- IDEALFUEL -

Lignin as a feedstock for renewable marine fuels

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Deliverable Report

D4.3 – Storage stability of Bio-HFO fuels

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Written By	Sangeetha Ramaswamy (OWI), Chaimae Ait Tararint (OWI)	28-04-2024
Checked by	Sangeetha Ramaswamy (OWI)	29-04-2024
Reviewed by	Chandra Kanth Kosuru (T4F)	30.04.2024
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Publishable summary

The primary aim of 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 extremely low sulfur content, allowing it to be seamlessly integrated as a drop-in fuel in the existing maritime fleet.

The Task 4.3 focuses on evaluating the potential application of the developed Bio-HFO and their blends in marine engines concerning storage, aging, and degradation behavior (T4.3.1). Furthermore, the impact of aging on the compatibility of the fuels with these engine elements is studied. This deliverable presents an overview of the rapid aging trials conducted on bio-HFO fuels.

Two rapid ageing test rigs were used for the investigation of storage stability. One of the test rigs based on the principal of Rancimat was developed and validated as a part of the IDEALFUEL project. Due to the lack of availability of sufficient amounts of fuels, surrogate fuels were developed and tested based on the results from the GC-MS analysis of the produced lab scale Bio-HFO. The initial ageing trials have shown that the bio-HFO undergoes oxidation and separates into phases upon ageing. Further work should involve the analysis of the aged fuels for the investigation of the nature of the ageing products such as water, acids, which could have a negative effect on the fuel –material compatibility and their storage. Furthermore, the impact of additives that enhance the storage stability needs to be investigated.

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1 Introduction

The primary aim of 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 extremely low sulfur content, allowing it to be seamlessly integrated as a drop-in fuel in the existing maritime fleet.

The Task 4.3 focuses on evaluating the potential application of the developed Bio-HFO and their blends in marine engines concerning storage, aging, and degradation behavior (T4.3.1). Additionally, the investigation aims also to assess the compatibility of the fuel blends with essential components of marine engines that encounter the fuels during their application. These components include materials like polymers and metals (T4.3.2), as well as parts such as fuel pumps, filters, injectors (T4.3.3), and engine oil (T4.3.4). Furthermore, the impact of aging on the compatibility of the fuels with these engine elements is studied. This deliverable presents an overview of the rapid aging trials conducted on Bio-HFO fuels, focusing on their significant chemical and physical properties as part of T4.3. Additionally, it outlines the BigRanci method which was developed as a part of this project.

2 Methods and Results

2.1 Materials

Marine fuels are primarily classified into two categories: distillate marine fuel and residual marine fuel. Distillate marine fuel represents a lighter fuel oil that undergoes further refinement compared to heavier oils. On the other hand, residual fuel, is the remaining oil after distilling out the lighter grade components. The ISO 8217 standard describes the properties of these marine fuels, defining uniform conditions globally. In the initial stages of the project, the properties of the novel biofuels were uncertain. Therefore, two types of marine fuels were chosen as baseline references respectively: a distillate fuel, marine gasoil (MGO), also known as DMA in ISO 8217, and heavy fuel oils (HFO) RMD 80 and RMG 380. Additionally, considering the renewable biofuels perspective, the used cooking oil methyl ester (UCOME) was also selected as another benchmark fuel. Table provides a comprehensive list of all the tested baseline fuels.

Table 1: Summary of the tested fuels.

Fuel	Fuel category	Label
Baseline fuels	Distillate fuel / Light fuel oil	Marine gas oil (MGO)
		Used cooking oil methyl ester (UCOME)
	Residual fuel	RMD 80
		RMG 380
Surrogate Bio-HFO	see details below in 2.1.1	Bio-HFO
	Bio-HFO - MGO blend (20:80)	Bio-HFO+MGO

2.1.1 Surrogate fuel composition

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 below.

