



Refinery integration, scale-up and certification
for aviation and marine biofuels production

D4.5 – Evaluation of fuel blend related to marine fuel standards on the basis of analytical results

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Executive summary

This deliverable D4.5 Evaluation of fuel blend related to marine fuel standards on the basis of analytical results, describes the activities carried out in WP4 (T4.2) of the REFOLUTION project. This report summarizes the results of detailed analytics of all hydrodeoxygenated pyrolysis oil (HPO) products and the evaluation for their suitability as blending component for marine fuels.

Description of the deliverable content and purpose

The deliverable is intended to provide an overview of the samples produced in the Refolution project. Firstly, the parameters according to ISO 8217 have been included in order to demonstrate the basic suitability as a marine fuel. In addition, various tests have been carried out on the blending behaviour of an HPO sample. This is to assess the miscibility of HPO with conventional and alternative marine fuels. The purpose of this deliverable is to determine whether the HPO is compatible with marine fuels and thus in principle suitable as a marine fuel and a marine drop-in fuel.

Deviation from objectives

When the proposal was written the VTT workpackages and person months were wrong in WP3. So, the VTT part was then shifted to WP4. Due to the change from VTT to WP4 the HPO samples were sent firstly to UROS and later (MM16) to VTT, so that the VTT investigations of storage stability could be started lately. In addition, the partner UROS was undergoing remodelling measures, which meant that the laboratories were temporarily closed. As a result, some of the analyses could only be started very late. In Addition, there is a delay in WP2 and only HPO samples could be analysed so far. Samples from FCC co-processing have not yet been provided and therefore no analyses have been carried out. The project partner estimate the production of marine fuel fraction from FCC co-processing by quartal 1 in 2025. Than the results and investigations will be finished by quartal 2 in 2025. An SDPO was provided to investigate the suitability as a marine fuel (residual fuel). The final results for this activity are still outstanding and will be finished by M27.

Corrective actions (if relevant)

When the samples from the FCC co-processing are ready, the tests on the blend behaviour will be carried out after M24 and the deliverables will be continuously updated.

Introduction

Alternatives to fossil fuels are necessary for the long-term success of the energy transition and the climate protection. Ships built and launched in and around 2025 will still be in service well after 2040. This has several consequences. One of them is the necessity of retrofit measures, to obtain significant CO₂ emission reduction in already existing ships. Such retrofit measures may be introduced for instance in 2030 to ships being designed and built today. Fuel blending, in this case the mixing of a fossil base fuel with an alternative fuel, requires the mutual solubility of both components, at least within a reasonable concentration range. Furthermore, the physical and chemical properties of the blend should be identical or only slightly different to those of the traditional (fossil) fuel. This would allow the distribution of new fuels and fuel blends through the existing infrastructure and their application in the existing engines, i.e. the existing fleet of ships.

1. Objective

The aim of the deliverable is to assess the basic suitability of fuels produced in the Refolution project as marine fuels and to investigate the blending behaviour of these fuels with conventional and alternative marine fuels. The investigations are based purely on laboratory tests.

2. HPO characterization

The fuel assessment of the delivered samples was conducted according to the specification of marine fuels DIN EN ISO 8217. As an example of the analysis conducted to the samples, the characterization of four of the samples are presented in the following table. The most important fuel parameters are summarized in the Table I.

parameters	Unit	REF0010 BTG-3242 (distilled at flashpoint)	REF0011 BTG-3258 (distilled at flashpoint)	REF0021 BTG-4310 (distilled at flashpoint)	BTG-2024- 2955 (distilled at flashpoint)
Density	kg/m ³	900.0	878.7	891.4	908.9
Kin. Viscosity at 40°C	mm ² /s	4.12	4.33	3.99	4.72
Kin. Viscosity at 50°C	mm ² /s	3.29	3.44	3.26	3.72
Water content	ppm	31	16	24	28
Total acid number	mgKOH/g	0.06	0.05	0.05	0.08
Oxidation stability	h	-	7.04	>48	-
Flash Point	°C	78	82	61	75.6
Cloud Point	°C	-21.4	-21.7	-34.5	-31.3
Pour Point	°C	-21	-21	-36	-33
Sulphur content	ppm	<1	<1	<1	<1

Table I – fuel evaluation of 4 HPO samples according to standard parameters (ISO 8217).

