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HYBRID TANDEM CATALYTIC CONVERSION PROCESS TOWARDS HIGHER OXYGENATE E-FUELS

E-TANDEM - Deliverable report

Deliverable 3.2-Fuel ignition 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 essential to decarbonize the existing internal-combustion vehicle fleet. They are especially relevant for long-distance, heavy-duty uses such as cargo road and waterborne transport sectors where alternatives with comparable energy density are limited. This holds true also for aviation, which is out of the scope of this E-TANDEM project. Rapid deployment, however, faces hurdles beyond today's cost premium: equipment and infrastructure were built around fuels that meet established specifications, which sustainable substitutes do not always match by default. Blending new e-fuels with conventional products offers a pragmatic path, enabling a staged shift away from fossil feedstocks.

The E-TANDEM project is designing and bench-validating a first-of-its-kind direct route to selectively produce carbon-neutral higher (mid-long chain) oxygenate e-fuels (HOEF) intended as drop-in replacements for fossil diesel. The primary targets are difficult-to-electrify heavy-duty sectors, most notably waterborne transport, with relevance to heavy-duty, long-haul road transport as well. The fuel is a mildly oxygenated mixture of C_{5+} aliphatic alcohols and their corresponding aliphatic ether derivatives. It is synthesized using CO_2 as the sole carbon source and renewable electricity as the only energy input via a single-pass hybrid catalytic scheme: electrocatalytic generation of e-syngas followed by a tandem conversion that couples thermocatalysis over solid catalysts with molecular (homogeneous) chemocatalysis. The project demonstrates this process at bench scale and evaluates robustness under variable renewable power.

This deliverable D3.2 reports outcomes from Work Package 3 on auto-ignition behaviour of surrogate HOEF formulations developed in WP2. Two families are examined: (i) mixtures of higher alcohols (C_5-C_9) and (ii) mixtures of higher ethers (C_8-C_{18} or C_{10}-C_{18}). These surrogates, prepared from commercially available neat alcohols, closely mimic compositions expected from the project's tandem-catalysis pathway. Particular attention is given to blending with state-of-the-art marine gas oil (MGO) to assess practical "blend-ready" use. Properties of neat HOEF and HOEF/MGO blends are measured and discussed against applicable European fuel specifications for marine (ISO 8217) and heavy-duty road diesel (EN 590), highlighting areas of compliance and any deviations. The results illustrate that, particularly higher ether compounds appear as a promising e-fuel component, providing cetane enhancement and tailpipe soot emission reductions for blends with state-of-the-art marina gas oil.

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Abbreviations & Definitions

Abbreviation	Explanation
AFIDA	Advanced Fuel Ignition Delay Analyzer
CI	cetane index
HOEF	Higher-oxygenate e-Fuel
GS-MS	Gas Chromatography with combined Mass Spectrometry
MGO	Marine Gas Oil
YSI	Yield Sooting Index

Item	Definition
DMA	Marine Gas Oil grade: with low sulphur content, distilled and high Quality
DMB	Marine Gas Oil grade: with more remnants as DMA
DMX	Marine Gas Oil grade: often referred to as a special light distillate, DMX is designed for high-speed engines that require fuels with lower viscosity and density.
DMZ	Marine Gas Oil grade: 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 ignition behaviour of the herein proposed HOEF e-fuel, regarding its use as a diesel replacement in applications of waterborne and heavy-duty road 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 D3.2 addresses the second goal, while the goals 1 and 3 are reported in reports D3.1 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 ignition behaviour characterisation. 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 ignition and soot behaviour 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_5-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". Within this second (ether) HOEF realization, a specific batch (hereafter referred to as batch 3) was produced to have aliphatic ethers in the C_{10}-C_{18} carbon chain-length range, i.e. devoid of lower flash point C_8 and C_9 ether compounds.

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 (light and 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. However, these two standards do not cover all aspects of interest. Especially regarding the soot characteristics, the results of comparative investigations are provided within this report.

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.

As discussed in the earlier Deliverable D3.1, the rationales underlying the exclusion of particular fuel characteristics—as delineated in the ISO 8217 norm for marine gasoil and the EN590 norm for automotive diesel—have been thoroughly expounded. This phenomenon is not reiterated in this particular instance; however, selected aspects are incorporated within the present report, as they pertain to the combustion behavior of the fuel. As illustrated in Table 2.1, a comprehensive overview of the various fuel ignition parameters is presented, as outlined in the pertinent normative documents and incorporated within the scope of this study. The table provides a detailed exposition of the methodologies employed for their experimental assessment, along with a delineation of the limits stipulated in the respective normative documents.

Cetane number and ignition delay

The determination of ignition delay times and cetane number is critical for the characterization of the ignition quality of diesel-like fuels. The cetane number is a standardized measure of a fuel's propensity to undergo autoignition under compression, with shorter ignition delays corresponding to higher cetane numbers and hence improved combustion performance in a diesel internal combustion engine. These parameters have been demonstrated to exert a substantial influence on combustion efficiency and emission characteristics. Accurate measurement of ignition behavior is imperative for the development of suitable fuels and the compliance with environmental and performance regulations. It has been established that the Diesel norm acknowledges a variety of methodologies for determining the cetane number. However, in the event of a discrepancy, the EN ISO 5165 standard is to be regarded as the prevailing authority. The AFIDA device is utilized in the context of this project (DIN EN 17155).

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	Standardized Method	Method applied	MGO ISO 8217 DMA	**Diesel EN 590**
Flash point	°C	EN ISO 2719		≥60	≥55
Cetane number	-	EN ISO 5165, EN15196, EN16144, EN16715, DIN EN 17155			≥51
Cetane index	-	EN ISO 4264		≥40	≥46

The AFIDA (Advanced Fuel Ignition Delay Analyzer), fulfilling DIN EN 17155, is a constant volume combustion chamber (CVCC) apparatus designed to evaluate the ignition and combustion behavior of liquid fuels (Fig. 2.1). The primary function of the cetane number is the determination of the ignition quality of fuel. The cetane number is a standardized measure of fuel ignition quality [4]. CVCC devices enable the determination of ignition quality through the utilization of reduced sample volumes and a concomitant reduction in testing time when compared to engine-based methods. It has been demonstrated that the aforementioned procedures are suitable for the ignition quality of both petroleum-based and non-petroleum-based middle distillates.

The combustion chamber is a cylindrical vessel that is heated by nine ceramic rods, which can reach temperatures of up to 730 °C. The maximum setpoint pressure (pre-ignition) is 25 bar, permissible pressure for combustion is 50 bar. The fuel is introduced into the chamber using a piezoelectric diesel injector or a solenoid gasoline injector. The combustion process within the chamber is meticulously monitored by a pressure sensor. The ignition delay between injection and auto-ignition i.e. rapid pressure increase is determined automatically based on the recorded pressure data. This delay is then used to derive the fuel's ignition quality in a cetane number. Experiments were performed in the AFIDA 2805 apparatus, ASG Analytik-Service GmbH (ASG), Germany (Fig. 2.1).

The cetane number standard conditions are derived as follows: combustion chamber pressure: 17.5 bar and combustion chamber temperature: 580°C are utilized. However, the temperature and pressure are also subjected to variation to conduct a more thorough investigation into the characteristics of the ignition.

Cetane index

The cetane index (CI) is a parameter used to estimate the ignition quality of diesel fuels in the absence of a cetane engine. This method is especially advantageous when conducting engine testing is impractical due to limitations in sample quantity or equipment availability. The cetane index is defined by ISO 4264:2007, and it is calculated using a standardized four-variable correlation involving fuel density and distillation characteristics [5], which is detailed in section 2.3. It is imperative to note that the distillation data in accordance with EN ISO 3405 is mandatory, with a fuel quantity of 100 milliliters. Therefore, the determination was not always possible.

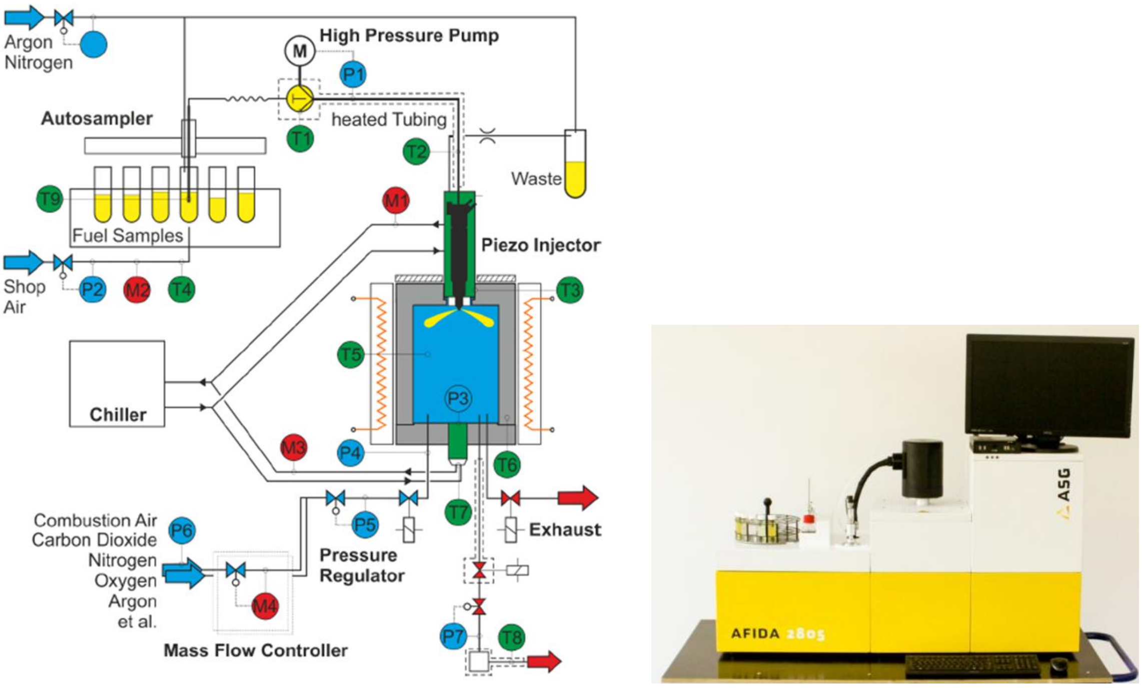


Figure 2.1 Advanced Fuel Ignition Delay Analyzer (AFIDA) device (right) and operating principle (left).

Bidimensional gas chromatography (GCxGC)

In the course of this project, the standard GC-MS (gas chromatography-mass spectrometry) technique is employed in conjunction with the customized bidimensional GCxGC method. An Agilent 7890A GCxGC gas chromatograph method was customized with a unique heating protocol on the secondary FID transfer column line for trace analysis, as described by [6]. The analysis was conducted under a reverse phase configuration, employing a primary Restek Stabilwax column (30 m, 0.25 mm internal diameter, 0.25 µm) and a Restek Rtx-5 column (1, 0 m, 0.18 mm internal diameter, 0.20 µm). The following characteristics are delineated:

GC Method

- Carrier gas: Helium
- Column flow rate: 1.4 ml/min
- Inlet split type: Split
- Inlet split: 50

- Inlet temperature: 300 °C
- Primary oven temperature programme:
- Initial: 40 °C, 3 min hold.
- Ramp: 6.5 °C/min up to 240 °C, 5 min hold.
- Secondary oven temperature: +65 °C over primary oven.
- Modulator temperature:: +15 °C over secondary oven (cryogenically cooled with liquid nitrogen).
- Modulation programme: 8s; 2s hot pulse, 2s cold pulse
- Transfer line temperature: 250 °C
- Instrument: Agilent 7890A equipped with cryogenic liquid nitrogen modulator and secondary oven configuration.