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 (WP3) of the latest batch of bio-fuel 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 1 shows the components for the surrogate formulation, whereas in Table 2 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
<u>Ethers</u>
Trimethylene glycol monomethyl ether
<u>Esters</u>
Pentanoic acid, 4-oxo-, ethyl ester (Ethyl-Levulinate) (alternative chosen for Pentanoic acid, 4-oxo-, methyl ester to reduce costs)
<u>Ketones</u>
2(3H)-Furanone, dihydro-5-methyl- (Valerolacetone)
2,5-Hexanedione
<u>Aldehydes</u>
Furfural
2-Furancarboxaldehyde, 5-methyl- (Methyl-Fufural)
<u>Acids</u>
Pentanoic acid, 4-oxo- (Levulinic Acid)
Vanillic acid (alternative chosen for Homovanillic acid / 2-(4-hydroxy-3-methoxyphenyl)acetic acid to reduce costs)
<u>Alcohols</u>
2-Methoxy-4-Methylphenol (alternative chosen for 2-Methoxy-5-methylphenol which was out of stock)

Table 4. Surrogate bio-HFO recipe

Bio-HFO 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 Bio-HFO.	57
Heavy fuel oil RMG 380	The constituents of the Bio-HFO 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**

2.2 Methods

To study the ageing behaviour of fuels, fresh samples are aged using accelerated ageing methods. Two accelerated ageing test rigs were used with an open and a closed system.

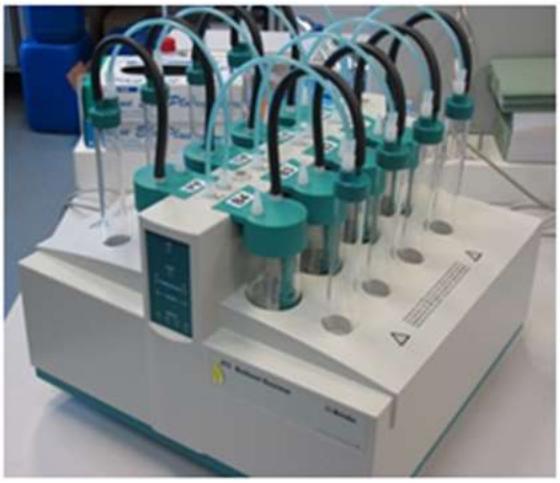
2.2.1 Big Oxy

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 1, left) according to standard DIN EN 16091. The fuel sample is heated together with oxygen in a 500 ml volume reactor (Figure 1, 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 1: Standard test method "PetroOxy" and reactor in "BigOxy" test rig.

2.2.2 BigRanci

The BigRanci test bench (Figure 2 right) has been developed in the IDEALFUEL project to accelerate the fuel oxidation and predict its degradation properties during extended storage periods. Furthermore, Bigranci would provide the aged sample to determine the properties of the fuel, such as viscosity, acid number, and water content in aged condition. The fuel samples are subjected to faster oxidation in the BigRanci test rig, facilitating the determination of aged fuel quality based on the analysis of fuel properties. In contrast to the BigOxy system, BigRanci operates by bubbling of air through the fuel, providing inducing forced oxidation of the fuels. Furthermore, the fuel can be easily sampled and analyzed at any point throughout the entire oxidation process, due to being an open system unlike BigOxy. The test rig is based on the Rancimat principle [EN 15751]. In the Rancimat test (Figure 2 left), fuel is heated up to 110 °C and then air is bubbled through the fuel. After passing the air through the fuel, the air then is lead through distilled water where the electric conductivity of the water is measured. During fuel aging, the oxygen in the air forms low molecular acids, which are carried into the water phase, and change the water's conductivity.



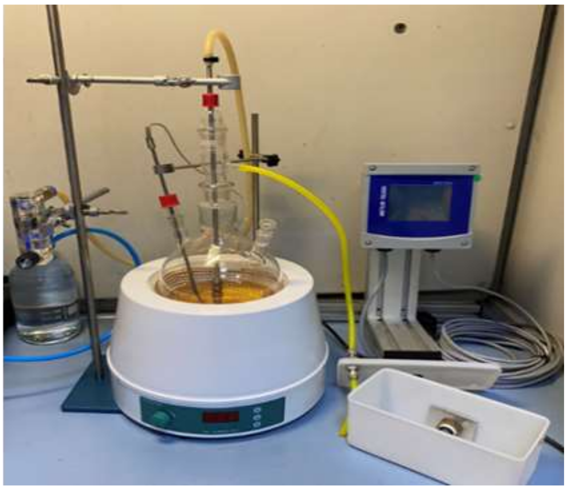


Figure 2. (left) Standard test method Rancimat, (right) Big Ranci test rig developed in the IDEALFUEL project