All measured values shown here comply with the standard (ISO 8217). The very low water content and the low acid number as well as the low sulphur content are particularly noteworthy. In addition, it can be said that all

the samples shown comply with the limit value for the flash point and exhibit excellent cold behaviour (cloud and pour point). It can therefore be said that, in purely formal terms, a suitable fuel fraction could be obtained from hydrogenated pyrolysis oil in accordance with the standard.

In addition, one of these HPO samples (BTG-4310) was measured using FT-ICR-MS (Fourier Transformation Ion Cyclotron Resonance Mass Spectrometry). Depending on the measurement conditions, this technique can be used to identify polar species as well as aromatic compounds and thus characterise the chemical composition of the HPO. By determining high-resolution masses, molecular formulae can be calculated and the composition (C, H, N, O, S) of organic molecules can be specified. Selected results are summarised in the following figure.

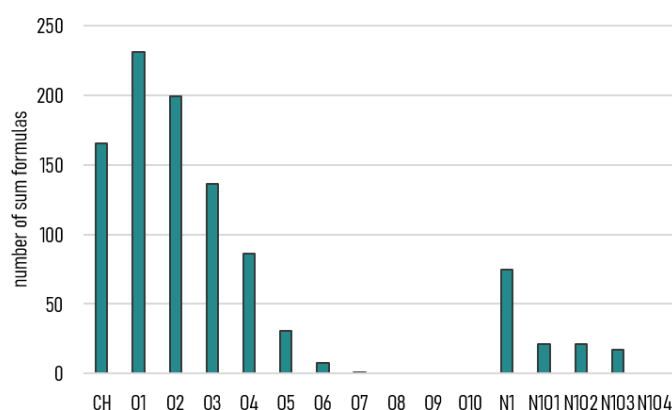


Figure I – number of sum formulas in BTG-4310 measured via FT-ICR-MS.

A total of approx. 1000 molecular formulae have been detected. Among them, mainly CH species, oxygen-containing molecules (up to 7 oxygen atoms per sum formula) as well as nitrogen-containing sum formulae have been identified.

In addition, double bond equivalents (DBE) can be calculated from the sum formulae. The results are shown in Fig. illustrated. In the diagrams shown in the figure, the measured carbon number is plotted against the double bond equivalent (DBE). The carbon number indicates the amount of carbon atoms in the measured molecules. The DBE is a measure of the aromaticity of the measured molecules. The higher the DBE value, the more double bonds or aromaticity are present in the molecule. In addition to the carbon atoms, heteroatom containing molecules (oxygen, nitrogen, sulphur) can also be considered. Furthermore, the circles and their colour provide information about the intensity, i.e. the quantity, of the respective molecules.

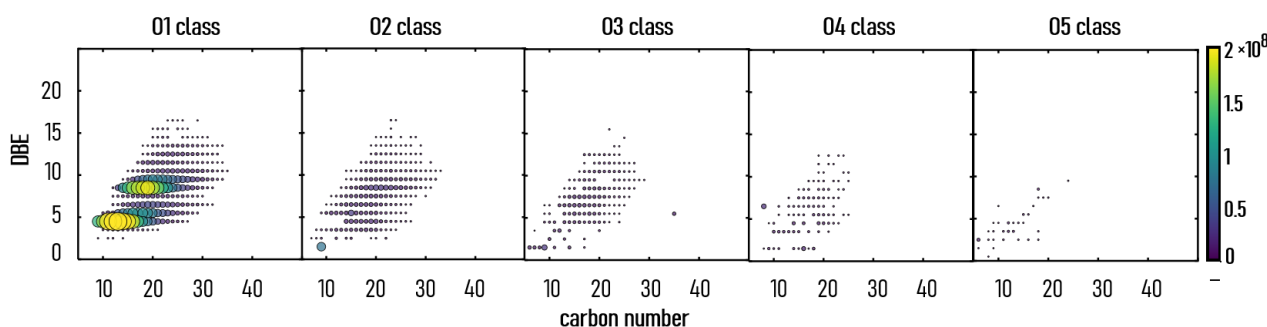


Figure II – DBE vs. Carbon number diagrams of BTG-4310.