MS Method

- Mass spectral range: 45-500 amu
- Electron energy (volts): -70
- Ion source temperature: 250 °C
- Instrument: LECO Pagasus 4D Classic

Soot Formation

In an effort to curtail CO_2 emissions and pollutants in the transport sector, the implementation of more stringent standards, such as EURO 7, is currently under deliberation. Soot formation is a significant contributor to pollution, and given its high susceptibility to fuel composition, the development of novel climate-neutral fuels holds promise for reducing particulate emissions. However, extant measurement methods, particularly those grounded in engine-based approaches, have been principally designed for the purpose of vehicle and fleet testing. These methods are time-consuming and impractical for routine use outside of research environments.

The project utilizes the Yield Sooting Index (YSI) [7] to predict particulate emissions from alternative fuels and blends. To address these challenges, a simplified stationary burner test has been developed to reduce complexity and accelerate the development process. All data, including fuel properties, are stored in a database to support a predictive emission model. This approach provides a direct, combustion-based measurement that reflects the full fuel properties. This method facilitates expeditious and dependable assessments of soot formation for real-world fuel blends.

The Yield Sooting Index quantifies the soot-forming tendency of a chemical substance by measuring soot concentration in a standardized methane/air flame after adding a small amount of the test compound. To minimize the influence of experimental variability, such as concentration, burner type, or flame conditions, the soot values are rescaled linearly between reference compounds with assigned YSI values. For example, in the unified YSI Scale, n-hexane and benzene are typically chosen as the reference substance, with YSI values of 30 and 100, respectively. A similar concept is employed in the octane number system for quantifying fuel knock resistance and also in the cetane number system.

The concentration of the test compound can be expressed by mole or mass fraction. For complex fuels with unknown molecular weights, the mass-based definition is preferred. A key advantage of the YSI method lies in the high dilution of the test fuel, which is typically referred to as flame “dopant” (0.5% by mass), which is added to the fuel stream of a baseline methane/air coflow non-premixed flame. The small addition perturbs the flame just enough to produce soot precursors from the tested fuel or fuel blend, and the resulting increase in soot yield is recorded and converted to the YSI. Keeping the dopant very dilute minimizes dilution/thermal effects and thus it ensures that the soot yield is primarily influenced by the intrinsic chemical properties of the test fuel rather than by secondary effects such as dilution or flame temperature variation. Furthermore, the minimal sample volume required (~100 µL) makes the method highly efficient and repeatable. Finally, a comprehensive online database of over 400 measured YSI values as a reference are available.

This project employed a well-established experimental setup centred on a Yale-Coflow burner to investigate the sooting tendencies of pure compounds and fuels [7]. On this Coflow burner an axisymmetric, laminar, nonpremixed methane/air flame is generated, and soot volume fractions were measured using color-ratio pyrometry. The maximum soot volume fraction (fv,max) is used to calculate the Yield Sooting Index (YSI) of each tested compound.

The fuel mixture is made up of methane (58.3% by mass), nitrogen (41.2%), and a dopant (0.5%), which is delivered through a 4 mm inner diameter tube and reacted with air through an annular gap within a 74 mm diameter concentric aluminum chimney. The dopant is added at a constant mass fraction via a syringe pump, with liquid-phase flow rates of 109-142 µl/h depending on density.

Dopants are injected into the fuel line through a septum in a stainless-steel T-connector. The line and tube were maintained at about 150 °C to ensure complete vaporization and homogeneous gas-phase mixing. A stabilization period of at least 30 minutes was observed before data collection.
An issue of appearing smoke, which was initially observed, was addressed through a methodical approach. This approach entailed alternating with the reference substances and repeating the measurements.

Flame imaging is performed using a Canon EOS D 60 camera with a 50 mm lens. A Schott BG-7 optical filter is set on the lens to block UV and IR interference. To ensure repeatability, the camera is positioned at a fixed distance of 500 mm from the flame´s symmetry axis. A hood was used to block light from the laboratory environment.

Two-dimensional soot volume fraction (f_v) maps are obtained using color-ratio pyrometry, following the method of Das et al. [8] without significant modification. According to this literature, $f_{v,\,max}$ is defined as the soot concentration averaged over the sootiest parts of the flame. All results of the soot formation relate to this value $f_{v,\,max}$.

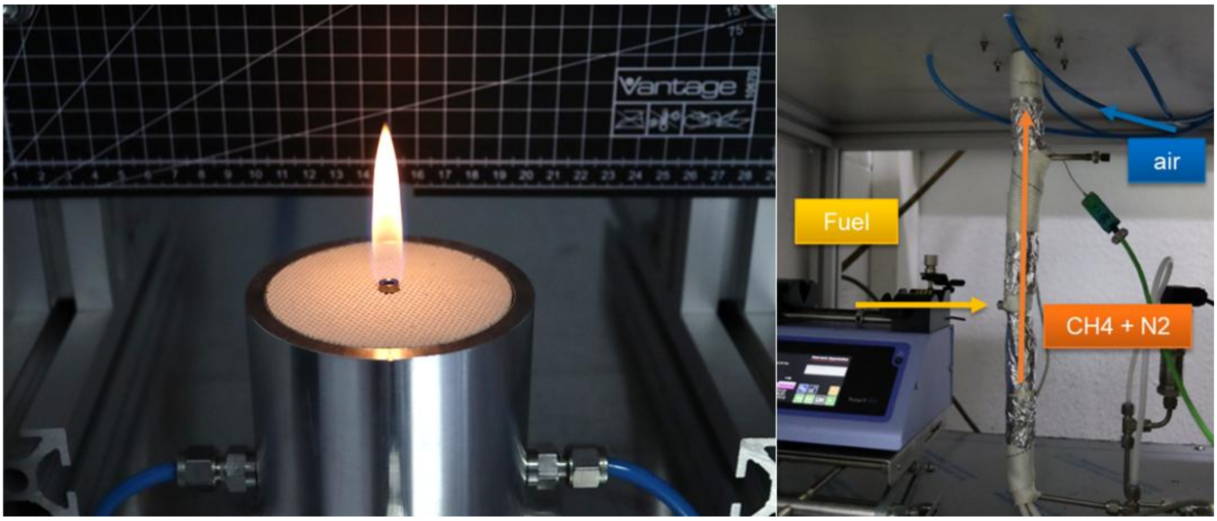


Figure 2.2 Yale-Coflow burner (chimney not attached) with established flame (left) and dopant dosing unit and heated fuel line underneath the burner (right)

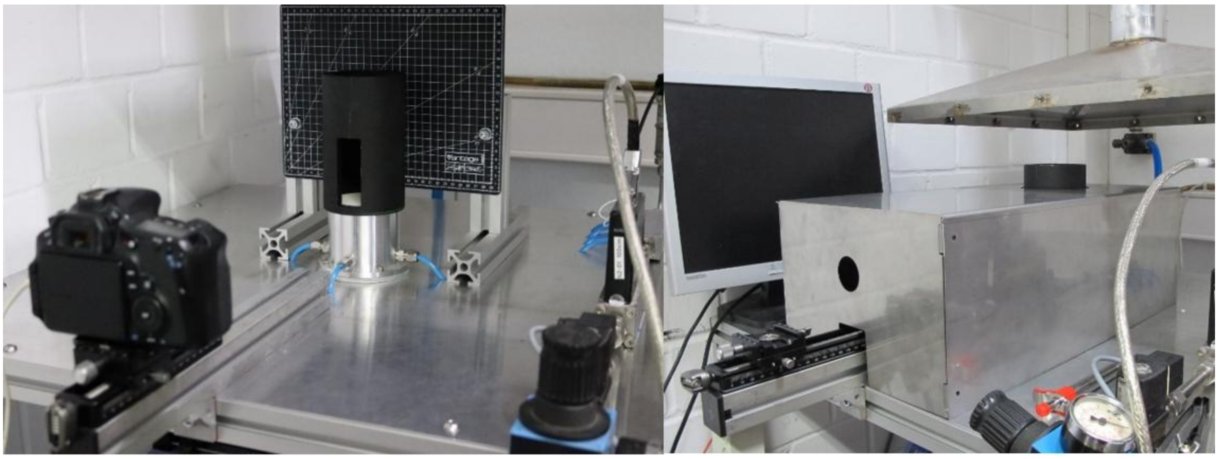


Figure 2.3 Camera set in front of the Coflow-burner (left) and light preventing hood (right).

Image processing and soot volume fraction (f_v) calculation are performed in Python using open-source code described by Dreyer et al. The flame images represent two-dimensional line-of-sight projections of the three-dimensional soot distribution. These projections are reconstructed into radial distributions using the BASEX Abel transform method. A flame-heated Type-S thermocouple is used as a calibrated light source to generate a temperature lookup table, relating pixel intensities and color-channel ratios to absolute flame temperatures.

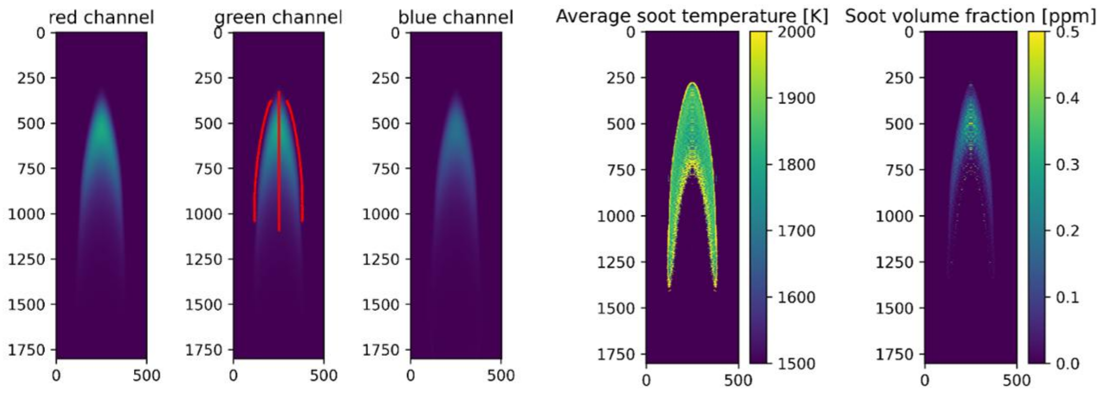


Figure 2.4 Intensities of the individual colour channels (R, G, B) of one picture of a flame doped with 1,2-dimethylbenzene (3 pictures on left) with added flame edge detection and centerline in red (second left). Average soot temperature and soot volume fraction fv derived from two-colour pyrometry of a flame doped with 1,2-dimethylbenzene (two pictures on right).

In a few cases, the test methods mandated by the relevant fuel specifications could not be followed exactly. These departures were driven mainly by instrument access and, critically, limited sample volumes. **Oxidation stability,** included in this report, is a key example. The marine gas oil (MGO) standard references ISO 12205, but this procedure requires more material than we could allocate for the surrogate e-fuels in this study. Accordingly, oxidation stability was measured using two approaches: ISO 12205 where sufficient sample was available, and ISO 1609 (selected for its lower volume requirement) otherwise.

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 is the case for the **Cetane Index** determination**.** This index is not measured but calculated as describe in the standard ISO 4264. It is based on the measurement of the density at 15 °C as well as the distillation test, where the 10, 50 and 90% (v/v) evaporation levels are considered.