During a 24-hour test run at 110°C, the conductivity changes in the test fuel (7% FAME in heating oil) exhibit similarities to those observed in the commercial Rancimat device, which measures an induction time and provides insights into the oxidation stability of fuels. Various blends of Bio-HFO with baseline fuels will also undergo rapid oxidation testing in the BigRanci system. These findings serve as indicators for establishing appropriate storage and shipping conditions for the fuel, as well as determining the maximum allowable storage duration.

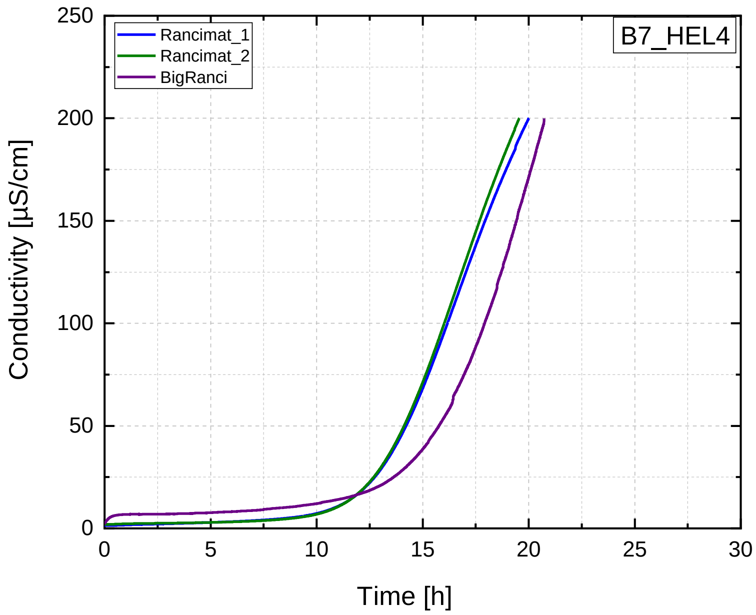


Figure 3. Ageing trials of Heating oil with Big Ranci test rig validated with the Rancimat method

3 Results and Discussion and Conclusions

3.1 Baseline Fuels

One of the aims of these trials was to check if the test rig is compatible with marine fuels esp., HFO. The baseline fuels MGO, UCOME, HFO RMD 80 and HFO RMG 380 were aged in the Big Oxy reactor test rig. The pressure-time curve of HFO RMG 380 is illustrated in Figure 4. Three test runs were completed, and it was found that the ageing behaviour of the three samples were similar.