The figure shows that mainly O1 species are present. The identified molecules have carbon numbers of up to

approx. 35 and also a high aromaticity, which indicates the presence of polynuclear aromatics. In addition, it can be seen from the diagrams that the carbon number and aromaticity decrease with increasing oxygen content within the molecules.

3. Blending pre tests

The pre blending tests have been carried out with marine diesel fuel, FAME (fatty acid methyl ester), HVO (Hydrotreated vegetable oil) and methanol in small scale (ratios: 25:75, 50:50, 75:25 m:m %). The blends were stored at 50°C for 14 days.

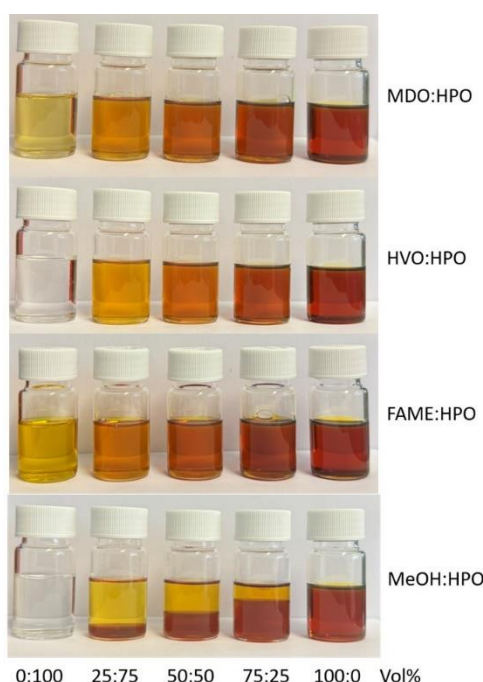


Figure III - Blending pre tests conducted with sample BTG-4310 from BTG and different conventional and alternative renewable fuels.

The following figure shows an example of the results of the blending tests. Four different blend fuels (MDO, HVO, FAME and methanol) were blended with the HPO fuel sample provided by BTG at different blending rates. The figure shows that HPO has good miscibility with MDO, HVO and FAME. The only exception in these tests was the miscibility of HPO with methanol. As was to be expected, these two fuels are not completely miscible with each other. Nevertheless, a low miscibility can be demonstrated. This could be a possibility to make methanol a future marine fuel. Methanol itself does not ignite in the engine. Either a spark plug is required or it must be ignited with a pilot fuel. HPO could therefore be a climate-friendly alternative as an ignition fuel.

In addition, the blends were stored at 50°C for 14 days. It was found that the FAME and MDO blends formed precipitates over the storage time. The precipitates were only minor. This behaviour will be investigated further in the course of the project.

4. Blending – Methodology (VTT)

In this chapter methodology for the hydrodeoxygenated pyrolysis oil (HPO, BTG-4310) produced in the project and its blends with marine diesel oil (DMB), hydrotreated vegetable oil (HVO) and fatty acid methyl ester (FAME) are described.

Selected physico-chemical properties of HPO oil as such and as various blends were determined using the methods (Table 1) developed mainly for FPBOs. [1] In a previous study these methods showed good correlation among values obtained with methods for Marine fuels.[2] HPO composition was analysed by GC/MS after dissolving in isopropyl alcohol. Water extraction followed by GC/MS analysis was used to determine polar compounds. The measured values of HPO and its blends were compared with the ISO 8217 that defines specifications for marine fuels, marine distillate fuels (DM grades), and marine residual fuels (RM grades). These fuels may also contain renewable hydrocarbons, e.g., hydrotreated vegetable oil (HVO) or biomass to liquid (BTL). The DF grades may contain up to 7 vol % FAME, while DM and RM grades may contain FAME only, in maximum, at the “de minimis” level.