The cetane index is derived through a four-variable empirical equation:

$$CI=45.2+0.0892T_{10N}+(0.131+0.901B)T_{50N}+(0.0523-0.42B)T_{90N}+0.00049(T_{10N}^2-T_{90N}^2)+107B+60B^2$$

Where:

- T_{10}: temperature in °C, at which 10% volume of the product has evaporated;
- T_{50}: temperature in °C, at which 50% volume of the product has evaporated;
- T_{90}: temperature in °C, at which 90% volume of the product has evaporated;
- $T_{10N}=T_{10}-215$;
- $T_{50N}=T_{50}-260$;
- $T_{90N}=T_{90}-310$;
- $B = [\exp(-0.0035D_N)] -1$;
- D_N = D-850;
- D is the density at 15°C in kg/m³.

2.4 Overview on fuels tested

The following Table 2.2 offers a synopsis of the fuels examined. This encompasses both the alcohol and ether surrogates for HOEF, in their neat form (as received from WP2) and the fuels formulated by blending the former with MGO. It is noteworthy that, in contrast to the corresponding table in Deliverable D3.1, this table incorporates an additional batch of ether surrogate (ether surrogate-3) and a blend thereof with MGO (50%-50%). As it shall be further detailed below, this 3rd batch of ether HOEF surrogate was produced aiming at depriving the e-fuel mixture of lower flash-point compounds, specifically C_8 and C_9 aliphatic ethers. Therefore, the new ether HOEF batch 3 was synthesized from C_5-C_9 alcohols, effectively yielding the corresponding mixture of C_{10}-C_{18} ethers.

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
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.
Ether surrogate-3	0.65	Batch3. Total amount received for testing
Volume amount after 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 30% (v/v) alcohol surrogate & 70% MGO-2.
50% alcohol blend	3	Blend of 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
50% ether blend	0.7	Blend of 50% (v/v) ether surrogate-3 & 50% 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.

Due to limited fuel availability, we constrained the number of tests per sample, especially for methods with high sample-volume demands. The rationale and methodology guiding these choices, including when to repeat or omit tests based on preliminary findings, are detailed in the next chapter and align with the approach set out in Deliverable D3.1. Table 2.2 summarises the sample volumes required for each analytical method.

3 Results & Discussion

This chapter first complements earlier report D3.1 with an update on specific physicochemical fuel properties (section 3.1). Then the corresponding results on the ignition behaviour are provided in section 3.2. Finally, section 3.3 covers the results on the soot investigation.

3.1 Update on the physicochemical characterization of HOEF e-fuel realizations and blends thereof with MGO

This section presents an update on the physicochemical characterization of the HOEF e-fuel realizations and blends thereof with MGO. This update was motivated by two factors:

(i) Initially, the oxidation stability was assessed solely according to methods indicated in ISO 16091 (D3.1). The unconventional results suggested extending the analysis of at least selected fuel samples to ISO 12205. The new results, following ISO 12205 have been incorporated herein.

(ii) Earlier results on the flash point (D3.1) suggested that the presence of low flash-point ethers could draw the flash point of even MGO-rich blends below the minimum stipulated in the ISO 8217 DMA norm for MGO and the EN 590 norm for automotive Diesel, i.e. 60ºC and 55ºC, respectively. Therefore, it was deemed interesting to produce a new batch 3 of the ether HOEF surrogate devoid of C_{9-} ethers. A second batch (labelled as batch-2) was produced. However, it became apparent soon after its synthesis that a suboptimal temperature control during the alcohol dehydration process step had resulted in an unusually high concentration of low-boiler light olefin side-products. Based on this observation, this batch was discarded and not further investigated. A third batch (batch-3) was then produced fixing the issue of the temperature control. The characterization results for this batch are presented and discussed in this report.

Although this report adds new results only for oxidation stability and flash point (relative to Deliverable D1.3), we reproduce, for completeness, all values from Deliverable D3.1 in Tables 3.1 and 3.2, as well as in Appendix C (fuel appearance images). The discussion below focuses exclusively on the new data; for previously reported results, the reader is referred to D3.1.

Because the available quantity of the batch-3 ether HOEF surrogate was limited (~600 mL), not all parameters could be measured for this composition. To extend testing, we prepared a 50:50 blend of the batch-3 ether HOEF surrogate with MGO batch 2. A portion of this blend was used for supplementary accelerated-ageing investigations, as described in Deliverable D3.3. Filtering, as done for batch-1 (see Deliverable 3.1) was not needed nor performed for batch-3.

Table 3.1 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 batch-1	Ether surrogate batch-1 filtered	Ether surrogate batch-3	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	1.5	≥ 2; ≤6	≥ 2; ≤4.5
Density @ 15 °C	kg/m^3	787	787	796	≤890	≥ 820; ≤845
Acid number	Mg KOH/g	4.1/0.2	0.7[*]/0.8/ 3.6/0.02	0.24	≤ 0.5	-
Corrosive effect on copper (3h @ 50 °C)	Corrosion grade class	1b	1b	-	-	1
Oxidation stability	g/m^3		11	-	≤ 25	-
	min	1401	14.3/12.2	10.8		
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	211	≤ 200[**]	≤ 200
Appearance	Rating	1 Light yellow	1 Light yellow	1 Light yellow	Clear & bright	-
Total contamination	mg/kg	181	53.5	-	-	≤ 24
Distillation				-		
(*v*/*v*) collected @ 250 °C	%	100	100		-	≤ 65
(*v*/*v*) collected @ 350 °C	%	100	100		-	≥ 85
95% (*v*/*v*) collected @	°C	217	217		-	≤ 360
Lubricity	µm	-	230	-	≤ 520	≤ 460
Net heat of Combustion	MJ/kg	-	38.7	-	-	-
	MJ/l		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 3.2 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. For all fuel blends, the percentage indicated in the sample label corresponds to the HOEF content, while the balance percentage corresponds to the MGO content.

Property	Unit	MGO-2	10% ether HOEF batch-1 blend	20% ether batch-1 blend	50% ether batch-3 blend	MGO ISO 8217 DMA	Diesel EN 590
Kinematic viscosity @ 40 °C	mm^2/s	4.13	3.40	2.86	2.3	≥ 2; ≤6	≥2; ≤4.5
Density @ 15 °C	kg/m^3	853	847	840	825	≤890	≥820; ≤845
Acid number	Mg KOH/g	0.6/0.1	0.6/ 3.8/0.1	3.9/ 2.7/0.1	-	≤ 0.5	-
Corrosive effect on copper (3h @ 50 °C)	Corrosion grade class	1b	1b	1b	-	-	1
Oxidation stability	g/m^3 min	3 1179	4 1543	5 1568	7 -	≤ 25	-
Cloud point	°C	1	1	0	-	≤ -16	≤ -10
CFPP (Cold Filter Plugging Point)	°C	-16	-17	-18	-		≤ -20
Pour point	°C	-9	-12	-14	-	≤ -6	-
Water content	mg/kg	53	134	220	-	≤ 200 **	≤ 200
Appearance	Rating	1 (3) brown	1 brown	1 brown	1 light Brown	Clear & bright	-
Total contamination	mg/kg	181	40	176	-	-	≤ 24
Distillation					-		
(v/v) collected @ 250 °C	%	14/<5	26.5	33.2		-	≤ 65
(v/v) collected @ 350 °C	%	91/95	93.3	93.0		-	≥ 85
95% (v/v) collected @	°C	383/350	356	358		-	≤ 360

Lubricity	µm	360	390	400	-	≤ 520	≤ 460
Net heat of Combustion	MJ/kg MJ/l	42.5 38.8	42.2 35.7	42.0 35.2	-	-	-

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

Oxidation stability: The subject of oxidation stability is addressed in Deliverable 3.1. Earlier results following methods outlined in ISO 16091 had revealed marked differences in the oxidation stability for HOEF ether fuels prior to and after fuel filtration. Moreover, for some of the HOEF fuels, the oxidation stability was remarkably lower than that of neat MGO, as judged with the method recommended in this standard.

The lower oxidation stability observed for ether-based HOEF under ISO 16091 raised the possibility that reactive peroxide species might be forming and contributing to reduced stability. To probe this, ISO 16091 testing was repeated for selected fuels (Table 3.3), and—between the two repeats—the samples were independently screened for peroxides using a peroxide indicator strip. The repeat measurements broadly agreed with earlier results, except for the unfiltered ether-surrogate batch 1, which now correlated more closely with its filtered, neat HOEF counterparts (Table 3.1). In all cases, the peroxide indicator strips were negative, indicating no detectable development of peroxide species.

Concerns about the suitability of ISO 16091 for assessing the oxidation stability of an ether-rich, diesel-range fuel, whose composition differs markedly from standard MGO, led the OWI partner to extend testing to ISO 12205. Those results are included in this report. Beyond the values in Tables 3.1 and 3.2, the study also repeated tests for the 30% and 50% alcohol-HOEF surrogate/MGO blends. The new ISO 12205 measurements yielded oxidation-stability values of ≤ 14 g/m³ for all neat HOEF fuels and their blends with MGO, i.e., well below the 25 g/m³ maximum specified under the ISO 16091 MGO standard.

Table 3.3 Overview of oxidation stability repeat test according to ISO 16091 with immediate peroxide test.

E-Fuel	Oxidation stability according to ISO 16091 (min)
Alcohol surrogate	374
Ether surrogate, batch 1, unfiltered	15.5
Ether surrogate, batch 1, filtered	14.3
Ether surrogate, batch 3, unfiltered	12.7
50% ether surrogate batch 3, 50% MGO batch 2	1048

In view of the results discussed above, it can be concluded that, while different oxidation stability assessment methods may be required to probe ether-containing HOEF compared to methods established for conventional MGO, the ether-based HOEF surrogate fuels, and the blends thereof with MGO, largely fulfill the physicochemical requirements set for Automotive Diesel (EN 590) and waterborne MGO fuels (ISO 8217) norms.

3.2 Ignition behaviour of HOEF e-fuel realizations and blends thereof with MGO

Table 3.4, 3.5 and 3.6 summarize the characterization results for the surrogate HOEF e-fuels in their realizations I and II, i.e. a mixture of C_4-C_9 higher alcohols, and a mixture of higher ethers (batch-1 and 3), respectively, as well as blends thereof with MGO.

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

Table 3.4 Overview of the ignition 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. For all fuel blends, the percentage indicated in the sample label corresponds to the HOEF content, while the balance percentage corresponds to the MGO content.

Property	Unit	MGO-2	Alcohol HOEF surrogate	30% alcohol HOEF blend	50% alcohol HOEF blend	ISO 8217 DMA norm for MGO	EN 590 norm for Autom. Diesel
Flash point	°C	86	65	64	64	≥ 60	≥ 55
Cetane number	-	54	27	42	37		≥ 51
Cetane index	-	52	20	47	35	≥ 40	≥ 46

Table 3.5 Overview of the ignition 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 or blending. Values highlighted in blue indicate non-compliance with one or more standard specifications. For all fuel blends, the percentage indicated in the sample label corresponds to the HOEF content, while the balance percentage corresponds to the MGO content.

Property	Unit	Ether HOEF surrogate batch-1	Ether HOEF surrogate batch-1 filtered	10% ether HOEF batch-1 blend	20% ether HOEF batch-1 blend	ISO 8217 DMA norm for MGO	EN 590 norm for Autom. Diesel
Flash point	°C	38	44	65	58	≥ 60	≥ 55
Cetane number	-	97	101	59	62		≥ 51
Cetane index	-	-	41	59	52	≥ 40	≥ 46

Table 3.6 Overview of the ignition characterization results for ether HOEF surrogate , batch-3, as-received from the production process in WP2 or following blending with MGO. Values highlighted in blue indicate non-compliance with one or more standard specifications.

