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E-TANDEM - Deliverable report

Deliverable 3.1-Fuel analytics and blending behaviour

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Project summary

E-TANDEM's ambition is to unlock an efficient and direct production of a new higher-oxygenate diesel-like e-fuel for the marine and heavy-duty transport sectors. This oxygenated fuel is directly produced from water, CO_2, as the sole carbon source, and renewable power as the sole energy input, in a once-through hybrid catalytic conversion process integrating three major catalysis branches: (1) high-pressure electrocatalysis *syngas* production coupled to a tandem catalytic e-syngas conversion, encompassing (2) thermocatalysis with solid catalysts and (3) chemocatalysis with molecular

complexes. The project will demonstrate the new e-fuel production process at bench-scale and assess its capacity to cope with fluctuating energy inputs.

Executive summary

Carbon-neutral, high-energy density e-fuels are critical to de-fossilize the legacy fleet for all ICE-based applications and are in particular mandatory for long-haul, heavy-duty road, marine, and aviation transport, where high energy density solutions are required. The introduction of e-fuels for rapid market penetration faces several challenges. Apart from the higher cost of these products, additional challenges arise from the compatibility of existing and new applications, which have been designed on the assumption that existing standards will be met even if the source of the energy carrier is sustainable, which is generally not the case. Ideally, these new fuels could be blended with existing fuels, allowing a transition from fossil fuel to a sustainable product in the future.

The E-TANDEM project develops and validates, at bench scale, the first direct process for the selective production of carbon-neutral higher oxygenate e-fuels (HOEF) as a replacement for fossil diesel. The focus is on heavy-duty, hard to abate transport sectors, particularly waterborne transport, but also heavy-duty road transport. This mildly oxygenated fuel is composed of higher (C_{5+}), aliphatic alcohols and their derivative aliphatic ethers, and it is directly produced from CO_2 as the sole carbon source, and renewable power as the sole energy input, in a once-through hybrid catalytic conversion process integrating three major catalysis branches: electrocatalysis syngas production, coupled to a tandem catalytic e-syngas conversion encompassing thermocatalysis with solid catalysts and chemocatalysis with molecular complex catalysts. The project demonstrates the new e-fuel production process at bench-scale and assess its capacity to cope with fluctuating energy inputs.

This deliverable report D3.1 emerges from R&D activities performed in work-package (WP) 3. It summarizes the results from studies of the physicochemical properties of surrogate fuels mixtures in two HOEF realizations, i.e. (i) a mixture of higher (C_4-C_9) alcohols and (ii) a mixture of higher (C_8-C_{18}) ethers, which have been developed in WP2 from commercially available neat alcohol compounds, while closely simulating compositions obtained through the tandem catalysis e-fuel production concept developed in the project. Emphasis is placed on the blending behaviour of the HOEF with state-of-the-art marine gas oil (MGO), to ascertain the drop-in potential of the new e-fuel compositions. Physicochemical characteristics of the neat HOEF and its blends with MGO are determined and discussed with the aim to identify compliance or deviations from relevant fuel norms which are effective in the EU for waterborne transport (ISO 8217) and heavy-duty road (EN590) diesel fuels.

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Abbreviations & Definitions

Abbreviation	Explanation
CP	Cloud Point
CFPP	Cold Filter Plugging Point
FAME	Fatty acid methyl esters
HIL	Hardware-In-the-Loop test
HOEF	Higher-oxygenate e-Fuel
HVO	Hydrogenated Vegetable Oil
ICP-OES	Inductively coupled plasma optimal emission spectroscopy
GS-MS	Gas Chromatography with combined Mass Spectrometer
MGO	Marine Gas Oil
NHOC	Net Heat of Combustion
XRF	X-ray fluorescence

Item	Definition
DMA	Marine Gas Oil with low sulphur content, distilled and high Quality
DMB	Marine Gas Oil with more remnants as DMA
DMX	Often referred to as a special light distillate, DMX is designed for high-speed engines that require fuels with lower viscosity and density.
DMX	The heaviest among the distillates, DMZ is used primarily for emergency engines and some types of medium-speed engines

1 Introduction

This report relates to Work Package 3 (WP3) within the E-TANDEM project. WP3 deals with the characterization of the higher oxygenate e-fuel (HOEF), the analysis of their blending behaviour with base, state-of-the-art fuels, as well as the study of system compatibility aspects of HOEF and its blends.

The research summarized in this report thus covers the need to provide an early assessment of the physico-chemical properties of the herein proposed HOEF e-fuel, regarding its use as a diesel replacement in applications of marine and heavy-duty transport, as well as to assess the effects of its mildly oxygenated character on the tailpipe emission profile.

Specific goals set for WP3 are:

1. To physico-chemically characterize the higher oxygenate HOEF e-fuel in its two realizations, i.e. mixture of higher aliphatic alcohols (with hydrocarbons) or mixture of higher ethers and study its blending behaviour with baseline fuels.

2. To evaluate the ignition behaviour and soot formation characteristics of selected HOEF e-fuel formulae.

3. To assess the fuel-system compatibility for HOEF and its blends: interaction with materials, lubricants, etc., in current-fleet systems.

Specifically, this deliverable report D3.1 addresses the first goal, while the goals 2 and 3 shall be reported in upcoming reports D3.2 and D3.3, respectively.

The present report is organized as follows:

Chapter 2 describes norm-related considerations and method-selection, as well as the experimental methodology applied for fuel characterization tasks.

In Chapter 3 the experimental results are provided and discussed.

Finally, in Chapter 4, conclusions and recommendations are given.

2 Methods

This chapter outlines the norm-related considerations and the selected experimental methodologies used for the physico-chemical characterization of HOEF e-fuel. Section 2.1 provides background considerations, while section 2.2 describes the procedures. Where applicable, further data analyses are given in section 2.3.

2.1 Background

Within the project time planning the final e-fuel from the production process will only become available near the end of the project and at volumes which are insufficient to perform some of the fuel characterization tests and blending analyses which are of concern in this report. Therefore, so-called e-fuel surrogates have been produced in the context of the project's WP2, and provided for activities in WP3, early in the project. The background and production details on the surrogate HOEF in a multi-liter scale have been detailed in Deliverable report D2.1.

Two mixtures of known composition have been produced, as surrogates for two different realizations of the HOEF e-fuel:

(i) A first mixture, hereafter referred to as "alcohol surrogate", which consists of a mixture of linear and branched alcohols in the carbon chain-length range of C_4-C_9; and

(ii) A second mixture, hereafter referred to as "ether surrogate", which consists of a mixture of C_8-C_{18} ether derivatives and which has been obtained via catalytic dehydration of the alcohol mixture in the "alcohol surrogate".

These mixtures have been produced from commercially available alcohol compounds in neat form. In the first case just by blending; in the second instance via catalytic dehydration of higher alcohols to higher ethers. Moreover, the composition of the "alcohol surrogate" mixture has been designed to mimic closely that obtained in lab-scale tests of the e-fuel production process developed in E-TANDEM, both in terms of alcohol chain-length distribution as well as in terms of the molar ratio of linear (*n*) to branched (*iso, 2-methylated*) alcohols at each specific chain length.

With the objective of assessing the potential of these e-fuel compositions to be blended with existing fuels, as well as to comply (in neat or blended forms) with existing fuel regulations, which is a critical aspect for a fast adoption the following two reference standards have been considered as relevant:

(i) ISO 8217 norm for marine diesel (waterborne transport) [1]; and

(ii) EN590 norm for automotive diesel (heavy duty road transport) [2].

This approach enables early feedback on the e-fuel properties and provides an effective means for potentially guiding the optimization of the production process for the final e-fuel product.

2.2 Procedures

The above fuel standards specify key fuel properties that must be met for compatibility with modern engines. In the case of the MGO (Marine Gas Oil) standard, several grades are distinguished, each with its own set of requirements:

DMA Marine Gas Oil with low sulphur content, distilled and high quality;

DMB Marine Gas Oil with more remnants than DMA;

DMX Often referred to as a *special light distillate*, DMX is designed for high-speed engines that require fuels with lower viscosity and density;

DMZ The heaviest among the distillates, DMZ is used primarily for emergency engines and some types of medium-speed engines.

Herein, DMA was selected as the relevant fuel grade, given that it fits most ship vessel types. Furthermore, it reflects the maritime industry's broader shift towards more environmentally friendly operations, especially with the looming shadow of tighter global emission standards. [3] It should be noted that not all specifications outlined in the above standards were analysed. This decision was based on considerations of project efficiency as well as the limited quantity of surrogate fuel available. Project efficiency, in this context, refers to avoiding analyses that are unlikely to yield meaningful or relevant results.

In the following, justifications are provided for the exclusion of specific fuel characteristics listed in the ISO 8217 norm for marine gasoil from our study.

- ***CCAI (Calculated Carbon Aromaticity Index):*** this index is derived from other properties, like density and kinematic viscosity, which have been included in the analysis. CCAI was originally developed as an indicator of ignition performance. Therefore, this aspect is considered in greater detail in task 3.2 of this project and will be reported in an upcoming deliverable report D3.2.