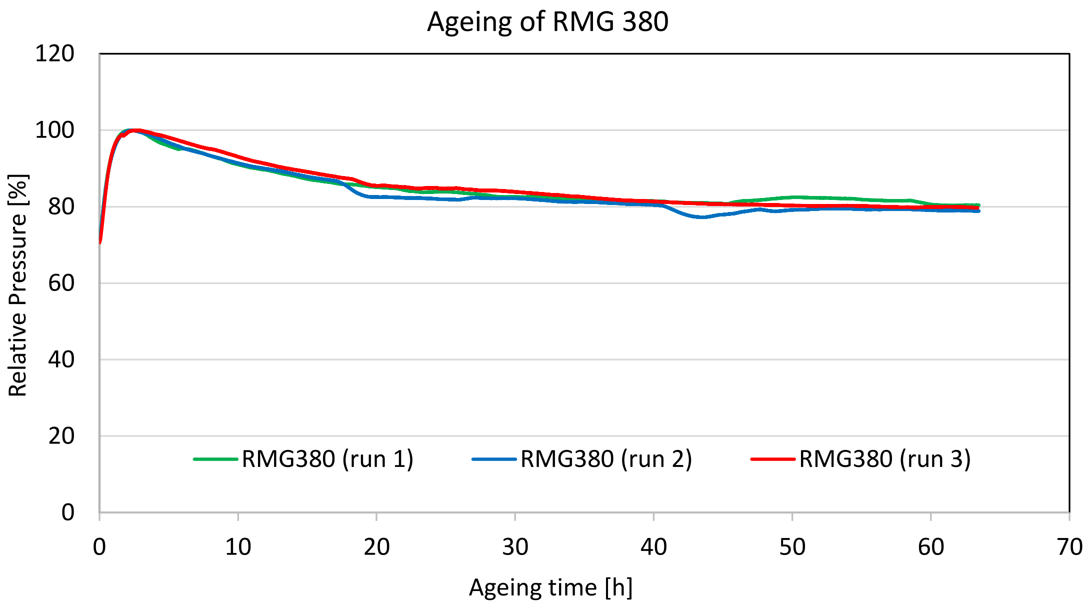


Figure 4 Ageing trials of RMG 380 – repeatability

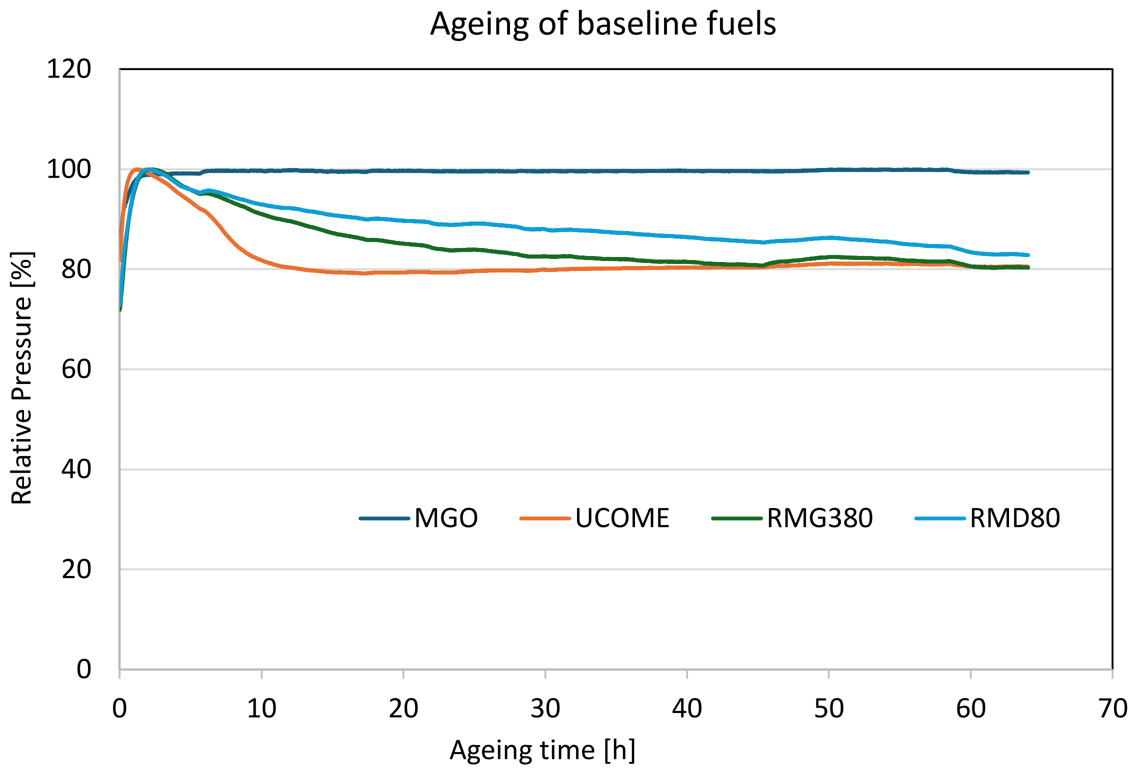


Figure 5. Ageing behaviour of baseline fuels – MGO, UCOME; RMG380, RMD80

To investigate and compare the ageing behaviour of MGO, UCOME, RMG380 and RMD80, an accelerated ageing of 64 hours was employed. The decrease in pressure indicates fuel oxidation. Notably, while MGO exhibits no pressure drop, in contrast to the other fuels tested, RMD80 shows a slower pressure decrease compared to UCOME and RMG380. This indicates that MGO has a better oxidation stability than the other baselines fuels. On the other hand, UCOME shows the fastest pressure drop, indicating rapid oxygenation and a lower storage stability.