4.1. Blending strategy

Blending strategy followed was adopted from the previous study.[2] For the tests marine diesel oil (DMB) was selected as the main component in the blends. As preliminary study HPO compatibility with DMB was tested at various concentrations (0 %, 5 %, 10 %, 25 %, 50 %, 75 % and 100 %) in a small scale prior to actual test and addition of other blending components to the mixtures. Main principle in all other tests was to use 30 % of HPO in the blends. Minor components in the blends were hydrotreated vegetable oil (HVO) having paraffinic nature and fatty acid methyl ester (FAME) obtained from vegetable oils by transesterification reaction with methanol. HVO is a renewable fuel, and it has already been used as blending component in marine fuels as well as FAME. FAME contains ester bond that is relative sensitive to degradation as result of interaction with the light, air, metal, or moisture during storage.[3] Increasing the temperature accelerates the decomposition reactions. Diesel fuel, EN590, as such was selected as reference marine fuel component.

4.2. Stability

Stability of the blends were followed by using accelerated aging test. Basis for the accelerated aging tests was ASTM D4625 standard, in which stability tests are performed at 43 °C for 12 weeks that resembles one year storage at room temperature. The results among room temperature and accelerated aging test has found to be consistent.[2] Storage test at 43 °C has been found to correlate well with actual fuel performance.[4] Stability test at 43°C has shown good correlation with the ageing test at 80 °C. That encouraged us to use higher temperature in the accelerated aging test for the oils, which initial boiling point was same with the marine distillation fuels (Figure 1). The higher temperature is also closer to the conditions used in fuel engines. Before the actual stability tests small scale accelerated aging test was performed at 80 °C for 24 hours for the HPO DMB blends (0 %, 5 %, 10 %, 25 %, 50 %, 75 % and 100 %) to ensure the applicability of the test conditions for HPO. Before and after the heat treatment viscosity and density were followed. For the not distilled HPOs with low initial boiling point temperature of 43 °C are still applied. Many of the accelerated aging tests has been applied as test method to determine sediment formation, which indicate negative engine performance. Formation of sediment has been followed either visually or gravimetrically.

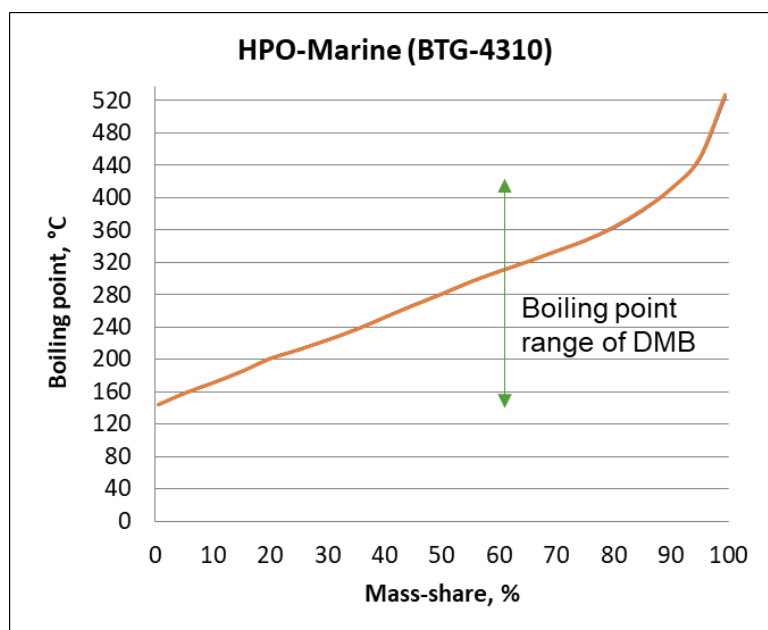


Figure IV - Boiling point range determined by simulated distillation for the HPO used for blending and stability tests.

Accelerated aging tests have been performed in both vented and non-vented borosilicate bottles. In these study non-vented bottles were used and bottles were filled leaving 20 vol% air space. Substances such as copper and water may accelerate fuel stability and were added in test set-ups. Copper might be present in the materials which are in contact with marine fuel and water in fuel tanks. [2] Before the analyses, water was separated. Parameters that were followed in storage:

- Visual appearance
- Homogeneity by microscope (top, bottom, and after mixing)
- Viscosity, density by ASTM D 7042 (top, bottom, and after mixing)
- Water content (ASTM E203)
- Acid number (ASTM D 664)

4.3. Results

The obtained results for distilled HPO (BTG-4310) used for the stability test were well in line with the limits set in ISO 8217 and values obtained by other laboratories in the project. The studied HPO was composed of hydrocarbons, mostly cyclic, aliphatic and aromatic. Polar compounds were not detected by GC/MS analysis and both the acid number and water content was well below the limits set in ISO 8217. Based on the chemical composition it was expected that HPO mixes well with marine distillate fuel and renewable fuels having non-polar nature.