- **Sulphur content (maximum mass 1%):** fuel characterization is performed on surrogate fuels. The "alcohol surrogate" is produced from high-purity alcohol compounds. Therefore, it is sulphur-free. For the "ether surrogate", however, it was realized that sulphur may be leached out of the acidic resin catalyst applied for ether production. Therefore, sulphur content has become of significance for this specific surrogate e-fuel, and it was specifically addressed in sulphur analysis (see chapter 3).

- **Hydrogen sulfide (H_2S) content:** this parameter is excluded from the analysis as the surrogate e-fuels are produced from high-purity alcohol compounds and there is no source of H2S during the surrogate formulation and synthesis.

- **Flash point:** this is considered a combustion behavior-related parameter and therefore it will be covered in an upcoming deliverable report D3.2.

- **Total sediment by hot filtration**: For MGO, the standard states that this parameter is not of concern if a visual inspection of the fuel is performed and its appearance is clear and bright. Sediment is not expected to be of concern with the surrogate fuels studied herein.

- **Total sediment – Aged:** this is excluded for the same reasons listed above for the total sediment by hot filtration.

- **Fatty acid methyl ester(s) (FAME) content:** the analysis is performed on surrogate fuels formulated from pure compounds. These do not include any FAME; therefore, it can safely be assumed that FAME content is null.

- **Carbon residue**: the analysis is performed on surrogate fuels formulated from pure compounds. These do not include any solid carbon residue; therefore, it can safely be assumed that the content of carbon residue is negligible.

- **Vanadium (V) content**: there is no requirement on vanadium content for distillate marine fuels (including DMA), only for residual marine fuels. Furthermore, the analysis is performed on surrogate fuels formulated from pure compounds. These do not include vanadium compounds; therefore, it can safely be assumed that the content of vanadium is null.

- **Sodium (Na) content:** there is no requirement on sodium content for distillate marine fuels (including DMA), only for residual marine fuels. Furthermore, the analysis is performed on surrogate fuels formulated from pure compounds. These do not include sodium compounds; therefore, it can safely be assumed that the content of vanadium is null. It is noted, however, that an ICP-OES analysis is performed as part of the work in task 3.3 and therefore addressed in upcoming report D3.3.

- **Aluminum (Al) plus silicon (Si) content**: there is no requirement on Al+Si content for distillate marine fuels (including DMA), only for residual marine fuels. Furthermore, the analysis is performed on surrogate fuels formulated from pure compounds. These do not include aluminum or silicon compounds; therefore, it can safely be assumed that the content of Al+Si is null. It is noted, however, that the ICP-OES is performed as part of the work in task 3.3 and therefore addressed in upcoming report D3.3.

- **Ash content**: from the formulation/production method applied to obtain the surrogate fuel mixtures it is safe to assume the presence of ash is negligible.

- **Used lubricating oil (ULO):** There is no requirement for this parameter in distillate marine fuels (including DMA); it applies only to residual marine fuels. Additionally, the analysis was conducted on surrogate fuels formulated from pure compounds, which do not contain any used lubricating oils (ULO). Therefore, the presence of ULO can be considered negligible.

It is also noted that this requirement is further specified in terms of calcium, zinc, and phosphorus content. These elements are partially covered by the ICP-OES analysis conducted under Task 3.3 and are addressed in detail in Report D3.3.

In the following, justifications are provided for the exclusion of specific fuel characteristics listed in the EN590 norm for automotive diesel from our study.

- **Cetane number**: this parameter is considered related to the fuel's combustion behavior and therefore covered as part of the upcoming report D3.2.

- **Cetane index**: this parameter is considered related to the fuel's combustion behavior and therefore covered as part of the upcoming report D3.2.

- **Polycyclic aromatic hydrocarbons (PAH) content**: the analysis is performed on surrogate fuels formulated from strictly aliphatic pure compounds. These do not include PAH compounds and the latter are not considered to form during the ether surrogate fuel production; therefore, it can safely be assumed that the content of PAH is negligible.

- **Manganese (Mn) content**: the analysis is performed on surrogate fuels formulated from pure compounds. These do not include manganese compounds; therefore, it can safely be assumed that the content of Mn is negligible. It is noted, however, that an ICP-OES analysis is performed as part of the work in task 3.3 and it will be discussed as part of upcoming report D3.3.

- **Coke residue**: from the production method applied to obtain the surrogate fuels it is safe to assume coke presence is negligible.

Table 2.1 shows a summary of the different fuel physico-chemical parameters listed in the relevant norms and considered herein, the methods for their experimental determination, as well as indications as to the limits set in the corresponding norms.

Table 2.1 Overview on the different physico-chemical fuel parameters listed in the relevant norms, i.e. ISO 8217 for Marine Gasoil and EN 590 for Automotive Diesel, and considered herein, the methods for their experimental determination, as well as indications as to the limits set in the corresponding norms.

Property	Unit	Standardardized Method	Method applied	MGO ISO 8217 DMA	**Diesel EN 590**
Kinematic viscosity @ 40 °C	mm^2/s	ISO 3104	V	≥ 2; ≤6	≥ 2; ≤4.5
Density @ 15 °C	kg/m^3	ISO 3675 or ISO 12185	V	≤890	≥ 820; ≤845
Acid number	mg KOH/g	ASTM D664	ISO 14104	≤ 0,5	-
Corrosive effect on copper (3h @ 50 °C)	Corrosion grade	EN ISO 2160	V	-	Class 1
Oxidation stability	g/m^3 min	ISO 12205	V ISO 16091	≤ 25	≤ 25
Cloud point	°C	EN 23015	V	≤ -16	≤ -10
CFPP (Cold Filter Plugging Point)	°C	EN 116	V		≤ -20
Pour point	°C	ISO 3106	V	≤ -6	-
Water content	mg/kg	ISO 3733 (MGO) EN ISO 12937 (Diesel)	V	≤ 200 (see bullet point below)	≤ 200
Appearance	-	visual	ASTM D4176	Clear & bright	-
Total contamination	mg/kg	DIN 12662	V	-	≤ 24
Distillation (*v*/*v*) collected @ 250 °C (*v*/*v*) collected @ 350 °C 95% (*v*/*v*) collected @	 % % °C	EN ISO 3405 EN ISO 3924	V	 - - -	 ≤ 65 ≥ 85 ≤ 360
Lubricity	µm	EN ISO 12156-1	V	≤ 520	≤ 460
Net heat of Combustion	MJ/kg	-	ASTM D 240	-	-

In certain instances, the standardized methods referenced by the fuel standards differ from the measurement methods applied in this project. These deviations are primarily due to considerations associated to the availability of instrumentation and analytical facilities. The rationale for these methodological choices is explained and justified in detail below.

- The **kinematic viscosity and density** are determined in the same test device, in which the temperature is varied for a given range.

- **Acid number**: both fuel standards refer to methods which rely on the acid-base titration with potassium hydroxide (KOH), but use a different solvent approach [4]. ASTM D664 uses a mixture of toluene, isopropanol and water (125 mL); it requires a blank titration to ensure accuracy. ASTM D664 is defined for petroleum products. ISO EN 14104 uses a mixture of ethanol and diethyl ether solvents, which are less toxic. There is no need for a blank titration but it requires solvent neutralization with KOH in the presence of phenolphthalein as a pH-indicator. ISO 14104 is based on method EN ISO 660, which focuses on fuels containing FAME. For this project ISO 14104 is seen as equivalent to ASTM D664, yet, more readily available. However, at some point also ASTM D664 is performed for quality assurance reasons (see next chapter for more details).

- **Oxidation stability**: In this project, two different methods were used to determine the fuel´s oxidation stability. From the MGO-standard the ISO 12205 method is referred to in the norm. However, this would require fuel volumes which are not commensurate with the limited availability of surrogate e-fuels in this study. Therefore, often only the ISO 16091 method, with lower fuel volume requirements, has been performed.

- **Cloud point:** the MGO fuel grade DMX has been considered for this parameter. For the DMA grade, the parameter is only required to be reported, with the note that the purchaser should ensure its suitability based on the ship's design and intended voyage. Regarding the norm for automotive diesel, the lowest-class cloud point value was used as a minimum reference for arctic climates, given that no specific requirement is established for moderate climates.

- **Cold Filter Plugging Point (CFPP):** the highest-class F value for Diesel has been taken as maximum value for a moderate climate.

- **Water content**: The MGO standard refers to ISO 3733, whereas the Diesel standard refers to EN ISO 12937 tests, respectively. Here the EN ISO 12937 has been adopted, since it is more readily available.
  For the MGO standard (ISO 8217) no water content testing is required, provided that the fuel's visual appearance is clear and bright. The value set here is only required in case the fuel is dyed and not transparent.
  In the Diesel standard (EN 590) the unit selected to express water content is % (m/m), with 0.02% being equivalent to 200 mg/kg.

- **Appearance**: No specific standardized methods is referred to in the MGO norm on this topic, except a direct visual test. However, in this project the standard ASTM D4176 has been adopted, which is

a test based upon visual judgement using a card with lines and standard approved photographs for comparison. A minor deviation with respect to the standardized method needs to be noted, though: a somewhat narrower cylinder glass vessel (28 mm instead of about 100 mm indicated in the standard method) has been used, given the limited availability for some of the surrogate fuels and their blends with MGO at the time this test has been performed. Rather, it was preferred performing the test for all fuels with the same glass diameter. However, in cases where fuel availability sufficed, the measurement was repeated using a 100 mm-wide cylinder glass vessel, for comparison. The result is a haze level rating from 1 (bright and clear) up to 6 (densest haze), as well as a darkness/color indication.

