties of bio-HFO

4.1 Surrogate fuel composition and fuel characteristics

Due to the unavailability of final Bio-HFO (IDEALFUEL) in the necessary volumes for the storage stability testing, a surrogate fuel has been formulated along with the support of consortium. The key components of the surrogate Bio-HFO have been determined using the GC-MS measurements of the produced lab scale Bio-HFO, from partner CSIC. A list of the components which have mass fractions above 1% are shown in Table 2..

Table 2 Reduced list of chemical species in the lignin based biofuel

Formel	Compound name	Mass Fraction
$C_6H_{10}O_3$	Pentanoic acid, 4-oxo-, methyl ester	10.28
$C_{12}H_{26}$	n-Dodecane	7.71
$C_5H_8O_2$	2(3H)-Furanone, dihydro-5-methyl-	5.06
$C_8H_{10}O_4$	3-Cyclobutene-1,2-dicarboxylic acid, dimethyl ester	2.78
$C_9H_{12}O_3$	Homovanillyl alcohol	2.65
$C_8H_{10}O_2$	2-Methoxy-5-methylphenol	2.60
$C_6H_8O_2$	1,2-Cyclopentanedione, 3-methyl-	2.48
$C_{15}H_{24}O_2$	butyl guaiacol	2.18
$C_5H_4O_2$	Furfural	2.01
$C_6H_{10}O_2$	2,5-Hexanedione	1.59
$C1_0H_{14}O_2$	methoxyphenol propyl	1.32
$C_9H_{12}O_3$	3,5-Dimethoxy-4-hydroxytoluene	1.32
$C_6H_6O_2$	2-Furancarboxaldehyde, 5-methyl-	1.22
$C_7H_{10}O_2$	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	1.19
$C_{10}H_{14}O_2$	Phenol, 2-methoxy-4-propyl-	1.12
$C_{12}H_{16}O_4$	Syringylacetone	1.05
$C_9H_{10}O_4$	Homovanillic acid	1.02

From the GC x GC-MS Analysis (WP 3) of the latest batch of biofuel produced, more than 100 components were identified and the species 4-oxo-, methyl ester, pentanoic-acid was seen to have the highest mass fraction next to n-dodecane. The other components with the highest fractions belong to following chemical groups: esters, ethers, ketones, aldehydes, acids, and alcohols and vary with respect to their properties such as flammability and toxicity. Out of these components, the constituents that influence fuel-component compatibility were selected and used to formulate the surrogate. For this formulation and the quantity of these components, their fractions in the actual Bio-HFO and viscosity has been the key parameter of reference. The Table 3 shows the components for the surrogate formulation, whereas in Table 4 the details the recipe for the surrogate bio-HFO. This surrogate then in turn was mixed with the standard Marine HFO (Heavy fuel oil) to test for drop-in compatibility and investigate the interaction with diesel.

Table 3: components for the surrogate formulation

Surrogate components	**Density [kg / l]**	**Flashpoint [°C]**	**Potential hazards**
Ethers			
Trimethylene glycol monomethyl ether	1.03 (25 °C)	110	
Esters			
Pentanoic acid, 4-oxo-, ethyl ester (Ethyl-Levulinate) (alternative chosen for	1.01 (25 °C)	94	Irritant

Surrogate components	**Density [kg / l]**	**Flashpoint [°C]**	**Potential hazards**
Pentanoic acid, 4-oxo-, methyl ester to reduce costs)			
Ketones			
2(3H)-Furanone, dihydro-5-methyl- (Valerolacetone)	1.05 (25 °C)	110.5	Toxic to environment
2,5-Hexanedione	0.97 (20 °C)	79	Irritant, carcinogenic
Aldehydes			
Furfural	1.16 (25 °C)	58	Flammable, toxic, carcinogenic
2-Furancarboxaldehyde, 5-methyl- (Methyl-Fufural)	1.11 (25 °C)	72	
Acids			
Pentanoic acid, 4-oxo- (Levulinic Acid)	1.13	98	
Vanillic acid (alternative chosen for Homovanillic acid / 2-(4-hydroxy-3-methoxyphenyl)acetic acid to reduce costs)	1.06	208	Irritant, toxic to environment
Alcohols			
2-Methoxy-4-Methylphenol (alternative chosen for 2-Methoxy-5-methylphenol which was out of stock)	1.09 (25 °C)	99	Irritant

Table 4. Surrogate bio-HFO recipe

bioHFO surrogate component	**Description**	**Volume (%)**
Surrogate components	The constituents that were most relevant for fuel-system compatibility were selected from the GC-MS results of the bio-HFO produced by VERT. These chemicals or chemicals close to their chemical structure were sourced to form the main part of the surrogate bioHFO.	57
Heavy fuel oil RMG 380	The constituents of the bioHFO which were not relevant to the fuel system compatibility were also the heavier components of the bio-HFO. These constituents of the bio-HFO was substituted by the heavy fuel oil.	42.5
Water		0.5
Total		**100**

The flashpoint of the mixtures in Table 4 were experimentally evaluated per the ISO 2719. The results are shown in Table 5. As can be observed from the results, all the three blends show flashpoints above the minimum required 60°C limit.