Fuel parameters	Unit	Standard	BTG-4310	Marine distillate fuels ISO8217:2017
Appearance		Visual	Yellow, bright	
Water content	wt. %/vol%	KF ASTM E203	0.01 wt%	-/Max. 0.30 C

Density at 15 °C	kg/dm ³	ASTM D 7042	891	max. 900 C
Kinematic Viscosity at 40 °C	mm ² /s	ASTM D 7042 ^a	3.3	2.0–11.0 (at 40 °C)
Bromine number		ASTMD 2710	< 1	
Acid number	mg KOH/g	ASTM D 664	< 0.02	Max. 0.5 mg KOH/g
Oxygen (O)	wt %		< 0.2	-
Chlorine (Cl)	ppm	CIC	< 1.1	-
Sulphur (S)	ppm	CIC	< 1.3	Max. 5000

Table II – Characteristics of HPO (BTG-4310) (a Dynamic viscosity measured by Stabinger Viscometer. Kinematic viscosity calculated (dynamic= viscosity/density).

In preliminary small-scale test HPO blends in various concentrations with DMB (0%, 5 %, 10 %, 25 %, 50 %, 75 % and 100 %) were homogeneous. HPO and its blends (Figure V) showed good performance in short term stability test that was determined as viscosity and density change at elevated temperature (80 °C, 24 hour). No sediment formation during the heat treatment was observed in any of the blends.

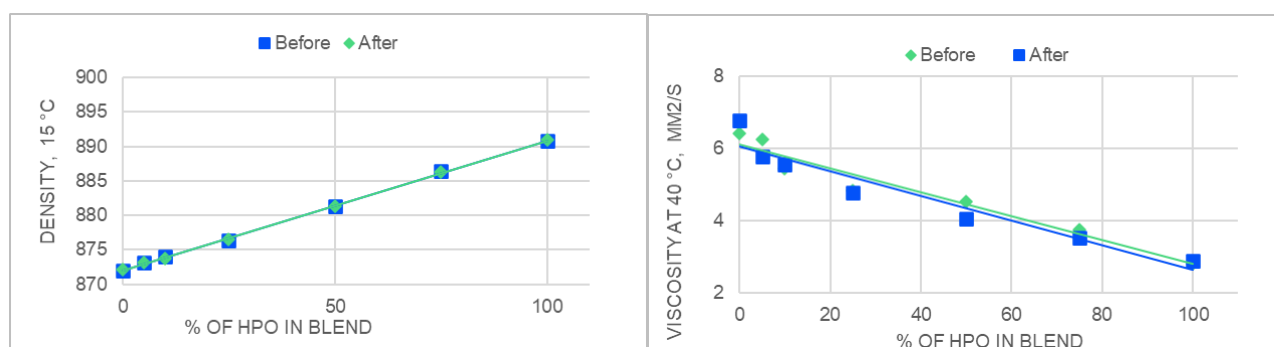


Figure V - HPO compatibility with DMB at various concentrations (0 %, 5 %, 10 %, 25 %, 50 %, 75 % and 100 %) density (left) and viscosity (right) before and after heat treatment.

All HPO blends with DMB and renewable fuel FAME were homogeneous. This was observed visually and with microscope. Exception was HPO blend with HVO. Small particles were formed to the blend after mixing (Figure VII). However, all blends met the limits set in ISO 8217 in terms of viscosity and density. Pure HPO have relative high density. However, as blending component high density value can be lowered.

During the accelerated aging test, no changes in viscosity or density values were observed, indicating good stability of the blends (Figure VI). Some variation in water content and acid number were observed, especially in those blends that contained FAME. The increase in acid number indicated degradation on FAME in storage. Lower acid number was detected when HPO was used as blending component with FAME, due to the low amount of FAME in the blends. This indicated that HPO does not catalyse FAME degradation. However, all values (acid number, water content) were well below the limit values.