- **Net heat of Combustion**: The MGO standard provides a formula for calculating specific energy for both residual and distillate fuels, based on parameters such as density, water content, ash content, and sulphur content. However, no specific minimum or maximum value is required. This aspect is discussed in more detail in Chapter 3.

2.3 Data Analysis

Most of the analyses performed yield direct numeric results, which are simply transferred into a consolidated overview. However, for certain instruments, the output requires additional explanation. The following cases are of note:

- **Acid Number**: The instrument used automatically determines the acid number during titration. A titration curve is displayed in real time, allowing for a visual quality check of the test. However, this curve is not logged or saved by the system and is therefore unavailable after the measurement. In some cases, a photo of the curve was taken. Further details on this are provided in Chapter 3.

- **Distillation:** The apparatus used for distillation provides results in the form of a data table and a corresponding graph, showing temperature as a function of volume fraction. The values reported here were extracted from this dataset.

- **Heat of Combustion:** The measurement was initially performed and reported on a mass basis. Since tank volume is a key factor in determining the operational range of a vessel or truck, the heat of combustion was recalculated on a volumetric basis using the experimentally determined fuel density.

2.4 Overview on fuels tested

Table 2.2, below, provides an overview of the fuels analysed. This includes both the alcohol and ether surrogates for HOEF, in neat form (as received form WP2) and the fuels formulated by blending the former with MGO. Fuel blends are highlighted in blue in the table. In turn, Table 2.3 offers an overview of the fuel quantities required for each type of analysis. This includes not only the tests discussed in the current report, but also those that will be reported in Deliverables D3.2 and D3.3.

It is important to note that the listed fuel amounts reflect an upper estimate, as they also account for duplicate or triplicate tests conducted for quality assurance purposes. The table illustrates that while some analyses require only minimal fuel volumes, others demand significantly larger quantities.

Due to the limited availability of fuel, it was necessary to restrict the number of tests conducted for each sample—particularly for those requiring larger volumes. The rationale and methodology behind these decisions, including whether to repeat or omit certain tests based on preliminary results, are described in the following chapter.

Table 2.2 Overview of the volume availability and testing needs for different fuels and fuel blends.

Fuel	Amount (Liter)	Remark
Input volumes of surrogate and base fuels		
Alcohol surrogate	6.5	Total amount received for testing
MGO-1	15	Batch 1. Total amount received for testing.
MGO-2	200	Batch 2. Total amount received for testing.
Ether surrogate-1	15.5	Batch 1 for ether surrogate (no other batch is discussed in this report)
Ether surrogate-1 filtered	0.1* + 12.5	A ca. 135 mL fuel loss was calculated and attributed to fuel remaining in the filters and/or loss due to vaporization during vacuum filtration.
Volume needs for fuel blend formulation		
10-50% alcohol blends	5 x 0.04	Blends of 10, 20, 40, 30, 50% alcohol surrogate & MGO-1 (blended for cetane number tests)
30% alcohol blend	3	Blend of aprox. 30% (v/v) alcohol surrogate & 70% MGO-2.
50% alcohol blend	3	Blend of aprox. 50% (v/v) alcohol surrogate & 50% MGO-2.
10% ether blend	30	Blend of 10% (v/v) ether surrogate-1 & 90% MGO-2
20% ether blend	30	Blend of 20% (v/v) ether surrogate-1 & 80% MGO-2

*Values of a first small amount (100 ml) of filtered ether surrogate, the second value results from the large amount of 12.5 Liter.

Table 2.3 Overview of the fuel volumes required per type of analysis test.

Analysis	Amount (ml)	Remark
Kinematic viscosity @ 40 °C	2x3	
Density @ 15 °C	0	Included in the kinematic viscosity test
Flash point	2x70	
Acid number	2x25	
Corrosive effect on copper (3h @ 50 °C)	2x30	
Oxidation stability	400 2x5	According to ISO 12205 According to ISO 16091
Cloud point	45	
CFPP (Cold Filter Plugging Point)	2x125	
Pour point	50	
Water content	3x2	
Appearance	0	After non-destructive visual inspection, fuel available for another test
Total contamination	2x315	
Distillation	100	
Lubricity	200	
Net heat of Combustion	50	
XRF /GC-1D	5	
GC2D	5	
Compatibility test	6x500	6 refreshments included 4 metals, 2 polymers and blind probe
Big Oxy compatibility test	500	Per variant
Cetane number	40	Per variant
Soot Formation	0.1	
HIL	15	

3 Results & Discussion

This chapter presents and discusses the results of the physicochemical analyses performed according to the methodology provided in the previous chapter. First, the results of the "alcohol surrogate" and related blends with MGO are presented and discussed in section 3.1. Then the corresponding results for the "ether surrogate" and related blends are covered in section 3.2.

3.1 Characterization of HOEF e-fuel realization I (higher alcohols) and blends thereof with MGO

Table 3.1 summarizes characterization results for the surrogate HOEF e-fuel in its realization I, i.e. a mixture of C_4-C_9 higher alcohols, and blends thereof with MGO. The data indicate that the alcohol surrogate meets most, but not all, of the specifications established in the corresponding standards for MGO and Automotive Diesel fuels. Although a detailed discussion on cetane number will be provided in the upcoming Deliverable D3.2, preliminary considerations regarding cetane performance were taken into account to formulate two distinct blends using the base (fossil) MGO fuel from batch 1. These blends contain 30% and 50% (v/v) alcohol surrogate, respectively. Moreover, it is noted here that the blending strategy was guided by the intention to create one formulation that meets, and one that does not meet, the cetane index requirement, thus providing contrast for further evaluation.

Table 3.1 Overview of characterization results for surrogate HOEF e-fuel Realization I (a mixture of higher alcohols) and its blends with MGO. Values highlighted in blue indicate non-compliance with one or more standard specifications.

Property	Unit	MGO-1	30% alcohol blend	50% alcohol blend	Alcohol surrogate	ISO 8217 DMA norm for MGO	EN 590 norm for Autom. Diesel
Kinematic viscosity @ 40 °C	mm^2/s	3.48	3.18	3.32	4.20	≥ 2; ≤6	≥ 2; ≤4.5
Density @ 15 °C	kg/m^3	856	846	840	826	≤890	≥ 820; ≤845
Acid number	mg KOH/g	0.1	0.25	0.13	0.07/0.13	≤ 0.5	-
Corrosive effect on copper (3h @ 50 °C)	Corrosion grade class	1a	1a	1a	2b	-	1
Oxidation stability	g/m^3 min	2 1043	11 123	13 158	- 359	≤ 25	-

Cloud point	°C	-2	-2	0	-39	≤ -16	≤ -10
CFPP (Cold Filter Plugging Point)	°C	-20	-20	-22	-38		≤ -20
Pour point	°C	-	-	-	-	≤ -6	-
Water content	mg/kg	54	217	247	386	≤ 200*	≤ 200
Appearance	Rating	2 Dark brown	1 Light brown	1 Light brown	1 Light colourless	Clear & bright	-
Total contamination	mg/kg	89.6	0	3.3	2.1	-	≤ 24
Distillation (*v*/*v*) collected @ 250 °C (*v*/*v*) collected @ 350 °C 95% (*v*/*v*) collected @	 % % °C	 14/27 91/63 383/350	 43.3 94.5 376	 60.2 95 372	 100 100 195	 - - -	 ≤ 65 ≥ 85 ≤ 360
Lubricity	µm	-	-	-	-	≤ 520	≤ 460
Net heat of Combustion	MJ/kg MJ/l				36.2 29.2	-	-

*Only norm-relevant if the fuel/blend is not clear and bright.

A parameter-by-parameter discussion of compliance with the relevant standards is provided below.

- **Kinematic viscosity:** this parameter is fulfilling the requirements in the fuel standards for all 4 fuels tested. Somewhat remarkable is, that for both blends the value is lower than the original alcohol surrogate and MGO components, respectively, suggesting unconventional blending effects brought about by the markedly different polarity of compounds in HOEF and MGO components, respectively, on viscosity.

- **Density:** this parameter fulfills the standards for all analyzed fuels.

- **Acid number**: this parameter fulfills the standards for all analyzed fuels.

- **Corrosive effect on copper**: for the neat "alcohol surrogate" the result (2d grade) is not fulfilling the requirement for the EN 590 Diesel standard. Although not required for MGO, the test was also performed for the available MGO and HOEF-MGO blends, revealing that blending improves the corrosive effect on copper. I In case of Diesel a blend with e.g. HVO gives a similar effect was not investigated.

- **Oxidation stability**: values determined according to the ISO 12205 test for the HOEF-MGO fuel blends fulfill the MGO standard. Values determined according to the ISO 16091 test are below the value for the neat MGO-1 and alcohol surrogate components, respectively. Here again the above-mentioned polarity aspect is seen as the most likely explanation for these markedly non-lineal blending effects.