Table 5 Flashpoint measurements of different blends

Fuel	**Flash point in °C (DIN ISO 2719)**
Bio HFO (Surrogate mixture with RMG 380) [1]	85°C
Bio HFO + 80 % MGO (Surrogate mixture with MGO)	66°C
Pure Surrogate + n-dodecane [3]	65.8°C

Although the flashpoints of all three mixtures are above the required limit, an additional evaluation of evaporation behavior of the volatile species in Table 3 should also be considered to ensure that enrichment of the atmosphere above the lower explosion limit does not take place. In addition to the explosion limits, danger in terms of spread of possible toxic gases must also be considered. It is however to be noted that heating of the fuel to temperatures that are normal for heavy fuels will cause evaporation of the more volatile components like furfural which may cause the headspace atmosphere in the fuel tank to be flammable, as is observed by comparison of the LEL which intersects the curve of furfural at around 60°C, whereby the HFO may be heated to temperatures around 72°C. The autoigntion temperatures of the major species are also seen to lie much higher than the temperatures that would be normally encountered in the spaces before the engine.

4.2 Storage stability

Figure 11 shows the ageing behaviour of the surrogate bioHFO and its blend with MGO.

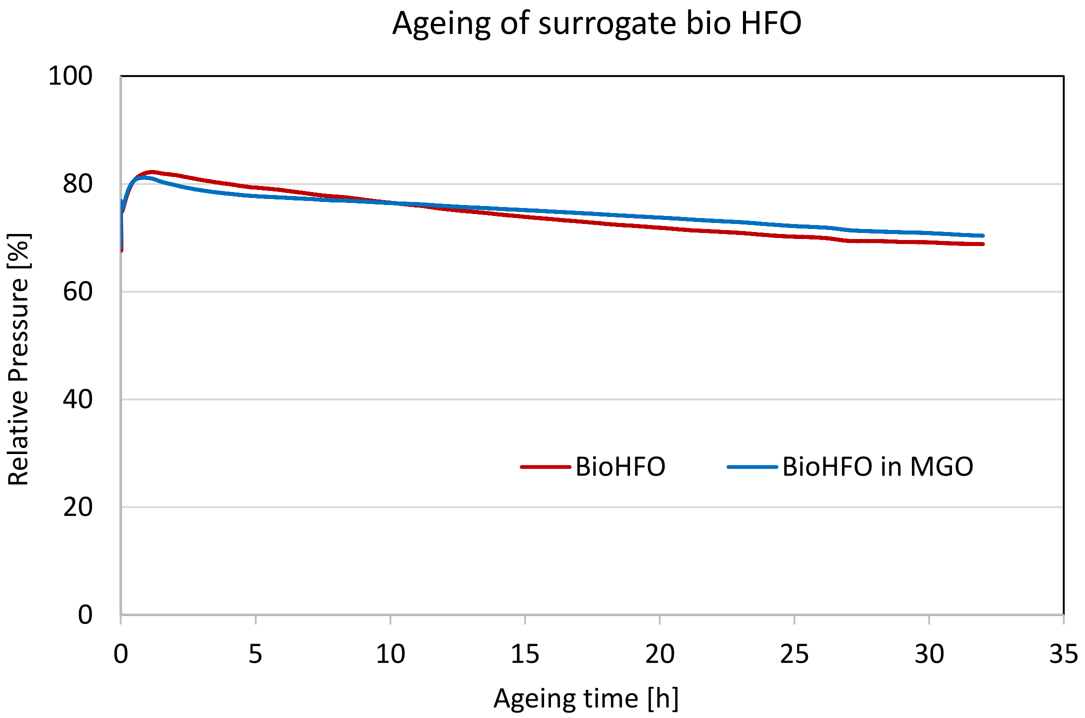

Figure 11. Ageing behaviour of surrogate bioHFO and its blend with MGO

A pressure drop of approximately 15 % was observed during a 32 hour ageing period. After the 32 hour ageing in the Big oxy reactor, both the fuels had changed physically with a separation of a low viscosity and high viscosity phase. This indicates that the oxidation has caused the formation of ageing products (long chain polymers) that can sediment in the surrogate fuel samples. Comparing pressure curves of MGO and Bio-HFO, the Bio-HFO tend to drive the oxidation of the fuels as blends.

4.3 Interaction to engine components

In the test with 10 % Bio-HFO blend, no significant abnormalities have been observed inside the high pressure pump, (Figure 12). Thus, no functional problems have also been observed. Although in Figure 13, the fuel has shown sedimentation in the tank and on the low pressure pump. However, the sediments have been filtered out through the filter before the high pressure pump and no influence on the high pressure pump was observed. Thus in the final formulation the usage of additive to avoid the sedimentation in the tank is suggested.

Figure 12: The High pressure pump components from test run with 10 % Bio-HFO.

Figure 13: The fuel sediments in the tank and on the low pressure pump from test run with 10 % Bio-HFO.

5 References

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Acknowledgement

The author(s) would like to thank the partners in the project for their valuable comments on previous drafts and for performing the review.

Project partners:

#	Partner short name	Partner Full Name
1	TUE	Technische Universiteit Eindhoven
2	VERT	Vertoro BV
3	T4F	Tec4Fuels
4	BLOOM	Bloom Biorenewables Ltd
5	UNR	Uniresearch B.V.
6	WinGD	Winterthur Gas & Diesel AG
7		(Formerly SeaNRG, is now GOODFUELS #12)
8	TKMS	Thyssenkrupp Marine Systems GMBH
9	OWI	OWI – Science for Fuels gGmbH
10	CSIC	Agencia Estatal Consejo Superior De Investigaciones Cientificas
11	VARO	Varo Energy Netherlands BV
12	GOOD	GoodFuels B.V.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 883753