The baselines fuels aged using Big-Oxy were analysed for properties such as acid content, water content, and viscosity. The change in properties of fresh and aged baselines fuels serve as a benchmark for the degradation performance for the bio HFOs. Both distillates (MGO and UCOME) and residual fuels (HFO RMD 80 and HFO RMG 380) have been chosen as baseline fuels and the aged fuels have been tested according to standard ISO 8217. Figure 5 and Figure 6

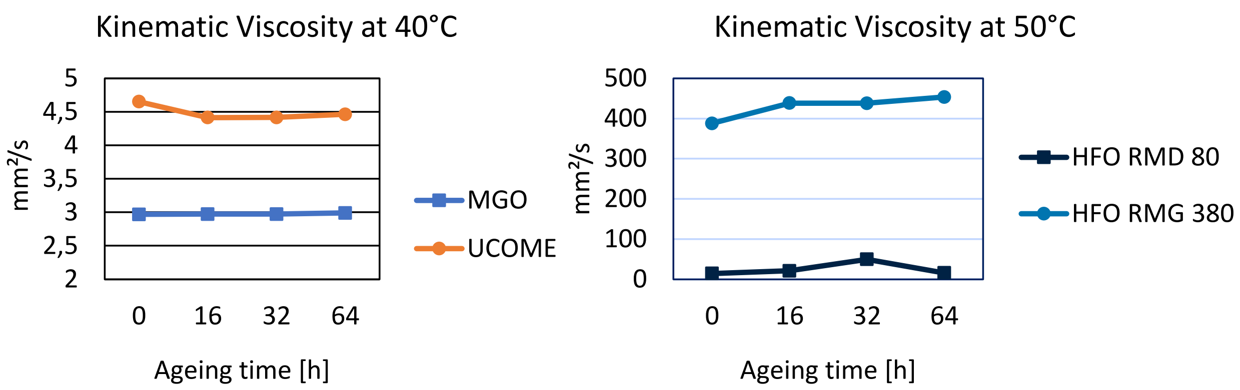


Figure 6. Kinematic viscosity of fresh v/s aged fuels

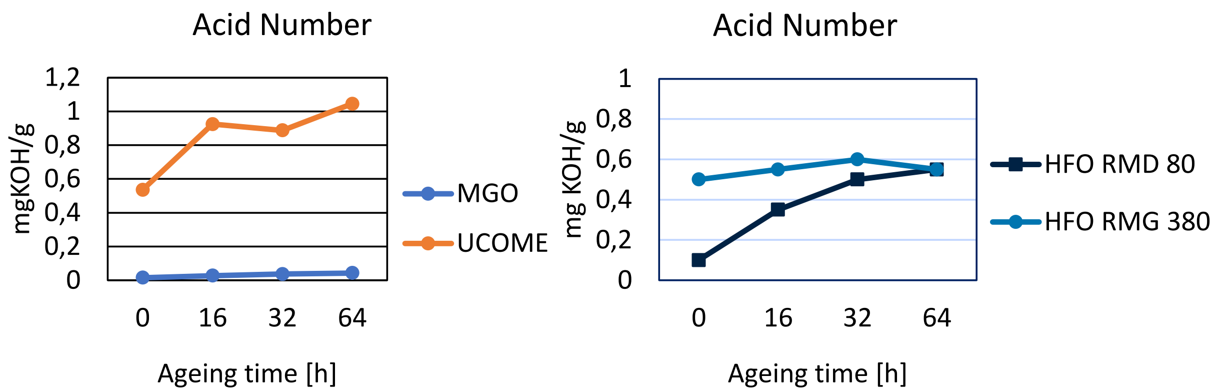


Figure 7. Acid number of fresh v/s aged fuels.