- **Cloud point**: the analyzed fuel blends do not meet the requirements of either the EN 590 standard or the ISO 8217 DMX standard. Interestingly, the neat alcohol surrogate complies with both standards, whereas the fossil MGO used as the base fuel in this project does not. However, this does not preclude the use of this particular MGO, as the MGO DMA standard only requires that the purchaser verify the suitability of the cloud point value in relation to the ship's design and intended voyage.

- **Cold Filter Plugging Point (CFPP)**: this was tested for all fuels, although there is no requirement according to the ISO 8217 standard for MGO. The neat alcohol surrogate fulfills the EN590 Diesel standard.

- **Pour point**: this was not determined for these fuels.

- **Water content**: neither the neat alcohol surrogate nor its blends with MGO fulfill the EN 590 Diesel standard as to this parameter. This reflects the intrinsically higher hygroscopic character of the alcohol compounds compared to the non-oxygenated components in fossil MGO. It is noted that for HVO, an alternative, also renewable Diesel fuel which has already been regulated, a higher water content is accepted, up values of 500 mg/kg, which is already notably higher than those determined herein for the HOEF and its blends. Regarding the ISO 8217 norm for MGO, the standard states that the water content determination is not required, as long as the fuel is clear and bright, which is the case for all the e-fuel surrogates and blends analyzed here (see next bullet point).

- **Appearance**: all fuels and fuel blends are a single-phase, clear and bright in appearance (rating 1) in a cylinder glass vessel of 28 mm diameter. Pictures of the test are provided in Appendix B. The neat "alcohol surrogate" is colorless, whilst the HOEF-MGO blends become light yellow, due to the (dark) brown color of the base MGO fuel. It is noted that the rating for MGO-1 decreases substantially, from 2 to 6, whereas the rating for MGO-2 remains 1 when a wider glass tube vessel of 100 mm diameter is used, as recommended in the standardized test.

- **Total contamination**: This test was performed for all fuels. There is no requirement regarding this parameter for MGO fuels (ISO 8217). Regarding the EN 590 standard for Automotive Diesel fuels, the neat HOEF as well as its blends with MGO delivered total contamination values in the range of 0-3.3, well below the maximum values stipulated in the norm (24), thus fulfilling the fuel standard.

- **Distillation**: the result for the alcohol surrogate only partially fulfils the EN 590 fuel standard. Already more than 65% (indeed essentially 100%) of the fuel had been distillated at 250 °C. This

result is not surprising given the lower boiling points expected for the higher alcohol components in the e-fuel surrogate. Although this test is only applicable to the EN 590 diesel standard, it was also conducted for the MGO base fuel and the HOEF–MGO blends for completeness. In the case of the blends, the temperature at which 95% of the fuel was distilled exceeds the diesel specification; however, this is not relevant for marine fuel applications. A repeat test was later performed on the MGO, revealing some variation in results. This difference was not further investigated at this stage but is consistent with observations from other compatibility tests, which shall be discussed in detail Deliverable report D3.2, and which suggest chemical evolution of the MGO with storage time.

- **Lubricity**: This parameter was not studied for these fuels.

- **Net Heat of Combustion (NHOC)**: This was only determined for the neat alcohol surrogate. The obtained value of 29.2 MJ/L is about 23% lower than that for neat MGO (38.8 MJ/L, see Table 3.3). In the HOEF-MGO blends, the NHOC is anticipated to deviate from that of MGO to a lower extent. For a vessel voyage, the captain should ensure compensation for differences in NHOC to attain the desired shipping range.

Overall, it can be concluded that most parameters for the HOEF alcohol surrogate, and particularly its blends with MGO, meet the specification requirements indicated in the relevant norm/s. However, the higher hygroscopicity inherent to the higher alcohol fuel components results in higher uptake of atmospheric water and water contents which do not consistently meet the limits set for Automotive Diesel and Marine Gasoil in EN590 and ISO 8217 (only if fuel is not clear) standards, respectively. This aspect does not appear to be critical, given that even higher water contents are accepted for recently regulated alternative diesel-like fuels such as HVO. Additionally, the alcohol surrogate clearly fails the copper corrosion test according to those requirements stipulated in the EN 590 norm for Diesel fuels.

3.2 Characterization of HOEF e-fuel realization II (higher ethers) and blends thereof with MGO

Table 3.2 Overview of characterization results for surrogate HOEF e-fuel Realization II (a mixture of higher ethers), either as-received form the production process in WP2 or following filtration. Values highlighted in blue indicate non-compliance with one or more standard specifications.

Property	Unit	ether surrogate -1	Ether surrogate filtered	ISO 8217 DMA norm for MGO	EN 590 norm for Autom. Diesel
Kinematic viscosity @ 40 °C	mm^2/s	1.02	1.03*/1.38	≥ 2; ≤6	≥ 2; ≤4.5
Density @ 15 °C	kg/m^3	787	787	≤890	≥ 820; ≤845
Acid number	Mg KOH/g	4.1/0.2	0.7*/0.8/ 3.6/0.02	≤ 0.5	-
Corrosive effect on copper (3h @ 50 °C)	Corrosion grade class	1b	1b	-	1
Oxidation stability	g/m^3 min	 1401	 14.3/12.2	≤ 25	-
Cloud point	°C	-40	-40	≤ -16	≤ -10
CFPP (Cold Filter Plugging Point)	°C	Time limit exceeded	Time limit exceeded		≤ -20
Pour point	°C	-	<-60	≤ -6	-
Water content	mg/kg	852	1080*/804	≤ 200 **	≤ 200
Appearance	Rating	1 Light yellow	1 Light yellow	Clear & bright	-
Total contamination	mg/kg	181	53.5	-	≤ 24
Distillation (*v*/*v*) collected @ 250 °C (*v*/*v*) collected @ 350 °C 95% (*v*/*v*) collected @	 % % °C	 100 100 217	 100 100 217	 - - -	 ≤ 65 ≥ 85 ≤ 360
Lubricity	µm	-	230	≤ 520	≤ 460
Net heat of Combustion	MJ/kg MJ/l	-	38.7 30.5	-	-

*Values of a first small amount (100 ml) of filtered ether surrogate, the second value results from the large amount of 12.5 Liter (see Table 2.2).

**Only relevant if the fuel is not clear and bright.

Table 3.3 Overview of characterization results for surrogate HOEF e-fuel Realization II (a mixture of higher ethers, after filtration) and its blends with MGO. Values highlighted in blue indicate non-compliance with one or more standard specifications.

Property	Unit	MGO-2	10% ether blend	20% ether blend	ether surrogate filtered	MGO ISO 8217 DMA	Diesel EN 590
Kinematic viscosity @ 40 °C	mm^2/s	4.13	3.40	2.86	1.03* /1.38	≥ 2; ≤6	≥2; ≤4.5
Density @ 15 °C	kg/m^3	853	847	840	787	≤890	≥820; ≤845
Acid number	Mg KOH/g	0.6/0.1	0.6/ 3.8/0.1	3.9/ 2.7/0.1	0.7*/0.8/ 3.6/0.02	≤ 0.5	-
Corrosive effect on copper (3h @ 50 °C)	Corrosion grade class	1b	1b	1b	1b	-	1
Oxidation stability	g/m^3 min	13 1179	1543	1568	14.3/12.2	≤ 25	-
Cloud point	°C	1	1	0	-40	≤ -16	≤ -10
CFPP (Cold Filter Plugging Point)	°C	-16	-17	-18	Time limit exceeded		≤ -20
Pour point	°C	-9	-12	-14	<-60	≤ -6	-
Water content	mg/kg	53	134	220	1080*/804	≤ 200 **	≤ 200
Appearance	Rating	1 (3) brown	1 brown	1 brown	1 Light yellow	Clear & bright	-
Total contamination	mg/kg	181	40	176	53.5	-	≤ 24
Distillation							
(*v*/*v*) collected @ 250 °C	%	14/<5	26.5	33.2	100	-	≤ 65
(*v*/*v*) collected @ 350 °C	%	91/95	93.3	93.0	100	-	≥ 85
95% (*v*/*v*) collected @	°C	383/350	356	358	217	-	≤ 360
Lubricity	µm	360	390	400	230	≤ 520	≤ 460
Net heat of Combustion	MJ/kg MJ/l	42.5 38.8	42.2 35.7	42.0 35.2	38.7 30.5	-	-

*Values of a first small amount (100 ml) of filtered ether surrogate, the second value results from the large amount of 12.5 Liter (see Table 2.2).

**Only relevant if the fuel is not clear and bright.

A parameter-by-parameter discussion of compliance with the relevant standards is provided below.

- **Kinematic viscosity**: this parameter is not fulfilling for neat ether surrogate. However, in blends with MGO, the viscosity value is within the requirement in the ISO 8217 standard.

- **Density**: this parameter is fulfilling the ISO 8217 for the ether-based HOEF as well as blends with MGO. Regarding the EN 590 Diesel standard, the density of the neat ether surrogate is below the requirement. It is not investigated whether a blend would solve this issue.

- **Acid number**: the acid number of the ether surrogate does not meet the required specification. Furthermore, the requirement is also not fulfilled in the corresponding blends. Some measurements exhibited unusual behavior (Figure 3.1), where an initial decrease of pH upon addition of the base titrating agent, was followed by an increase in the pH, as expected. This irregular behavior persisted even upon repeating the tests, resulting in significant variation in the measured values.