Property	Unit	Ether HOEF surrogate batch-3	50% ether HOEF batch-3 blend	ISO 8217 DMA norm for MGO	EN 590 norm for Autom. Diesel
Flash point	°C	52	62	≥ 60	≥ 55
Cetane number	-	113	73		≥ 51
Cetane index	-	-	-	≥ 40	≥ 46

Flash point: The data demonstrate that the alcohol surrogate and its blends comply with the flash point requirement for both MGO and diesel. However, the flash point values of the ether surrogate, as received, and following filtration, were 38°C and 44°C, respectively. These values are considerably lower than the minimum requirements stipulated by ISO 8217 (≥60°C) and EN 590 (≥55°C). In comparison, Marine Gas Oil (MGO) exhibited a flash point of 86°C, underscoring a pronounced disparity in their respective volatility profiles. The low flash point of the ether surrogate poses a substantial safety concern, particularly in terms of storage, handling, and fire risk. Notwithstanding the blending with MGO, it was observed that a flash point of 65°C was only attained by the 10% blend, while the 20% blend exhibited a reading below the ISO standard (58°C). These findings underscore the necessity for meticulous consideration of flash point when incorporating ether surrogates into marine fuel formulations, as excessively volatile components can compromise the overall safety of the fuel.

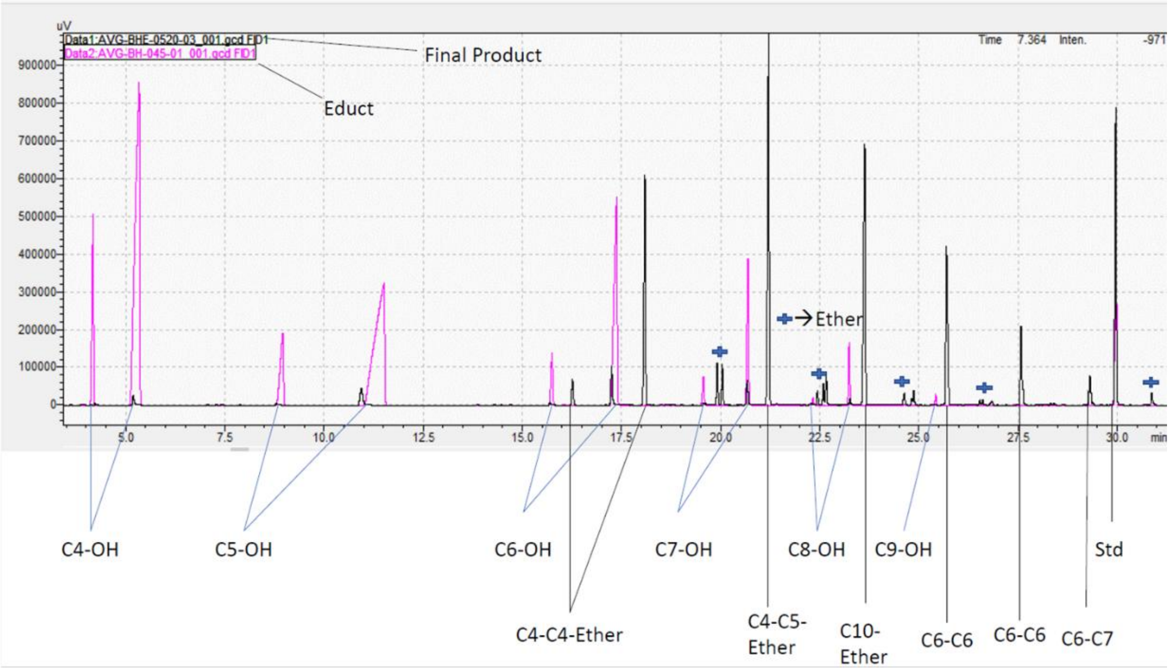


Figure 3.1 GC-MS analysis on the starting elements and the obtained ether surrogate, batch 1.

Gas chromatography of the ether-HOEF surrogate (batch 1) revealed minor constituents with inherently low flash points as neat compounds (Figure 3.2). These are primarily unreacted C_4-C_5 alcohols and C_8-C_9 ethers, which—per Table 3.6—have neat flash points below the minimum specified in ISO 8217.

Table 3.7 Overview of chemical elements identified in the ether surrogate batch 1 realization, based upon the GC-MS analysis.

GC-MS identifier	Chemical name	Amount in % (m/m)	Flashpoint in °C
C_4-C_4-Ether	Di-n-butyl ether	12.6	25
C_4-C_5-Ether	Di-n-pentyl ether	20.5	57
C_4-OH	1-butanol	trace	35

A more detailed analysis was also performed using GCxGC-ToFMS. The results for several fuels are included in Appendix B. This motivated the synthesis of a new ether HOEF surrogate batch-2, devoid of C_8-C_9 ethers, by starting from a C_5-C_9 rather than a C_4-C_9 alcohol mixture precursor. For this new ether HOEF batch, however, the presence of an abnormally high content of volatile olefins was observed by GC, which was tracked back to a suboptimal temperature control during the ether synthesis by alcohol dehydration (WP2). Further, GCxGC results showed that, subsequent to the filtration of the ether HOEF surrogate batch-2, there was a decrease in the low flashpoint olefin content; however, the composition of other components remained relatively unaltered. In light of the aforementioned results, a subsequent iteration of the ether surrogate was conducted, designated as batch-3. For this new batch, the temperature issue was solved and the content in light olefin side-products reduced to traces. As illustrated in Table 3.6, the HOEF batch-3 demonstrated a substantial enhancement in flash point, to 52ºC, approaching the requirement of the standards.

Cetane number: A variation in blending was performed with the two different batches of received MGO with the alcohol surrogate (see Table 3.7). The data demonstrates a decline in the cetane number with an increase in the alcohol surrogate, thereby suggesting that the e-fuel exerts an unfavorable influence on this ignition parameter. A discernible distinction emerges between the MGO batches of 1 and 2, though this observation is not unexpected. As shown in Deliverable 3.1, preliminary physico-chemical data revealed discrepancies between the two production batches.

In contrast, the measured cetane numbers are approximately 54 for the MGO-2 and around 100 for the neat and filtered ether HOEF surrogate, batch-1 (Table 3.5), which is almost a doubling and indicates significantly higher ignition quality. Furthermore, blends containing 10% and 20% ether surrogate with MGO were examined, yielding values of 59 and 62, respectively. These values comply with the established standards for diesel emissions. The findings indicate that the incorporation of the ether HOEF into MGO can significantly impact the fuel's ignition performance, acting as a cetane booster.

Table 3.8 Cetane number for varied blend of MGO (batch 1 and 2) with the alcohol surrogate.

Alcohol-MGO blend ratio (v/v)	Cetane number with MGO-1	Cetane number with MGO-2
0%	49	54
10%	47	52
20%	42	49
30%	37	46
40%	-	43
50%	37	39
100%	25	25

It is noted that the cetane number requirement is exclusively applicable to automotive diesel. However, the determined values continue to offer significant insights relevant to ship applications. The same applies for the ignition delay investigation, which is elaborated in more detail in the following.

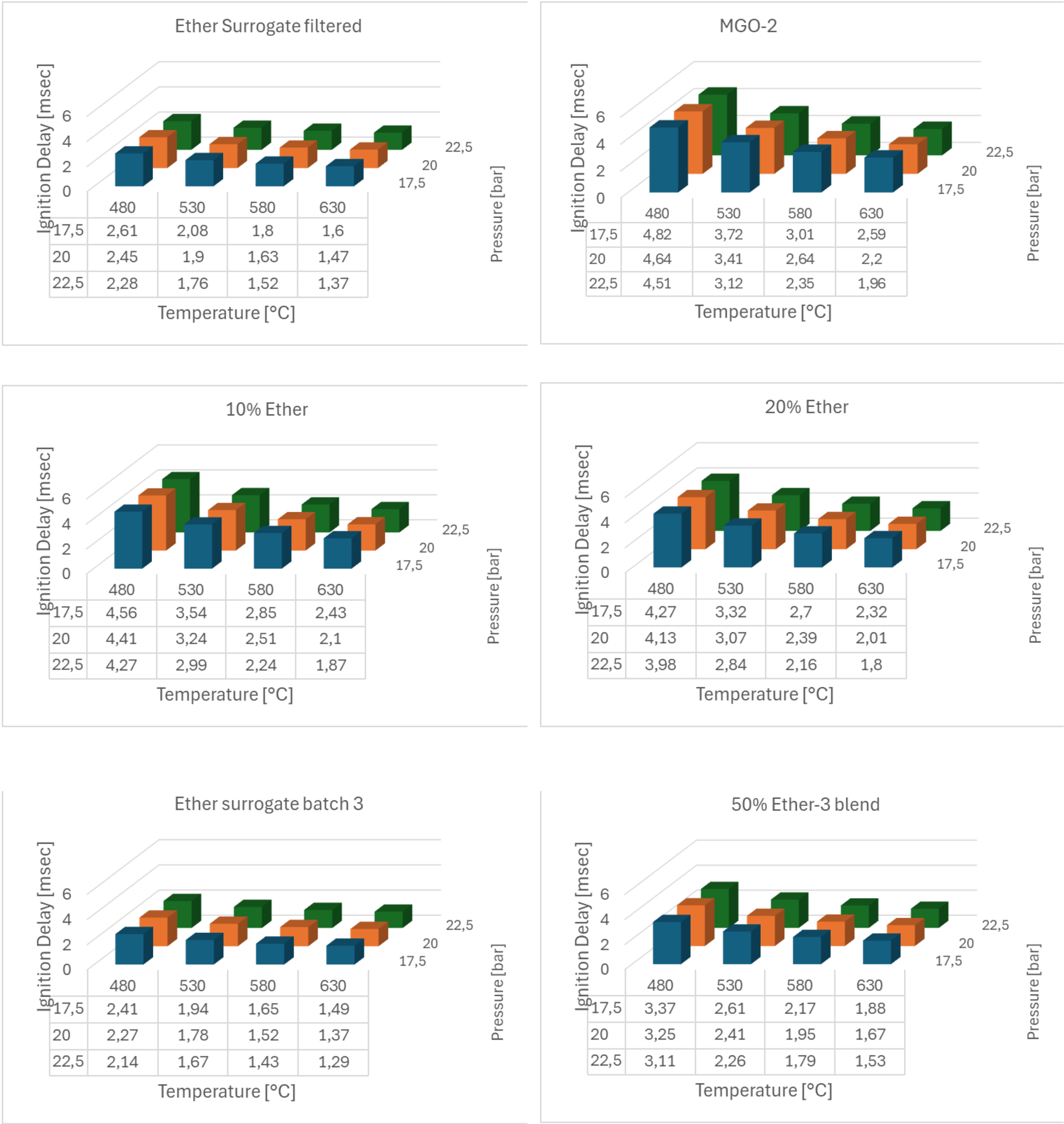
Finally, it is noted that the original blending strategy for the alcohol surrogate was guided by the intention to create one blend that meets, and one that does not meet, the cetane index requirement, thus providing contrast for further evaluation. However, in the end the available amount of surrogate determined the blend percentage investigated. The latter holds for both the alcohol surrogate and for the ether surrogates, batch 1 and 3.

Ignition delay: The ignition delay time refers to the time interval between the start of fuel injection and the onset of combustion. It is a critical parameter in evaluating the ignition quality of fuels, especially for compression ignition engines [4].

Ignition delay times were measured under various operating conditions, involving three combustion chamber pressures (17.5 bar, 20 bar and 22 bar) and four temperatures (480°C, 530°C, 580°C and 630°C). The results consistently show that increasing the chamber pressure and temperature leads to a reduction in ignition delay time for all tested fuels, including MGO, the ether HOEF surrogates, and the blends; see Figure 3.2.