The kinematic viscosity of MGO remains constant with ageing, whereas for UCOME it decreases with ageing. Furthermore, for UCOME, the acid number increases with ageing and exceeds the specified value of 0.5 mgKOH / g for aged samples. Because UCOME can be quickly oxidized in the air, its storage time should be as short as possible. The other fuels are in compliance with the limit specified by ISO 8217.

3.2 Bio-HFO Fuels

Figure 8 shows the ageing behaviour of the surrogate Bio-HFO and its blend with MGO described in Section 2.

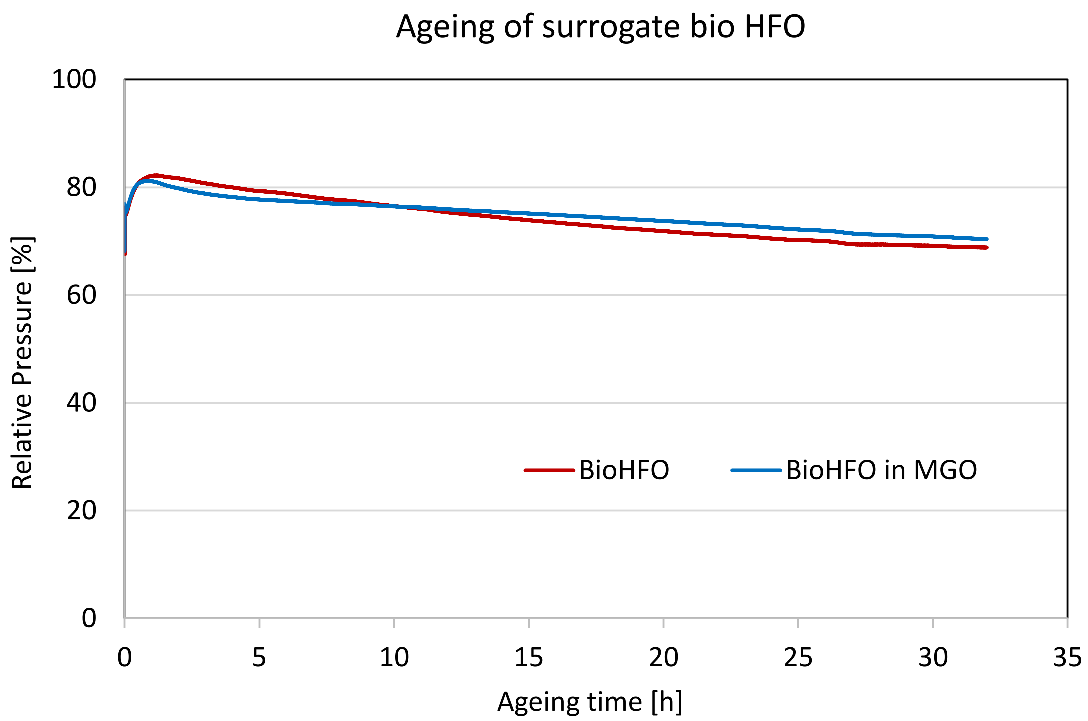


Figure 8. Ageing behaviour of surrogate Bio-HFO and its blend with MGO

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 Conclusions and future work

The current deliverable documents the results of task 4.3 which investigates the bio-HFO and baseline marine fuels and their blends with respect to their ageing behaviour and storage stability. The effect of ageing on the fuel properties of the baseline fuel is also studied. Two rapid ageing test rigs were used for the investigation of storage stability. One of the test rigs based on the principal of Rancimat was developed and validated as a part of the IDEALFUEL project. Due to the lack of availability of sufficient amounts of fuels, surrogate fuels were developed and tested based on the results from the GC-MS analysis of the actual Bio-HFO fuel. The initial ageing trials have shown that the surrogate Bio-HFO undergoes oxidation and separates into phases upon ageing. Further work should involve the analysis of the aged fuels for the investigation of the nature of the ageing products such as water, acids, which could have a negative effect on the fuel – component compatibility. Furthermore, the impact of additives that enhance the storage stability needs to be investigated.

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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.

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