  To further investigate the background of these unconventional titration behavior, it was decided to perform the same analysis by another external party according to the ASTM D664 standard. Table 3.4 shows the results for the fuel acid number as a function of the test date and methodology applied. For the base MGO fuels and the alcohol HOEF both tests provided similar results. In contrast, for all fuels/blends incorporating aliphatic ethers, marked differences in acid number were again obtained across different tests. It is therefore concluded that the methodology used according to ISO EN 14104 is not suitable for fuels with significant contents of aliphatic ethers.

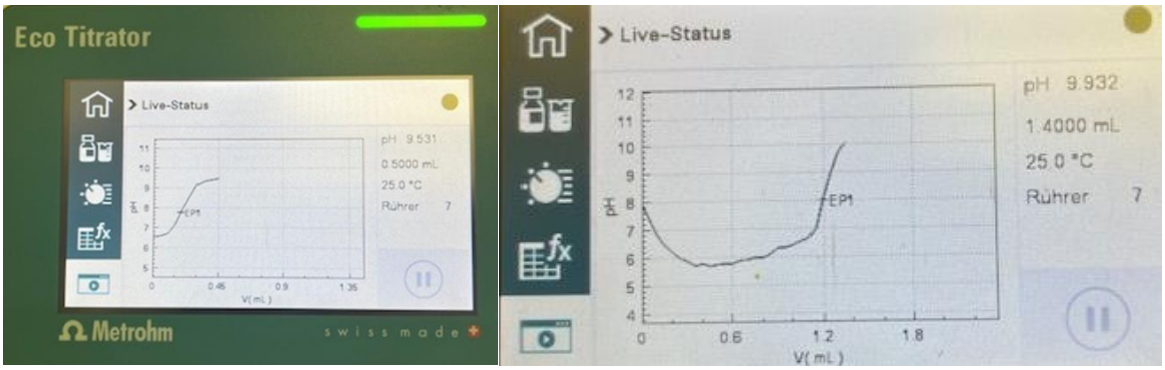

Figure 3.1 Snapshots during the collection of titration curves for the determination of the acid number for 10% ether surrogate blend with MGO (left) and 20% ether surrogate blend with MGO (right).

Given the unconventionally high acid number determined in an earlier experiment for the as-received (unfiltered) ether surrogate mixture, coinciding with the experimental detection of

significant amounts of sulphur upon a filter up to 1.6% by XRF (X-ray fluorescence), it was hypothesized that sulphonic species may have leached/detached from the acidic resin catalyst applied to synthesize aliphatic ethers from the corresponding mixture of aliphatic alcohol precursors. The sulfonic species are markedly Bronsted acidic and could thus be responsible for the experimental acid numbers. As a corrective measure, it was proposed to filter all the original ether surrogate. Filtration was performed at room temperature using a 0.45 µm filter under an absolute driving vacuum of 200 mbar, starting with a small test batch of 100 mL. This initial filtration clearly improved the acid number, lowering it from 4.1 to 0.66, leading to the decision to filter most of the remaining large surrogate fuel volume. Subsequently, the acid number for the larger quantity also decreased substantially, to 0.79, although it still did not meet the value stipulated in the ISO8217 norm (≤0.5).

Figure 3.2 shows the setup used for filtering a larger quantity of 12.L. A double filtration setup was employed to reduce processing time, operating in small batches and replacing the filters as soon as a noticeable decrease in flow rate occurred. When filters were used for extended periods, they showed a progressively darker brown coloration, as illustrated in Figure 3.4. Figure 3.3 compares the appearance of the ether surrogate before and after filtration, showing a somewhat clearer final product. The brown shade acquired by the filters is in agreement with the retention of sulphonic groups, which are dark brown coloured.

Table 3.4 Overview of acid number for various fuels as a function of test date and experimental standard adopted.

Substance	Date	Acid number	Standard	**Remark**
Alcohol surrogate	Oct-23	0.07	ISO EN 14104	
	Apr-25	0.13	ASTM D664	
MGO-1	Nov-23	0.1	ISO EN 14104	
	Apr-25	0.09	ASTM D664	
MGO-2	Dec-23	0.57	ISO EN 14104	
	Apr-25	0.09	ASTM D664	
Ether surrogate -1	Oct-24	4.1	ISO EN 14104	
	Apr-25	0.18	ASTM D664	
Filtered ether surrogate	Nov-24	0.66	ISO EN 14104	First 100 ml filtered
	Nov-24	0.79	ISO EN 14104	
	Mar-25	3.6	ISO EN 14104	After adding Amine
	Apr-25	0.02	ASTM D664	After adding Amine
10% Ether blend	Nov-24	0.58	ISO EN 14104	
	Mar-25	3.8	ISO EN 14104	
	Apr-25	0.10	ASTM D664	
20% Ether blend	Nov-24	3.9	ISO EN 14104	
	Mar-25	2.7	ISO EN 14104	
	Apr-25	0.11	ASTM D664	

Figure 3.2 Overview of the double set-up applied for fuel filtration.

Figure 3.3 Ether surrogate unfiltered (left) and filtered (right).

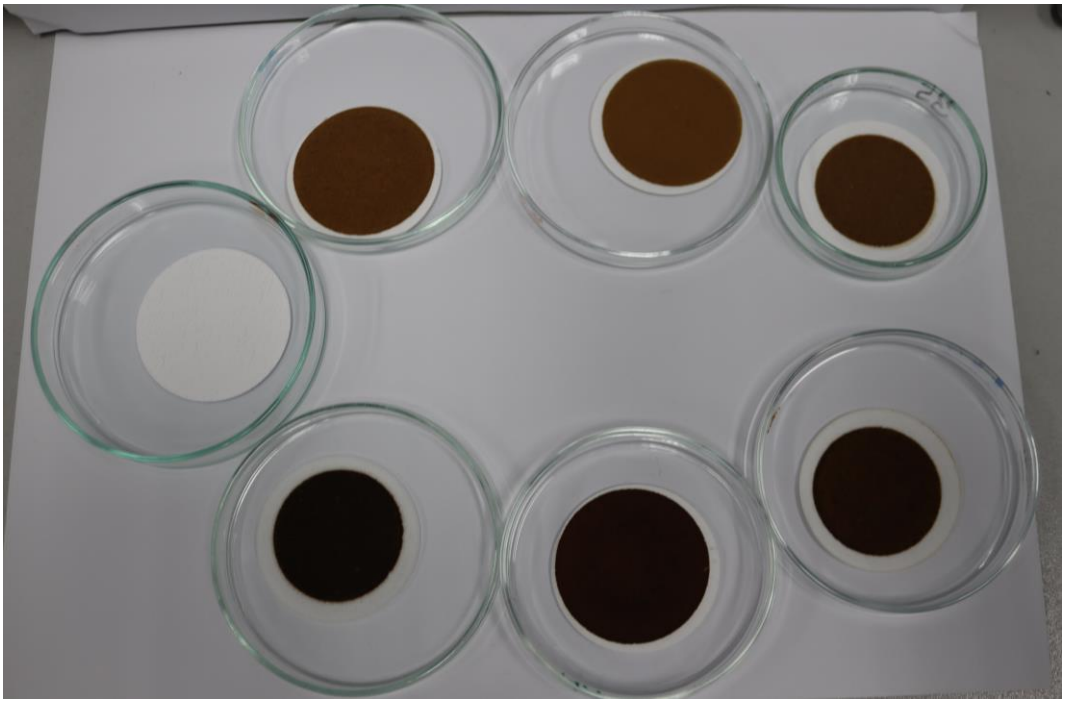

Figure 3.4 Clean (white) filter and used (brown) filters after filtering the ether surrogate.

To prove the hypothesis regarding the presence of acidic sulphur species in the as-synthesized ether surrogate fuel and the retention thereof in the filters, sulphur analyses were performed on several liquid and solid (filter) samples by XRF (X-ray fluorescence). The list of specimens analysed was as follows:

1. Clean filter material (VWR grade 698. bender free glass microfibre. particle retention 0.7 µm [5]
2. Filter used for the trial amount of ether surrogate
3. First filter used for the large amount of ether surrogate
4. Second filter used for the large amount of ether surrogate
5. MGO-2
6. Filtered ether surrogate

It is noted that the analyses were not limited to sulphur but additionally extended to other elements such as alkaline and alkaline earth and transition metals, Al, Si, etc. An overview of the results for those elements detected at significant amounts is listed in Table 3.5.

Table 3.5 Overview of XRF analysis results for different liquid (fuel) and solid (filter) specimens. Contents given in mg/kg (ppm).