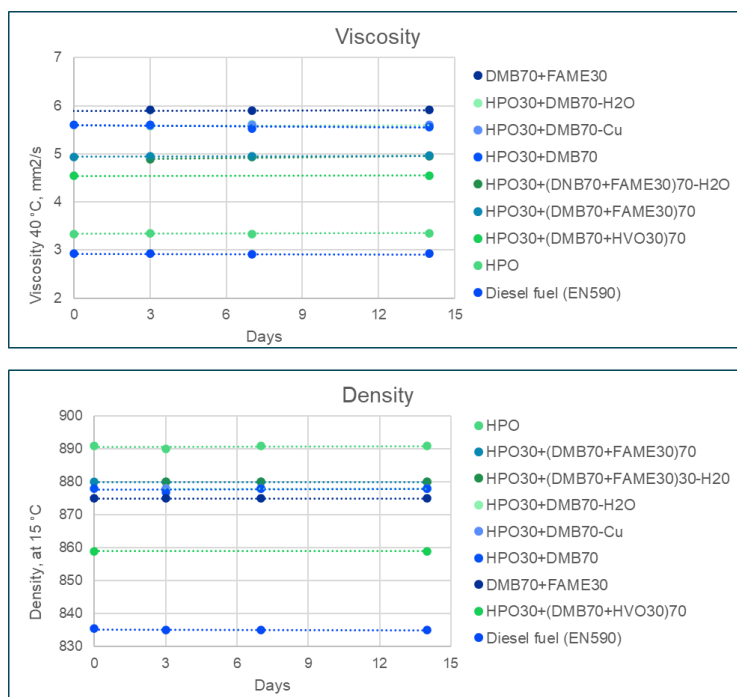


Figure VI - Stability of HPO in various blends density (below) and viscosity (above) determined during the accelerated aging test at elevated temperature (80 °C, for 14 days).

All blends were homogeneous at the beginning of the stability test, exception was blend which contained both HPO and HVO. Based on the microscope and visual evaluation some deposit formations (small particles) were observed in pure HPO halfway through the stability test (Figure VII). Similar phenomenon in stability test was observed in blends, which contained FAME as one of the blending components. Sediment formation was observed earlier (day 3) than pure HPO (day 7). In addition, copper seems to accelerate sediment formation. These insoluble sediments even present in small quantities may cause problems in engine performance and more research is required to understand the cause of their formation.

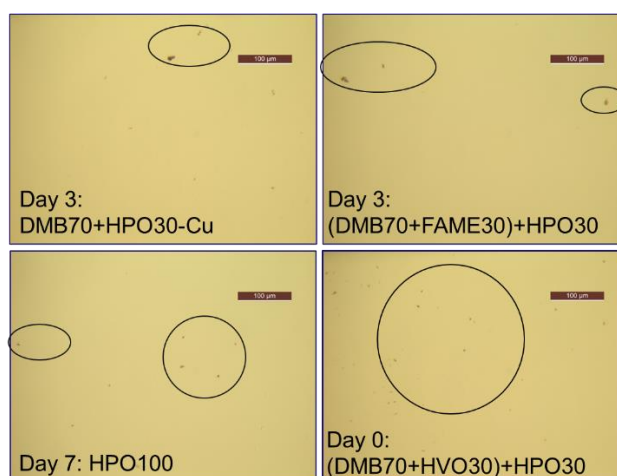


Figure VII- Small particles in blends by microscope in different stages of stability test (80 °C, for 14 days).

Conclusions

It can be said that, in purely formal terms, a suitable fuel fraction could be obtained from hydrogenated pyrolysis oil in accordance with the marine fuel standard. These fractions/samples were used to perform blending investigations. The fuel properties of HPO and its 30% blends with marine fuels remained stable over a storage period of one year determined by viscosity and density change. There were no issues in the water or acid contents, even though a small increase was observed for both in the blends containing FAME. However, sediment formation was observed especially in the pure HPO and its blends with HVO and FAME, but also when copper was present. More research is required to understand the reasons for sediment formation and possible ways to prevent it.

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