Across the full range of conditions tested, ether HOEF surrogates demonstrated significantly reduced ignition delay times in comparison to MGO, in line with their greater cetane number. For instance, the ignition delay time for MGO at low-temperature and low-pressure conditions of 480°C and 17.5 bar was measured at 4.8 milliseconds, while the ether HOEF surrogate batch-1, ignited in 2.6 milliseconds, which is a reduction of about 45%. It was observed that the ether HOEF surrogate batch-3 ignited at an accelerated rate, with a mean ignition time of 2.4 milliseconds. The ether-MGO blends also exhibited a reduced ignition delay time relative to neat MGO, a tendency that has been attributed to the higher reactivity of the ether additive.

Furthermore, at lower temperatures, the ignition delay time of the ether surrogate exhibited a steeper pressure dependence compared to MGO. As the pressure increased, the ether HOEF surrogates exhibited a more precipitous decrease in ignition delay time, suggesting an increased propensity for ignition. Conversely, at elevated temperatures, the ignition delay times of MGO and the ether surrogate become more analogous, exhibiting diminished disparity between the two fuels.



Ether Surrogate filtered

	480	530	580	630
17,5	2,61	2,08	1,8	1,6
20	2,45	1,9	1,63	1,47
22,5	2,28	1,76	1,52	1,37

MGO-2

	480	530	580	630
17,5	4,82	3,72	3,01	2,59
20	4,64	3,41	2,64	2,2
22,5	4,51	3,12	2,35	1,96

10% Ether

	480	530	580	630
17,5	4,56	3,54	2,85	2,43
20	4,41	3,24	2,51	2,1
22,5	4,27	2,99	2,24	1,87

20% Ether

	480	530	580	630
17,5	4,27	3,32	2,7	2,32
20	4,13	3,07	2,39	2,01
22,5	3,98	2,84	2,16	1,8

Ether surrogate batch 3

	480	530	580	630
17,5	2,41	1,94	1,65	1,49
20	2,27	1,78	1,52	1,37
22,5	2,14	1,67	1,43	1,29

50% Ether-3 blend

	480	530	580	630
17,5	3,37	2,61	2,17	1,88
20	3,25	2,41	1,95	1,67
22,5	3,11	2,26	1,79	1,53

Figure 3.2 Ignition delay analysis under various test conditions.

As demonstrated in the preceding analysis, a discernible disparity in the ignition behavior of MGO and the ether surrogate is evident. Furthermore, the analysis of high-resolution pressure trace data provides a more comprehensive understanding of the ongoing reaction processes. According to the standard DIN EN 17155, the ignition delay time and, consequently, the derived cetane number are determined from the pressure traces. The geometry of the curve provides insights into the ignition process and the temporal and chemical conversion of the fuel. As illustrated in Figure 3.3, following the injection of the substance, a minor pressure decline is initially observed, which is subsequently followed by a pronounced surge. This surge undergoes a steepening process following a brief period of retardation. The pressure curve for MGO and Ether blends demonstrate analogous trends, exhibiting negligible disparities in combustion behavior. Conversely, the neat ether surrogates exhibit a shorter ignition delay time and a reduced maximum pressure. Notwithstanding, all the tested fuels were found to ignite rapidly after injection, reaching their respective peak pressures within a brief time frame of 4 milliseconds. The incorporation of higher ethers into the MGO composition has been demonstrated to induce a beneficial alteration in the fuel's ignition performance. This has been shown to result in a reduction of the ignition delay.

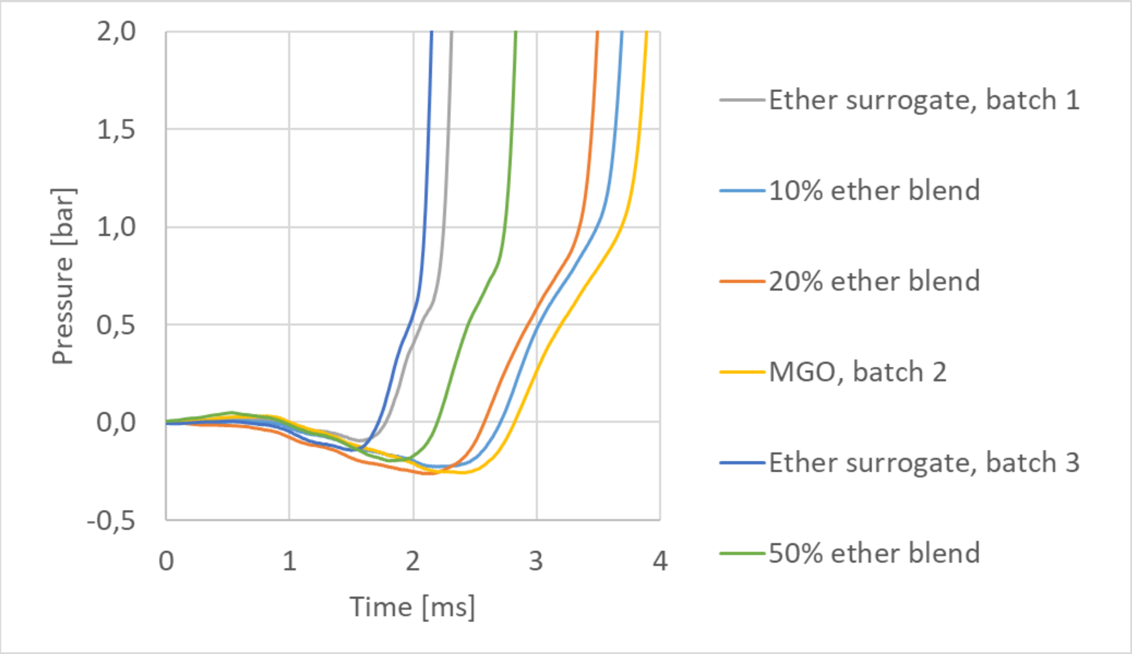


Figure 3.3 Pressure curves over time for the investigated e-fuels at start condition of 20 bar and 530 ºC.

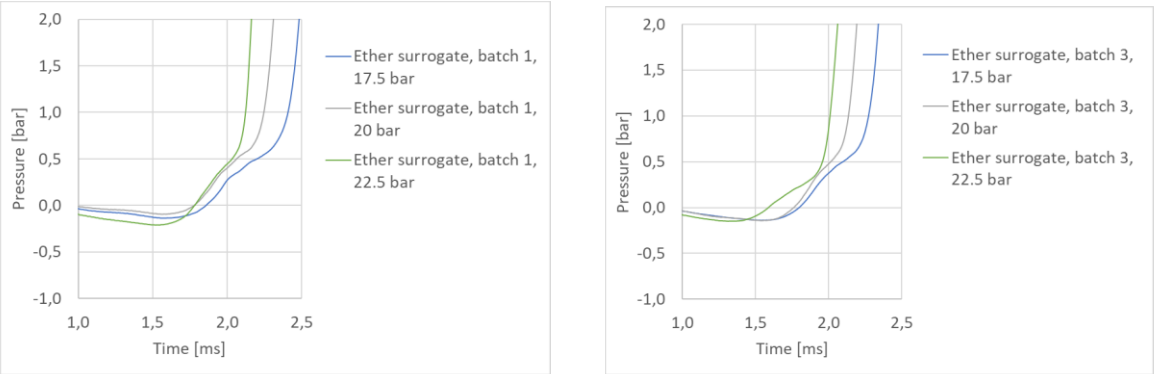


Figure 3.4 Pressure curves over time for the ether surrogate, batch 1 (left) and 3 (right) for varying initial pressure and initial temperature of 530 ºC.

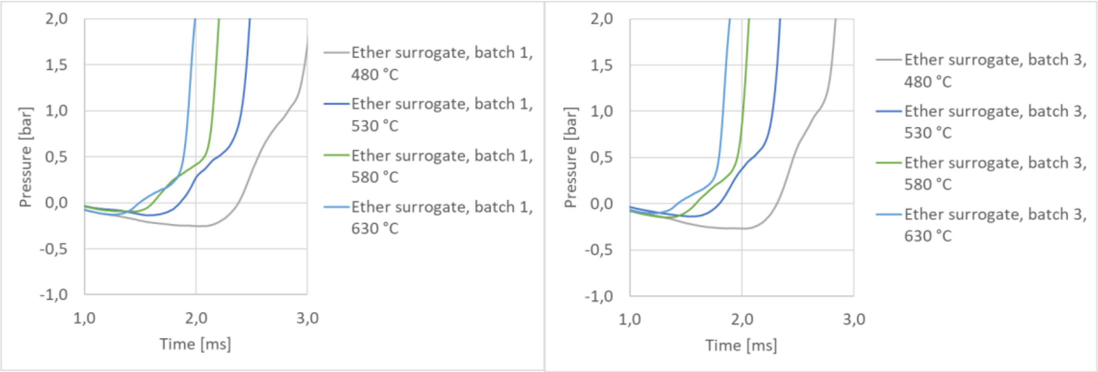


Figure 3.5 Pressure curves over time for the ether surrogate, batch 1 (left) and 3 (right) for varying initial temperature initial pressure of 17.5 bar.

In Figures 3.4 and 3.5, the pressure curves for the neat ether surrogates are shown, with varying initial pressure and varying initial temperature. As the pressure increases, the onset of the steep pressure rise becomes earlier. A similar phenomenon has been observed in the context of rising temperatures. A comprehensive evaluation reveals that the ether HOEF surrogate fuel, designated as batch-3, exhibits superior reactivity and concomitantly diminished ignition delays under all conditions.

Cetane index: with respect to the alcohol blends, the 30% blend meets the requirement for the cetane index; however, the 50% ether HOEF-MGO blend does not. The cetane index for the filtered ether surrogate is found to be in accordance with the standard for MGO; however, it does not align with the standard for diesel. With regard to the 10% and 20% ether blends, the cetane index readily complies with the MGO standard.

The amount of the leftover ether HOEF surrogate batch-3, as well as its 50% with MGO, was insufficient for the execution of a distillation test. The previously mentioned cetane number and ignition delay results were prioritized due to their perceived enhanced informative value.

Overall, the ignition behavior of the e-fuels and blends that were the focus of this investigation exhibited excellent values, highlighting the potential of e-fuels based on higher aliphatic ethers to enhance the ignition performance of MGO and Diesel fuels.

3.3 Soot characteristics of HOEF e-fuel realizations and blends thereof with MGO

Trends regarding the formation of particulate soot upon ignition of different fuel and fuel blends were established according to the Yield Soot Index methodology delineated in Chapter 2. Those fuels examined and the corresponding experimental YSI values are summarized in Table 3.8. The accuracy of this methodology is estimated to be approximately 10-15%. The findings indicate a discernible tendency toward a decline in soot emissions for both HOEF realizations. The results indicate that the values obtained for the unblended alcohol (19) and the ether (33 for batch-1 and 38 for batch-3) HOEF surrogates are consistently and significantly below the value determined for MGO (170). Blending HOEF with MGO is demonstrated to markedly diminish soot, even when utilizing a minimal amount of HOEF, e.g. 10% ether HOEF content in the blend results already in a 35% YSI reduction. Blending HOEF composed of higher aliphatic ethers into marine gas oil (MGO) reduces soot formation significantly, underscoring its potential to lower local particulate emissions in high-traffic waterways and port areas.

Table 3.9 Overview of the YSI testing on soot formation.