Element	Clean filter	Trial filtering	Light brown	Dark brown	Filtered ether surrogate	MGO-2
Al (Aluminum)	40970	40310	2733	64	192	166
Si (Silicon)	422900	409100	63040	8659	22	<0.7
S (Sulphur)	892	16090	344000	377700	169	1732
K (Potassium)	16940	14510	9311	676	<0.9	<0.9
Ca (Calcium)	8192	7119	5522	474	0.2	<0.8
Ti (Titanium)	419	369	0.3	21	<0.9	<0.9
Zn (Zinc)	6155	4720	7417	4583	0.06	0.22
Ba (Barium)	1527	1206	2025	1634	<11	17

From the results listed in the table, it is concluded:

1. Alkaline (earth) and transition metals (Potassium, Calcium, Titanium, Zinc, Barium) are already present in the clean filter, more diluted in the used filters, and essentially absent in the MGO and filtered ether surrogate liquid fuels. Therefore, these elements form part of the filter composition and are not transferred to the filtered fuels to any relevant extent.
2. The above is also valid for silicon (Si) and aluminum (Al).
3. Sulphur was clearly detected at higher concentrations (>340 g/kg) in the used filters compared to the clean filter. Based on these observations, it is concluded that the original ether surrogate contained substantial amounts of sulfur, likely originating from leaching of acidic sulphonic species from the sulphonated resin catalyst used during the alcohol dehydration process in ether production. These sulfur impurities were effectively retained by the filter during fuel filtration, reducing the sulphur content in the filtered fuel to <170 ppm and thus the fuel's acid number.

Finally, the sulphur content is compared with the MGO standard for which a 1% (m/m) content is allowed [1]. 1% corresponds to 10.000 mg/kg in the table 3.5. The filtered ether surrogate (169 mg/kg) and MGO-2 (1732 mg/kg) are easily fulfilling this requirement. Additional XRF analysis on the original unfiltered ether surrogate, batch 1, shows a value of 68 mg/kg, which is also well within the requirement of the MGO standard. Regarding the Diesel standard for sulphur the measured values are well above the required value of 10 mg/kg [2].

- **Corrosive effect on copper:** for all fuels and blends, the results met the requirements set by the EN 590 diesel standard. Although not mandatory for MGO, the analysis was also performed on the available MGO and the HOEF-MGO blends, all of which likewise met the classification criteria.

- **Oxidation stability:** Figure 3.5 shows a collection of pressure vs time curves during oxidation stability tests for the ether surrogate and its blends with MGO. From these curves, the oxidation stability (min) is determined, as summarized in Table 3.6.

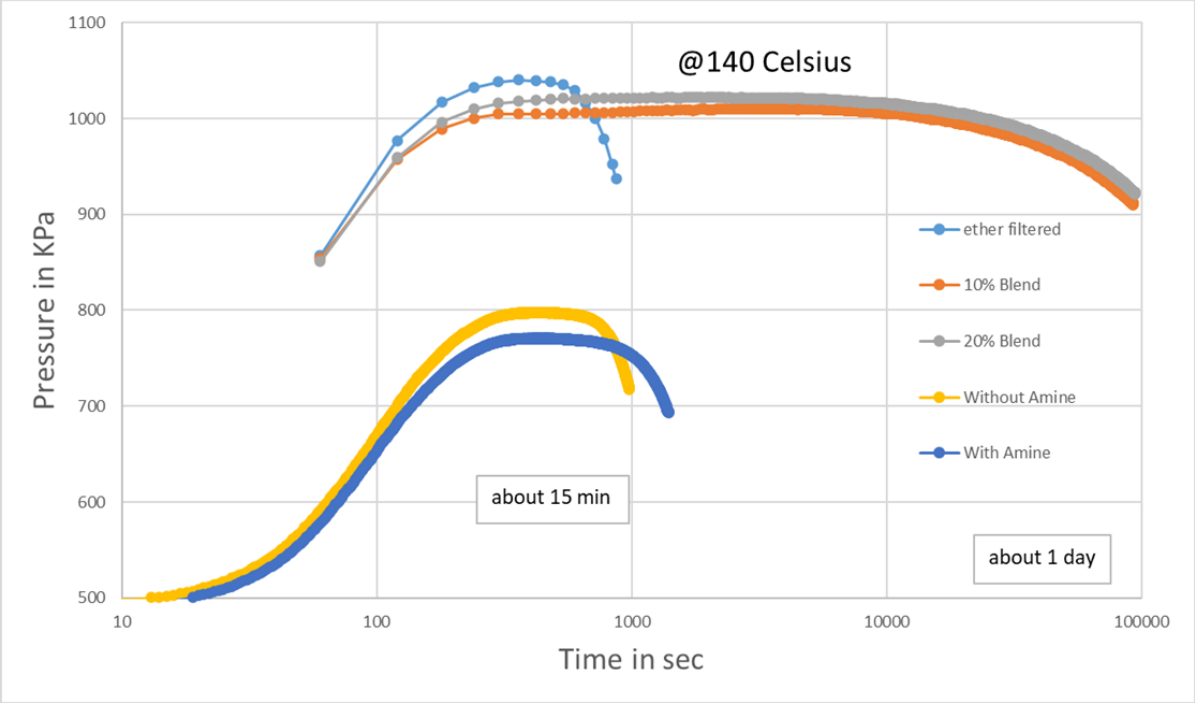

Figure 3.5 Pressure vs time curves registered during the oxidation stability tests for the ether surrogate in different states, as well as its blends with MGO. "With amine" indicates that the filtered ether surrogate had been re-additivated with diethylenetriamine (50 ppm).

Table 3.6 Overview on oxidation stability test results for ether surrogate HOEF and its blends with MGO.

Property	Unit	Ether surrogate	ether surrogate filtered	ether surrogate filtered + new Amine	ether surrogate Batch 2
Oxidation stability	min	1401	14.3/12.2/ 16.3	23.3	11.3

The as-received (unfiltered) ether surrogate exhibited a remarkable oxidation stability of 1401 minutes. However, following filtration, aimed at removing acidic sulfur contaminants introduced during the ether production process, the oxidation stability significantly decreased to 12–16.3 minutes across several test repetitions. Two hypotheses were proposed to explain this behaviour:

(i) The sulfur contaminants removed by filtration contributed to stabilizing the ether fuel against oxidation.

(ii) Filtration had also removed the diethylenetriamine (50 ppm) oxidation stabilizer, which had been added to the freshly produced ether surrogate to prevent the formation of peroxide species through autocatalytic ether oxidation, thereby substantially reducing oxidation stability.

To test the second hypothesis, a colorimetric test was conducted to detect the potential formation of peroxide species in the filtered ether surrogate HOEF. As shown in Figure 3.6, this test ruled out the presence of peroxides, which would have indicated destabilization of the fuel due to autocatalytic oxidation.

Figure 3.6 Result of the peroxide test on the filtered ether surrogate.

Additionally, OWI acquired diethylenetriamine and re-additivated the filtered HOEF by adding 50 ppm of the amine stabilizer. However, oxidation stability tests performed immediately before and after re-additivation yielded very similar results: 16.3 minutes and 23.3 minutes, respectively. These findings ruled out the unintended removal of the amine stabilizer during filtration as the cause for the observed drop in oxidation stability.

It can thus be inferred that the sulfur contaminants removed during filtration had contributed to stabilizing the ether fuel against oxidation. Consequently, the lower oxidation stability values in the range of 15–25 minutes better represent the intrinsic properties of the neat ether HOEF. These results indicate the oxidation stability of the neat ether e-fuel is a technical aspect

to consider carefully, which can likely be adjusted via the selection of suitable oxidation stabilizer additives. However, when blended with MGO, the oxidation stability for the HOEF-MGO blends increased significantly to >1500 min, even exceeding the oxidation stability determined for the base MGO fuel.
Furthermore, as it can be seen from the lower pressure values in Figure 3.6., a decrease in the vapor pressure point for the ether surrogate was detected over the storage time (about 4 months passed until the amine additive became available to re-additivate the fuel and repeat the test). This points to a loss of volatile components by evaporation, an aspect which shall be discussed in greater detail in the upcoming report D3.2.

- **Cloud point**: the (filtered) ether surrogate fulfills the standards for MGO DMX (ISO 8217) and Diesel (EN 590). However, the neat MGO base fuel, as well as the HOEF-MGO blends do not fulfill the MGO DMX standard. This does not exclude usage of the MGO taking the MGO DMA standard as reference, the latter norm merely stating that the purchaser should confirm that the fuel's cloud point value is suitable for the ship's design and intended voyage.

- **Cold Filter Plugging Point (CFPP)**: this test was performed for all fuels, including MGO and its blends with HOEF, even though there is no requirement specified in the ISO 8217 fuel standard for MGO. Moreover, the neat ether surrogate fulfills the EN 590 Automotive Diesel standard, since a time limit exceedance during the measurement can be interpreted as a CFPP below -40 °C, i.e. well below the -10ºC limit established in the norm.

- **Pour point**: all fuels and fuel blends tested showed pour points <-9ºC, and therefore fulfill the ISO 8217 MGO standard, which requires a pour point ≤-6ºC.

- **Water content**: the ether HOEF surrogate showed a water content of 804 mg/kg in neat form, exceeding the 200 mg/kg limit stipulated in the EN590 standard for Automotive Diesel. Blends with MGO showed lower water uptakes ≤220 mg/kg. It is noted that higher water contents up to 500 mg/kg are accepted in the regulation for the case of diesel fuels incorporating HVO biofuel as blending component. Therefore, it is speculated that a fuel blend incorporating both higher ether HOEF e-fuel and HVO biofuel components could be norm-complying as to the water content. Regarding the ISO 8217 standard for MGO fuels for waterborne transport, it is stated that the water content determination is not required provided that the fuel is clear and bright. This was the case for the neat HOEF and those blends with MGO formulated and analyzed herein (see next bullet point).

  To investigate the hygroscopic behavior of the HOEF e-fuel surrogates, in their two realizations, the following tests were performed:

  1. To repeat measurement of the water content.
  2. To apply a molecular sieve material 3Å [6] for about 20 hours to remove water by adsorption.
  3. To redo the water content analysis immediately after the water removal process.

4. To leave the fuel in open contact with the air, enabling water reabsorption.
5. To redo the water content analysis after further exposure to atmospheric water for about one week.

The results of these tests are provided in the following Table 3.7. It clearly shows that all HOEF surrogates are hygroscopic, which agrees well with their mildly oxygenated character. Moreover, the higher alcohol HOEF surrogate proved to be more hygroscopic, thus take atmospheric water faster and to higher contents, than its ether-based HOEF counterpart. The difference between the originally tested value and the value measured before drying already indicates this phenomenon, even though the substances were stored in closed bottles and canisters and only opened briefly to extract the required amount for planned tests. This behavior agrees well with the capacity of alcohol compounds to establish hydrogen bonding with water molecules, a property which ether compounds lack.

Figure 3.7 provides a graphical representation of the experimental water content over time. It shows that, after drying, the water content of all fuels increased quite rapidly within the first day of exposure to open air. The alcohol surrogate and its blends clearly exhibited the highest water uptake, while the ether surrogate and its blends showed a smaller increase. For some fuels, a maximum value of water content was reached after about two days, after which the water content decreased again. Even though, in general, the final water content in the fuels was higher than that in the as-dried fuel, blending HOEF (alcohol or ether-based) with MGO, which is intrinsically less hygroscopic, substantially reduced the water uptake for both types of HOEF.

Table 3.7 Overview of water content results for different fuels prior to and right after drying by water adsorption on a solid molecular sieve, and as a function of the time of exposure to ambient humidity over different periods of time.

Substance	Original tested value	Before drying	After drying	Day 1	Day 2	Day 5	Day 14
Alcohol surrogate	386	1395	4324	4324	4609	3516	931
Alcohol 30% blend	217	255	935	934.9	1436	1346	66
Alcohol 50% blend	247	367	1212	1212	2146	2602	102
Ether surrogate. batch 1	852	1400	716	716	751	418	796
	Original value	Before drying	After drying	Day 1	Day 2	Day 7	Day 9
Ether surrogate filtered	1080	1183	27	471	652	931	1055
Ether surrogate 10% blend	134	129	26	188	62	66	65
Ether surrogate 20% blend	220	205	23	70	77	102	156

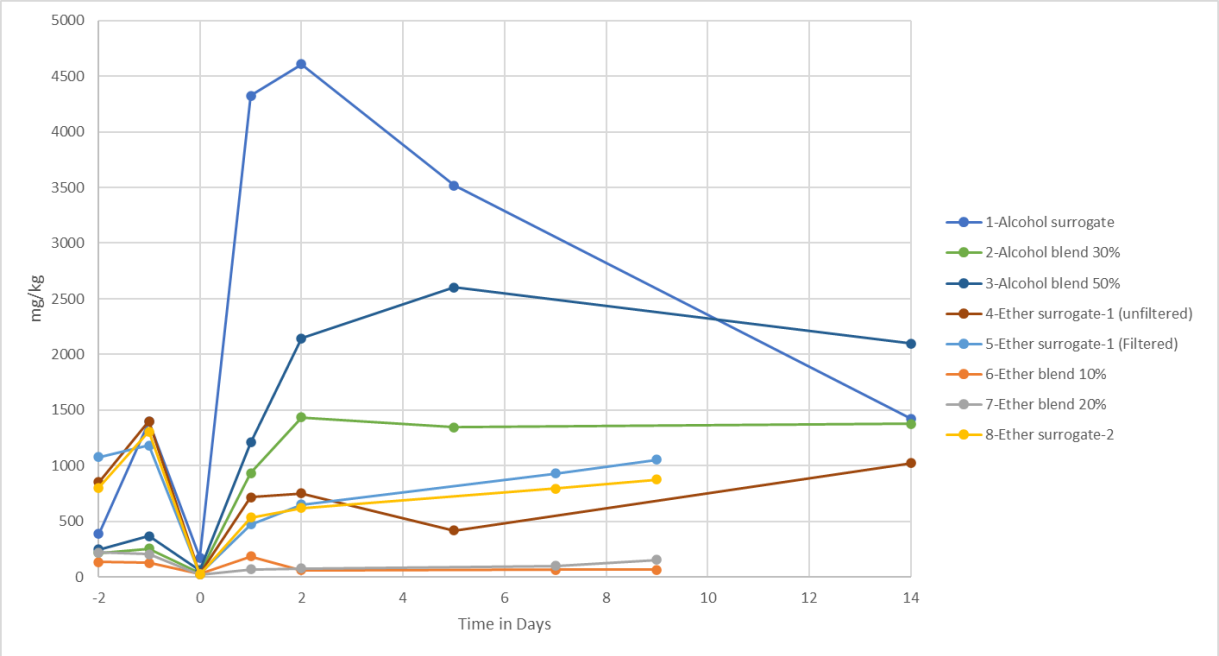

Figure 3.7 Time resolved evolution of water content results for different fuels after drying by water adsorption on a solid molecular sieve. Day -2 refers to the test on the as-received fuel or as-formulated fuel blend.

- **Appearance**: all fuels showed to be clear and bright appearance (rating 1) in a cylinder glass of 28 mm. Photographs of the tests are provided in Appendix B. The neat ether surrogate is yellow, whilst its blends with MGO showed a brown shade, given the dark brown color of the MGO base fuel. For a cylinder with 100 mm diameter the rating of the MGO-1 and its blends with the ether HOEF are still rated 1. Based on this, it can be justified that the ether surrogate and its blends can be rated 1 according to the standardized method.

- **Total contamination**: This standard test for the EN 590m Diesel norm was performed for all fuels, although there is no requirement regarding total contamination for MGO fuels for waterborne transport. The neat ether surrogate fulfills the standard. However, after filtration, the contamination level of the ether surrogate increased, which was unexpected. For the 10% ether blend with MGO, the total contamination decreased more than anticipated, while for the 20% ether blend, a value comparable to that of MGO was measured. A repeat test was not possible for all substances due to the limited fuel availability.

- **Distillation**: the result for the neat ether surrogate only partially fulfils the EN 590 fuel standard. Already more than 65% (indeed essentially 100%) of the fuel had been distillated at 250 °C. This result aligns with the comparatively lower boiling points expected for some of the ether components in the surrogate HOEF compared to some of the heaviest components in fossil Automotive Diesel. Although this test is only applicable to the EN 590 diesel standard, it was also conducted for the MGO base fuel and the HOEF–MGO blends for completeness. For the MGO-2 base fuel repeat tests were performed, showing some differences in the results. These were not further investigated at this point.

- **Lubricity**: this parameter showed values fulfilling the ISO 8217 MGO standard for the neat ether surrogate and all HOEF-MGO blends.

- **Net Heat of Combustion (NHOC)**: For the neat alcohol surrogate, the obtained value of 30.5 MJ/L is about 21% lower than that for neat MGO (38.8 MJ/L). For the HOEF-MGO blends, higher NHOC were determined, in the range of 35.2-35.7 MJ/L). For a vessel voyage, the captain should ensure compensation for differences in NHOC for different synthetic fuels, to attain the desired shipping range.

In view of the results discussed above, it can be concluded that the ether-based HOEF surrogate, and the blends thereof with MGO largely fulfil the physicochemical requirements set for Automotive Diesel (EN 590) and waterborne MGO fuels (ISO 8217) norms. Similarly to the alcohol-based version of the HOEF surrogate, the higher hygroscopicity inherent to the higher ether fuel components results in higher uptake of atmospheric water and water contents which do not consistently meet the limits set for Automotive Diesel and Marine Gasoil in the EN590 standard. This aspect does not appear to be critical, given that even higher water contents are accepted for recently regulated alternative diesel-like fuels such as Diesel containing HVO biofuel as blend component. On the other hand, the ISO 8217 standard for Marine Gasoil fuels states that water content limits are only applicable if the fuel is not clear, a physical requirement that the ether-based HOEF and its blends with MGO, as studied here, successfully meet. Additionally, the oxidation stability of the ether-based HOEF and its blends is a second physico-chemical aspect which requires further attention. The addition of diethylenetriamine (50 ppm) as an additive to the ether HOEF, effectively prevents the autooxidation of aliphatic ether compounds and thus the development of peroxide species, through storage for the periods of time studied in this project. However, this does not suffice to attain satisfactory fuel oxidation stability and this fuel parameter may need improvement, potentially through the selection and addition of (additional) suitable additives.

3.3 Contribution to project (linked) Objectives

The results included in this report contribute to the achievement of the following project objectives:

Objective 4. To characterize the newly proposed higher oxygenate e-fuel (HOEF). in its two realizations i.e. a mixture of either higher aliphatic alcohols or higher aliphatic ethers. and assess its drop-in characteristics for current-fleet marine and heavy-duty road internal combustion engines. This comprises:

Subobjective (4a) to design blending strategies with baseline fuels, and additivation to attain drop-in and backwards compatibility with reference to ISO8217 and EN590 current regulations for marine and road heavy-duty diesel fuels.