Fuel	YSI-value
MGO-2	170
Alcohol surrogate	19
30% alcohol surrogate MGO blend	85
50% alcohol surrogate MGO blend	77
Ether surrogate, batch 1, unfiltered	33
Ether surrogate, batch 1 filtered	37
10% ether surrogate-1 MGO blend	110
20% ether surrogate-1 MGO blend	100
Ether surrogate, batch 3	38
50% ether surrogate-3 MGO blend	88

3.4 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.

Subobjective (4c) to quantify the effects of the neat oxygenates e-fuel and selected blends thereof on the ignition behaviour, efficiency, with emphasis on soot emissions profile via the Yield Sooting Indices (YSIs) formalism.

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

3.5 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
Steps to facilitate exploitation	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 the ignition properties and soot characteristics 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.

With respect to the alcohol-based HOEF and its blends with MGO: it is concluded that the specification requirements indicated in the relevant fuels norms are fulfilled with regard to oxidation stability and flash point. The cetane number (CN) and cetane index (CI) are not satisfied for the neat alcohol HOEF surrogate; nevertheless, blending with MGO at a 30% HOEF content has been demonstrated to achieve the desired cetane index.

In consideration of the ether-based HOEF and its blends with MGO: it is concluded that the specification requirements stipulated in the pertinent normative documents are met with regard to oxidation stability and cetane number. The ignition delay shows significant reduction upon HOEF blending, emphasizing that higher aliphatic ethers may act as cetane boosters, improving combustion performance. Compliance with the flash-point requirement, however, still necessitates blending, even though an ether HOEF batch synthesized to be devoid of lighter (C_{9-}) ethers delivered a value approaching the limit.

Both realisations exhibit favourable soot behaviour, and even modest HOEF additions have been shown to significantly reduce the soot yield relative to state of the art MGO.

The results of the investigations reported herein indicate that the objective of a rapid market introduction of higher oxygenate e-fuels (HOEF) is indeed feasible, particularly upon blending the ether-based HOEF with state-of-the-art fossil fuels such as MGO.

Recommendation

The results presented in this report have implications for the design of the HOEF production process. In order to attain an ether HOEF composition for optimal performance upon blending with MGO, the e-fuel synthesis process should strive for:

(i) As high as possible chain-growth probability, thus favoring the production of longer-chain and higher flashpoint ether compounds; and,
(ii) as linear as possible higher alcohol intermediates, which result in higher yields to ethers and lower side-production of olefin side-products, the latter displaying undesirably low flash points.

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	Low flash point of some fuel blends due to even minority presence of volatile ethers or olefins.	1	2	Tune HOEF production to favour longer-chain higher oxygenates, and blending with suitable diesel/MGO fuels.
WP 3.2	High water uptake, due to increased hygroscopicity, for the HOEF (particularly if based on alcohols) and its blends.	1	3	For waterborne transport, check for each fuel charge, so that ship's captain can decide whether water content and overall fuel 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
D2.1 & D2.3	Describes the production of the surrogate HOEF fuels analysed and tested in D3.1. D3.2 and D3.3.
D3.1	Whereas D3.2 discusses results on the ignition performance and soot emissions, report D3.1 reports the details on the fuel physicochemical characterization.
D3.3	Whereas D3.2 discusses results on the ignition performance and soot emissions, report D3.3 reports on the fuel-system compatibility, hardware-in-the-loop and accelerated 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

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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
9	UZ	SVEUCILISTE U ZAGREBU. FAKULTET STROJARSTVA I BRODOGRADNJE
10	UCT	UNIVERSITY OF CAPE TOWN
11	KAUST	KING ABDULLAH UNIVERSITY OF SCIENCE AND TECHNOLOGY

Disclaimer/ Acknowledgment

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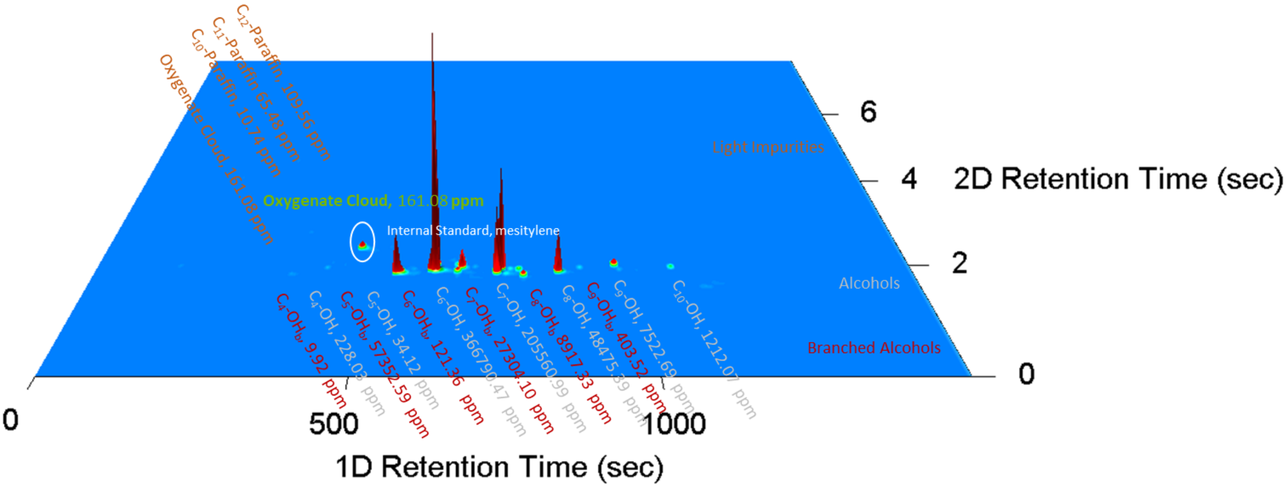
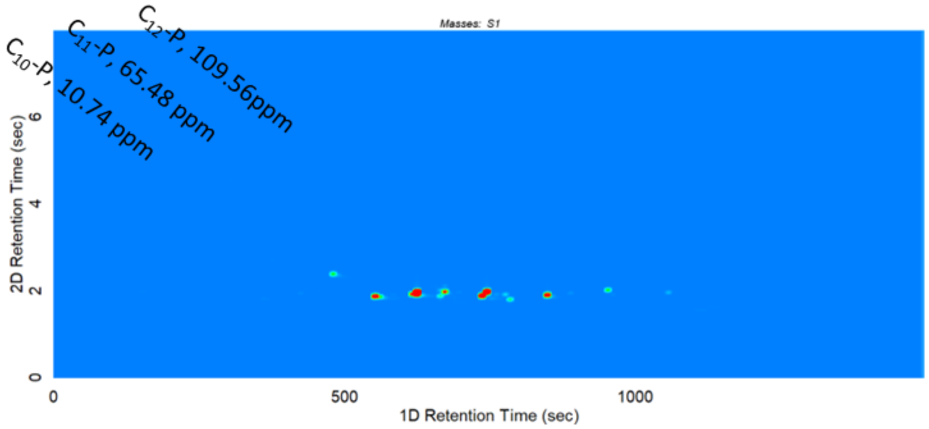
9 Appendix B – GCxGC test results

9.1 Alcohol surrogate

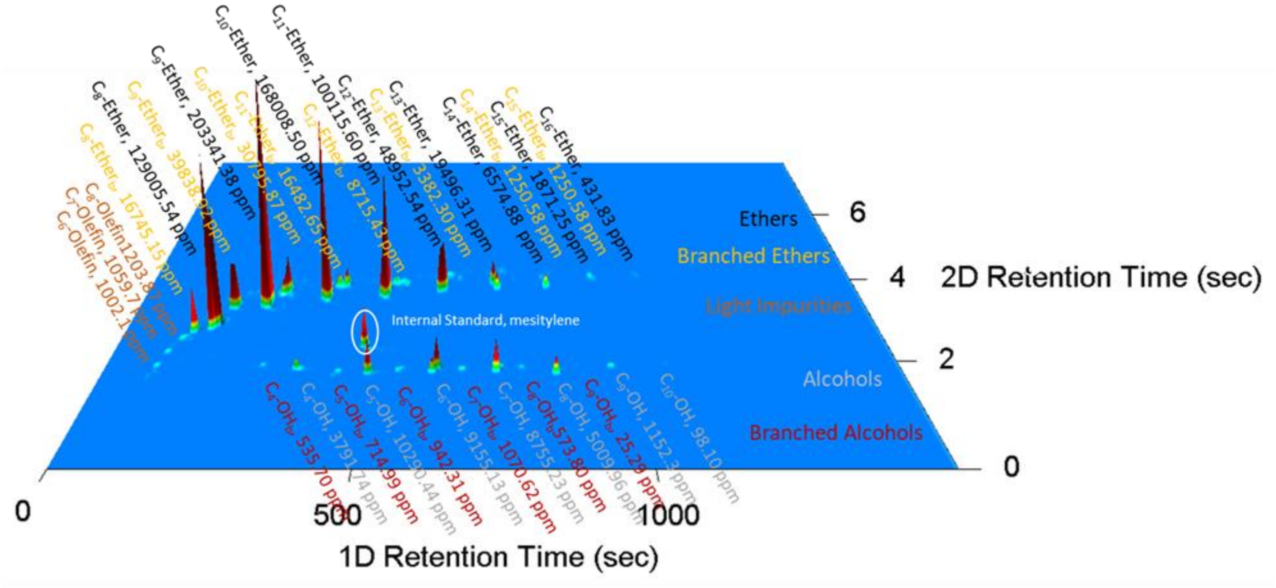


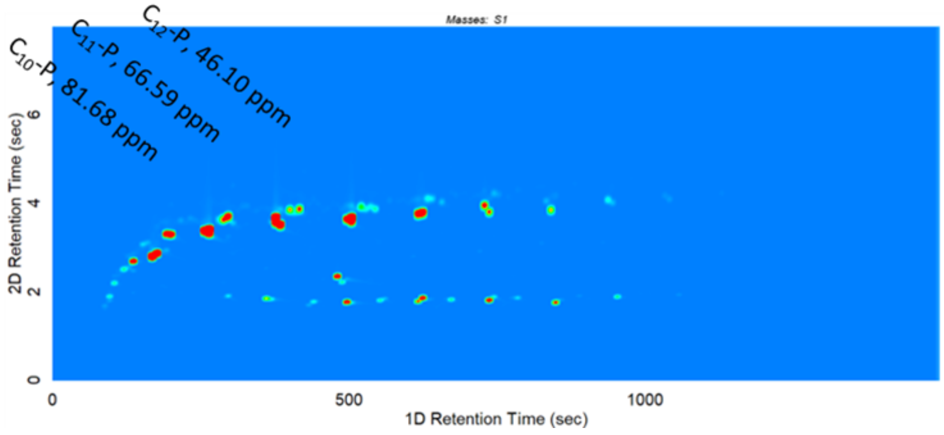


Notes:

- Besides both branched and linear alcohols, minimal low-flashpoint molecules were observed.
- The sample presented with C_{10-12} paraffins at low concentration (10.74, 65.48 and 109.58 ppm, respectively).
- A minor oxygenate cloud of 161.08 ppm was also observed.

9.2 Ether surrogate, Batch 1, unfiltered

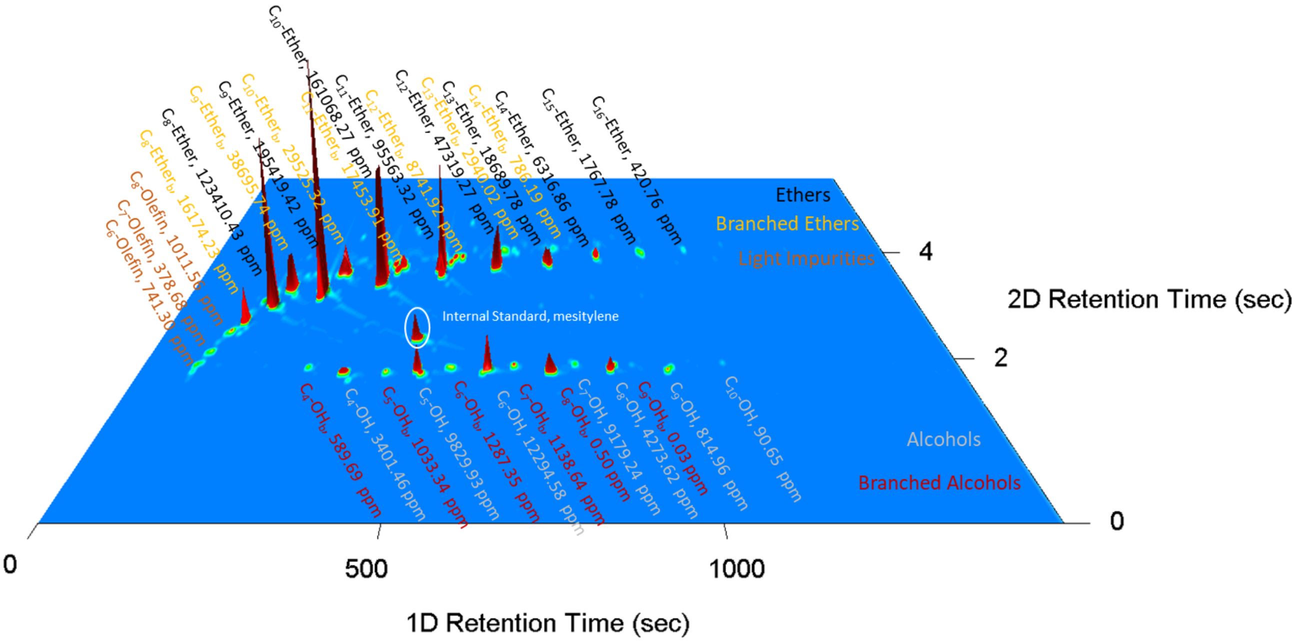


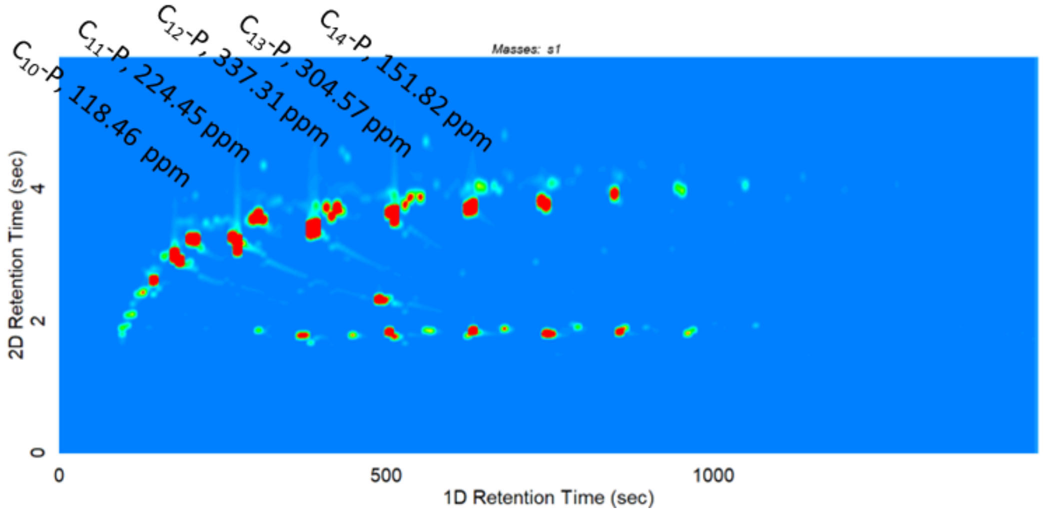


Notes:

- ➢ The sample presented with low flashpoint molecules, namely C_{6-8} olefins at 1002.1, 1059.7, and 1203.87 ppm, respectively).
- ➢ However, the e-fuel appeared clean and only presented with both alcohols (C_4 to C_{10}) and ethers (C_8 to C_{16}).

9.3 Ether surrogate, Batch 1, filtered

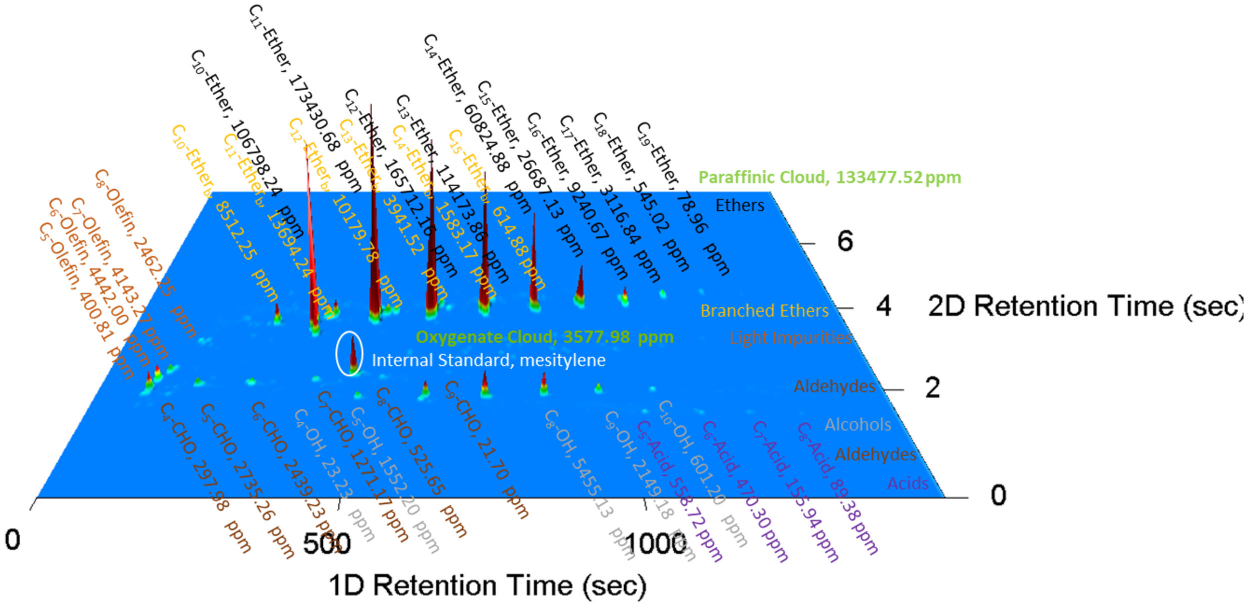


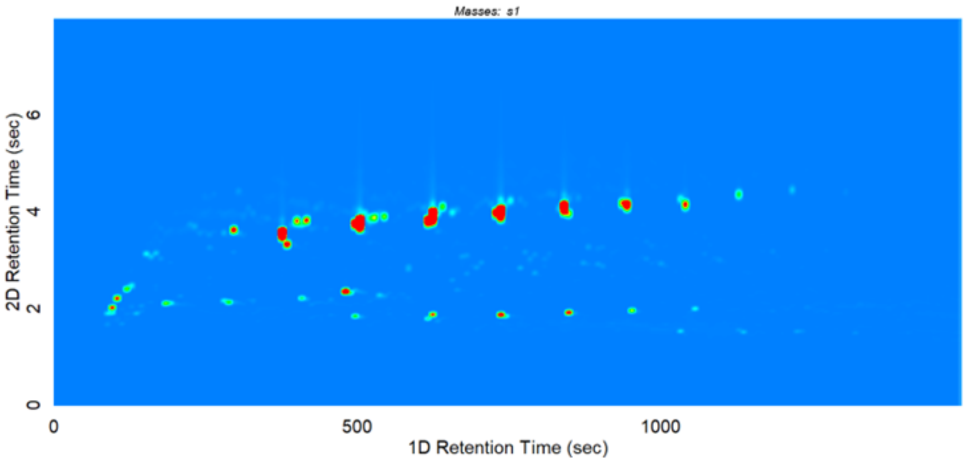


Notes:

- Filtering the Ether Surrogate slightly reduced the low flashpoint olefin content, ($C_{5\text{-}7}$ olefins at 741.30, 378.68, and 1011.56 ppm, respectively), yet all other components (linear and branched alcohols, and ethers) remained relatively unchanged because of filtering.
- The filtered ether surrogate was also found to contain linear paraffins (C_{10}-C_{14}).

9.4 Ether Surrogate, Batch 3

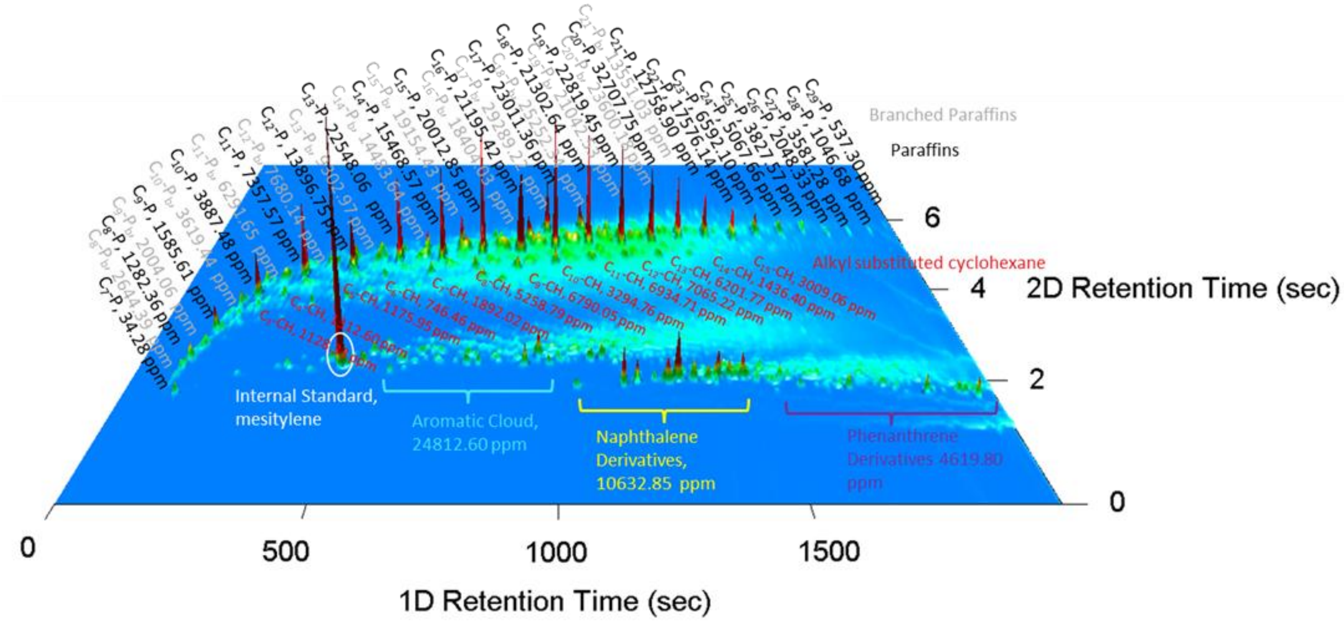


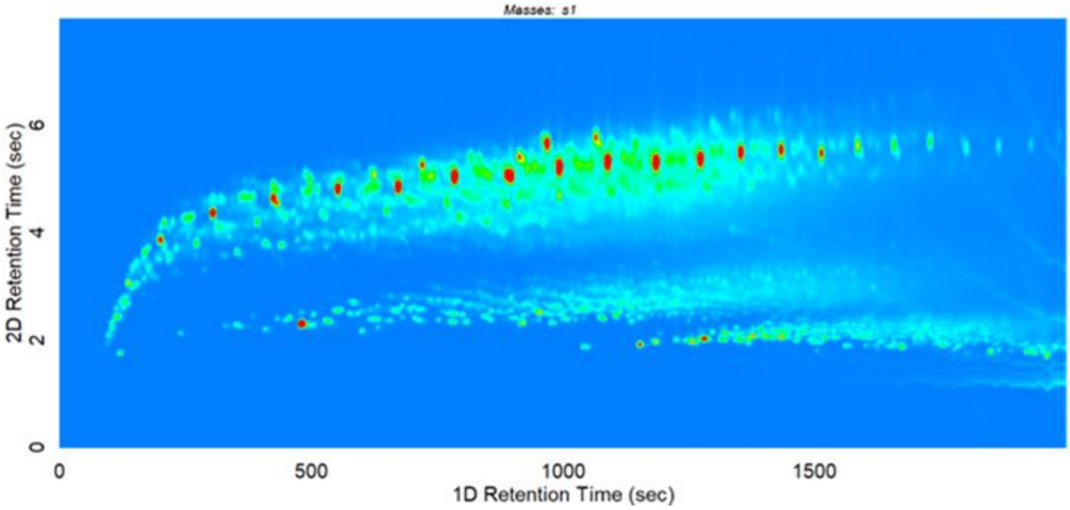


Notes:

- ➢ The sample presented with low flashpoint molecules ($C_{5\text{-}8}$ olefins [400.81, 4442.00, 4143.27, and 2462.25 ppm, respectively], $C_{4\text{-}9}$ CHO [aldehydes at 297.98, 2735.26, 2439.23, 1271.17, 525.65, and 21.70 ppm, respectively] as well as $C_{5\text{-}8}$ acids [558.72, 470.30, 155.94, and 89.38 ppm, respectively]).
- ➢ This particular Ether Surrogate was observed to also contain a higher linear ether and lower alcohol ratio compared to Ether Surrogate 1 but similar to Ether Surrogate 2.

9.5 MGO, batch 2

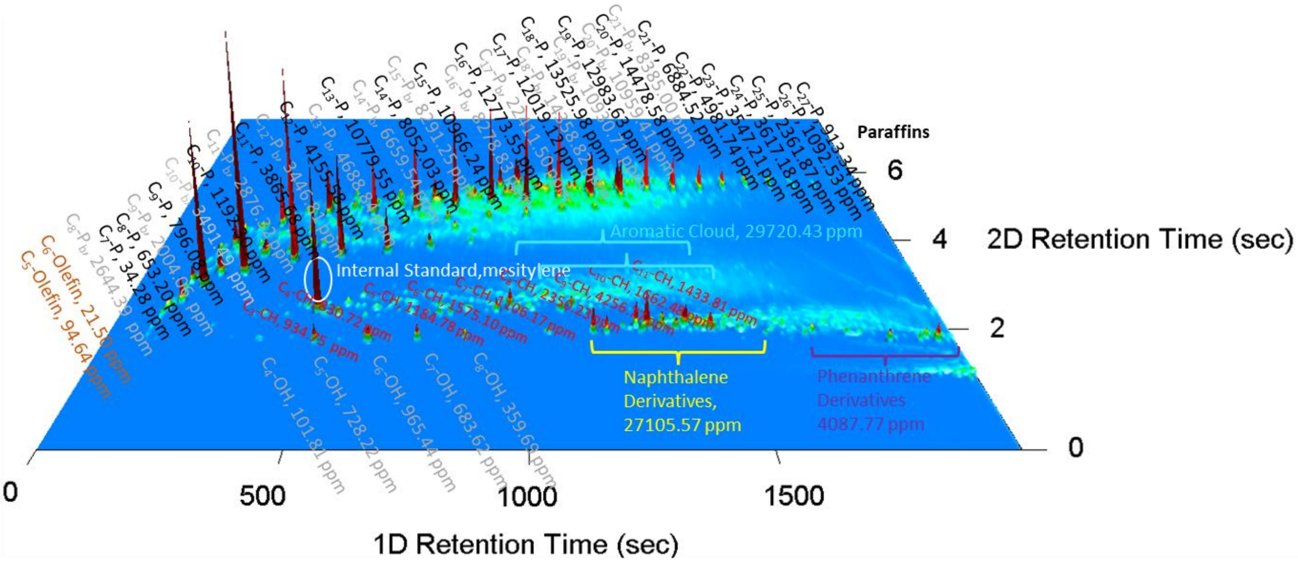


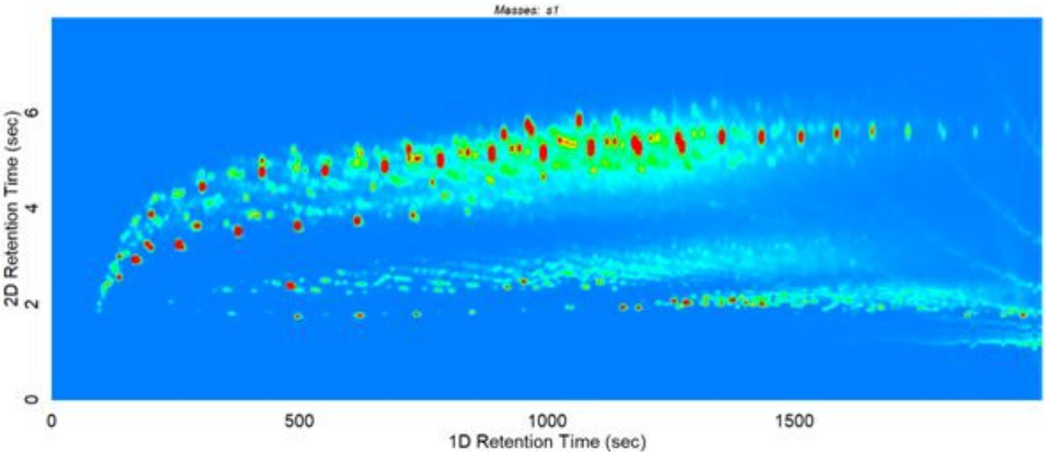


Notes:

- The MGO-2 oil was studied and contained low flashpoint molecules starting from heptane, in addition to C_{3-15} alkyl substituted cyclohexanes (C_{x}-CH), naphthalene and phenanthrene derivatives.
- The oil was found to contain no low flashpoint olefins.

9.6 10% ether surrogate blend

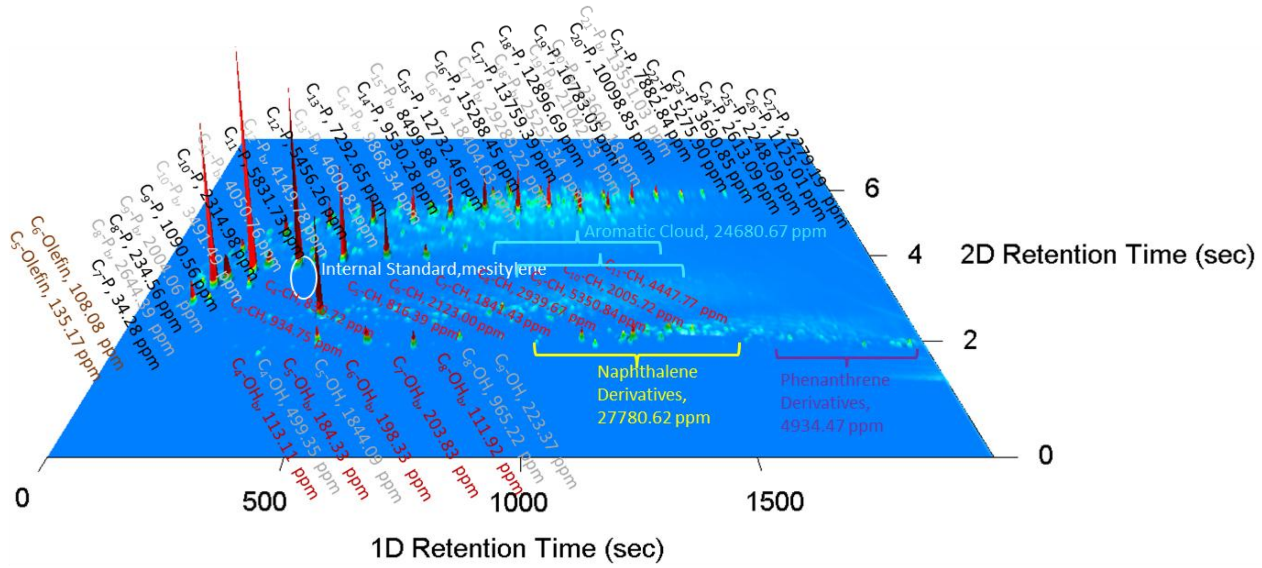


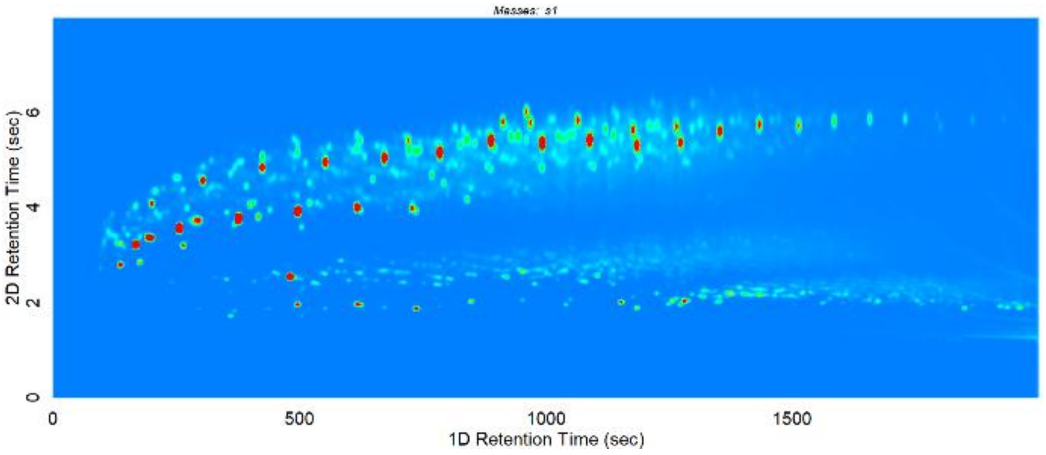


Notes:

- This blend was found to contain pentene and hexane at low concentrations (94.64 and 21.50 ppm, respectively).
- As with this 90:10 ratio, the ether content was lower than the 80:20 ratio.

9.7 10% ether surrogate blend





Notes:

- ➢ As with the 10% blend, the 20% blend was also found to contain pentene and hexane at slightly higher concentrations, 135.17 and 108.08 ppm, respectively.
- ➢ Ether content was higher than the 10% blend, due to the higher blending ratio.

10 Appendix C – Appearance test results

 Alcohol surrogate	 30% Alcohol/70%MGO Blend	 50% Alcohol/50%MGO Blend
 MGO batch 1	 MGO batch 2	
 Ether surr e, batch 1 (unfiltered)	 Ether sur ate, batch 1 (filtered+amine)	 Ether surrogate, batch 2

 10% Ether surrogate/90% MGO Blen	 20% Ether surrogate/80% MGO Blend	
 Ether Surrogate, batch 3	 50% Ether surrogate-3/ 50% MGO-2	