Given the focus of the project on e-fuel applications in waterborne transport, Marine Gasoil (MGO) has been selected as a relevant baseline fuel.

3.4 Contribution to major project exploitable result

The results included in this report identify the best state of the art purification method. As such these results contribute to attaining the following Key Exploitable Result:

KER	Fuel characterization
Owner	OWI, T4F
Alternative solution/Market Competition	Other research institutes in this area
Use model to go to the market	Provision of a service
Potential End user/market	Shipping industry, transport industry, e-fuel end users in general
Target market/companies	Fuel development, fuel production and fuel trade companies
Unique selling point	Knowledge on similar fuels, special self-developed methods and equipment
Time to go market	Immediately
Exploitation seps to achieve	Publications
Risk evaluation	Political change on climate policy: P: 30%, I: 50%, R=15%

4 Conclusion and Recommendation

This report presents the results for the assessment of norm-related physico-chemical parameter for the Higher Oxygenate E-Fuel (HOEF) in its two possible realizations: (i) a mixture of synthetic higher, aliphatic alcohols and, (ii) a mixture of synthetic higher, aliphatic ether compounds, as well as their blends with Marine Gas Oil (MGO) as a baseline fuel. Within the project time planning the final e-fuel from the production process will only become available near the end of the project and at volumes which are insufficient to perform some of the fuel characterization tests and blending analyses which are of concern in this report. Therefore, so-called e-fuel surrogates have been studied to enable an earlier assessment of the e-fuel suitability for target applications in maritime and road heavy duty transport sectors according to ISO 8217 and EN 590 fuel standards, respectively.

Regarding the alcohol-based HOEF, it can be concluded that most parameters for the HOEF alcohol surrogate, and particularly its blends with MGO, meet the specification requirements indicated in the relevant norms. However, the higher hygroscopicity inherent to the higher alcohol fuel components results in higher uptake of atmospheric water and water contents which do not consistently meet the limits set in the EN 590 standard for Automotive Diesel. This aspect does not appear to be critical, given that even higher water contents are accepted for recently regulated alternative diesel-like fuels such as HVO. On the other hand, the ISO 8217 standard for Marine Gasoil fuels states that water content limits are only applicable if the fuel is not clear, a physical requirement that the ether-based HOEF and its blends with MGO, as studied here, successfully meet. Additionally, the alcohol surrogate e-fuel clearly fails the copper corrosion test according to those requirements stipulated in the EN 590 norm for Automotive Diesel fuels.

Regarding the ether-based HOEF, it can be concluded that the ether-based HOEF surrogate, and the blends thereof with MGO largely fulfil the physicochemical requirements set for Automotive Diesel (EN 590) and waterborne MGO fuels (ISO 8217) norms. Similarly to the alcohol-based version of the HOEF surrogate, the higher hygroscopicity inherent to the higher ether fuel components results in higher uptake of atmospheric water and water contents which do not consistently meet the limits set for Automotive Diesel and Marine Gasoil in the EN590 standard. This aspect does not appear to be critical, given that even higher water contents are accepted for recently regulated alternative diesel-like fuels such as Diesel containing HVO biofuel as blend component. On the other hand, the ISO 8217 standard for Marine Gasoil fuels states that water content limits are only applicable if the fuel is not clear, a physical requirement that the ether-based HOEF and its blends with MGO, as studied here, successfully meet. Additionally, the oxidation stability of the ether-based HOEF and its blends is a second physico-chemical aspect which requires further attention. The addition of diethylenetriamine (50 ppm) as an additive to the ether HOEF, effectively prevents the autooxidation of aliphatic ether compounds and thus the development of peroxide species, through storage for the periods of time studied in this project. However, this does not suffice to attain satisfactory fuel oxidation stability and this fuel parameter may need improvement, potentially through the selection and addition of (additional) suitable additives.

It is recommended that to assure a quick market penetration the e-fuel production process is reviewed and possibly adapted to attain higher average hydrocarbon chain lengths for the higher oxygenate e-fuel components, thus reducing their hygroscopicity, given that too high water contents might

decrease e-fuel application for certain ship voyages and particularly as Diesel replacement for road transport. Additionally, improving the oxidation stability of the ether HOEF and its fuel blends, with a suitable additive, is recommended.

Based on the results of the investigations reported here, it is concluded that the objective of a fast market introduction of higher oxygenate e-fuels (HOEF) is feasible, particularly upon blending the ether-based HOEF with fossil fuels such as MGO.

5 Risks and interconnections

5.1 Risks/problems encountered

Risk No.	What is the risk	Probability of risk occurrence[1]	Effect of risk[1]	Solutions to overcome the risk
WP 3.1	High acid number for the HOEF	2	2	May require different methodologies to assess this parameter in fuels containing higher oxygenate compounds. The standard test methods chosen herein appear not to be appropriate for fuels containing ether substances.
WP 3.1	Low oxidation stability for the HOEF	2	2	Improve with a suitable additive.
WP 3.1	High water content for the HOEF and its blends	1	3	For waterborne transport, check for each fuel charge, so that ship's captain can decide whether water content and energy density is acceptable for the intended voyage.

[1)] Probability risk will occur: 1 = high. 2 = medium. 3 = Low

5.2 Interconnections with other deliverables

Report	Interconnection
D2.3	Describes the production of the surrogated analysed and tested in D3.1. D3.2 and D3.3
D3.2	Whereas D3.1 summarizes all analytic results. the report D3.2 reports the details on the ignition and emission behaviour.
D3.3	Whereas D3.1 summarizes all analytic results. the report D3.2 reports the fuel-system compatibility trials and hardware-in-the-loop aging tests

6 Deviations from Annex 1

There are no deviations from the description of this deliverable as given in Annex I of the Grant Agreement.

7 References

1. ISO 8217 Petroleum products-fuels (class F) – Specification of marine fuels. 6th edition. 2017-03. reference number ISO 8217-2017(E)
2. EN 590 Automotive fules – Diesel – requirements and test methods. German version EN 590:2013+A1:2017
3. Dmitry. What are MGO and MDO fuels? Fuels Explained. October 25. 2024. www.maritimpage.com/what-are-mgo-and-mdo-fules-marine-fules-explained/
4. E.P. da Silva Santos. E.F. De Souza. T.C.P Moreira Ramos. M.S. Silva. Evaluation of potentiometric methods for acid number determination in commercial biodiesel samples and proposal of alternative method. January 2018. Obirtal – The electronic journal of chemistry 10 (1). DOI 10.17807/orbital.v10i1.1034
5. VWR glass fibre filters. grade 698. bender free glass microfibre. www.de.vwr.com/store/product/7586583/null
6. Molekularsieb UOP Typ 3Å, Molekularsiebe, 3 Å beads, 4-8 mesh | Sigma-Aldrich

8 Acknowledgement

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Project partners:

#	Partner short name	Partner Full Name
1	CSIC	AGENCIA ESTATAL CONSEJO SUPERIOR DE INVESTIGACIONES CIENTIFICAS
2	MPG	MAX-PLANCK-GESELLSCHAFT ZUR FORDERUNG DER WISSENSCHAFTEN EV
3	DTU	DANMARKS TEKNISKE UNIVERSITET
4	OWI	OWI SCIENCE FOR FUELS GMBH
5	UNR	UNIRESEARCH BV
6	T4F	TEC4FUELS GmbH
7	AVL	AVL LIST GMBH
8	GF	GOODFUELS BV
9	UZ	SVEUCILISTE U ZAGREBU. FAKULTET STROJARSTVA I BRODOGRADNJE
10	UCT	UNIVERSITY OF CAPE TOWN
11	KAUST	KING ABDULLAH UNIVERSITY OF SCIENCE AND TECHNOLOGY
12	FE	FINCOENERGIES - BUSINESS INNOVATION BV

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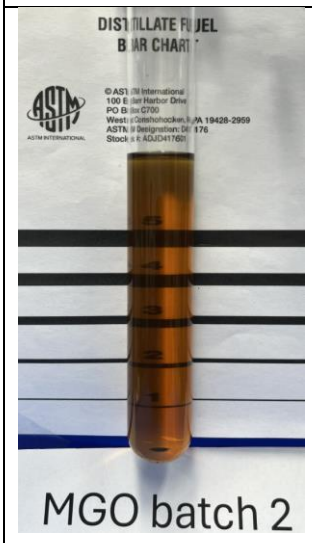
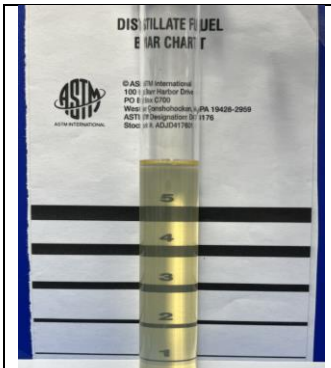
9 Appendix A – Appearance test results



 Ether surrogate, batch 1 (unfiltered)	 Ether surrogate, batch 1 (filtered+amine)	 Ether surrogate, batch 2
 10% Ether surrogate/90% MGO Blend	 10% Ether surrogate	
 20% Ether surrogate/80% MGO Blend	 20% Ether surrogate	