



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

Production of 200 L HPO



Project: REFOLUTION

Refinery integration, scale-up and certification for aviation and marine biofuels production
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1. Executive summary

Pyrolysis oils, oxygenated and heterogeneous, are hydrotreated to first yield a stabilized pyrolysis oil (SPO), at mild temperatures (200 – 250°C) and high pressures (near 200 bar) over a nickel-based catalyst (Picula™). The SPO is subsequently used to obtain a stabilized deoxygenated pyrolysis oil, which can further be ‘refined’ into what is referred to a hydrotreated pyrolysis oil (HPO). This deliverable report details the production of sufficient amounts of HPO product, thereby also addressing the specifications for the HPO.

Fresh samples will be prepared for combustion tests to be carried out by UROS in the next period, viz for analysis in their high pressure, high temperature marine injection chamber

- a) Shipment of around 15 L HPO product with proper quality ($< 925 \text{ kg/m}^3$) in Oct 2025 (BTG).
- b) Around 10-20 L SDPO product in Oct 2025 (BTG). This will be used both as a pure fuel, as well as ignition fuel in methanol blends.

For testing in the single cylinder marine engine:

- c) Preparation (BTG) of a new batch of around 200 L HPO product in Feb 2026.

1.1. Description of the deliverable content and purpose

REFOLUTION aims at the transformation of pyrolysis oils into advanced biofuels, through intermediate processing steps (fractionation, stabilisation) combined with downstream co-processing technologies at different levels of severities (temperature, hydrogen consumption, carbon yield) for targeting different applications: Fluid Catalytic Cracking (FCC) processing for aviation and marine sectors, and hydrotreating for the marine sector. This deliverable reports the results for the larger scale production of HPO, i) to generate data for a further modification of the existing hydrotreating plant ($\sim 1 - 2 \text{ kg/h}$ feed) into a prototype scale unit to be operated in an environment close to expected performance, and to obtain high quality hydroprocessed pyrolysis oils (HPO) for further blending purposes.

1.2. Deviation from objectives

A delay is noted in the submission of the deliverable. This was to obtain best possible alignment between BTG and UROS for sample distribution, including timing, quality and amounts. This delay has no effects on the progress of the overall project.

1.3. Corrective actions

This deliverable will be updated by BTG, if necessary, with information on the new HPO production run when it becomes available, expectedly beginning of 2026.

2. Introduction

Hydrotreatment is typically deployed to remove sulphur from petroleum feeds, deploying temperatures between 300 and 500 °C using molybdenum-based catalysts and hydrogen at elevated pressures. These conditions initially looked attractive for pyrolysis liquids as well. However, due to the heterogeneity of the oils

with the associated reactivity of the oxygenates, new innovative catalysts and processes for the pyrolysis treatment had to be developed. Catalysts first included expensive precious metals to reduce the reactivity of the oils (typically Ru, Pd and Pt), but these generally deteriorated severely even after repeated use. Instead, a specific nickel-based catalyst (Picula™) was developed for the first stabilisation step. In addition, the process was changed from a one-step into a two-step process; first reducing the ‘carbohydrate’ content by a selective hydrogenation (‘stabilisation’) at mild temperatures (200 – 250°C) and high pressures (near 200 bar) before processing at high temperatures (350 – 400°C) and mild pressures (typical 60 – 120 bar) to remove the oxygen (see Figure 1).

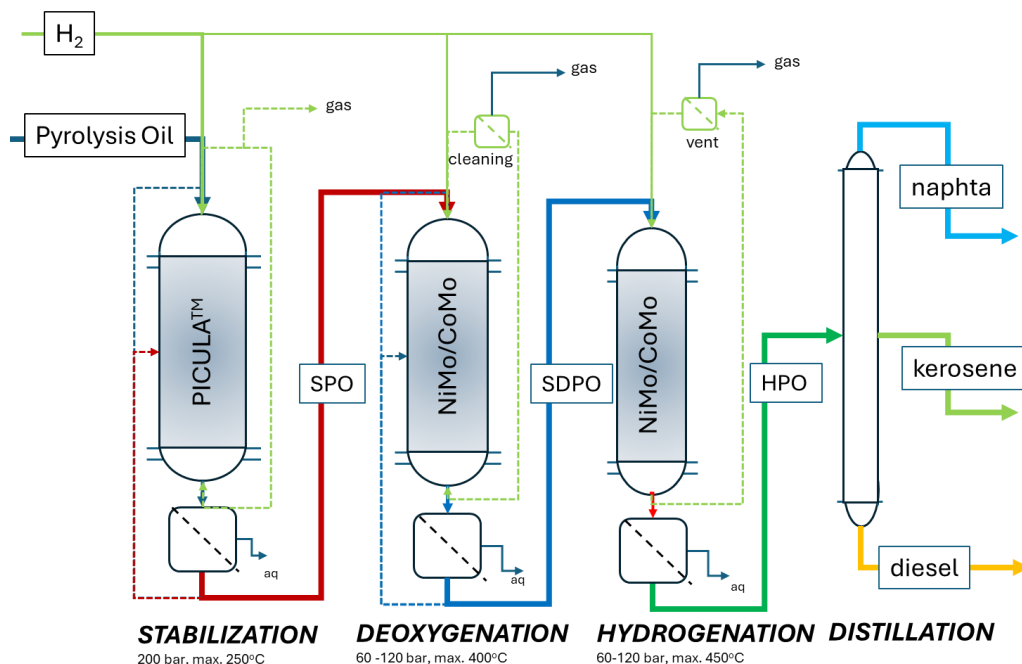


Figure 1. Transportation fuels through fast pyrolysis

The Picula catalyst is very effective:

- Water can be reduced to around 5-10 wt.%. This reduction is done by evaporating water from the product, yielding SPO. This cannot be done for a crude pyrolysis oil as this leads to a high viscosity product.
- The H/C is increased; hydrogen is typically used to hydrogenate the aldehydes to alcohols, which are stable at these conditions. The aldehyde concentration (in mmol carbonyl/g) correspondingly is reduced (typically with a factor of 2 – 4), resulting in a lower charring tendency (in MCRT).

The product from the stabilization step, the Stabilised Pyrolysis Oil (SPO) can be fully deoxygenated. This deoxygenation is successfully demonstrated applying commercial CoMo or NiMo catalysts, yielding liquids in the hydrocarbon range from marine diesel down to light alkanes.

The HPO products are much closer to known hydrocarbons:

- The molar ratio H/C (on dry basis) is close to hydrocarbons (1.6 - 1.8), and the oxygen reduced down to well below 1 wt.%.
- The viscosity is reduced well below 10 cSt.
- Charring tendencies typically < 1 wt.%, allowing the SDPO to be easily distilled, similar to a crude oil
- Liquid densities can be < 900 kg/m³.

Due to the apolar nature of the HPO, water spontaneously separates from the product stream (< 1 wt.% in the product). Major components in HPO are iso- and cycloalkanes, with some paraffins also present. REFOLUTION aims to transform pyrolysis oils into advanced biofuels, through intermediate process steps (fractionation, stabilisation) combined with downstream co-processing technologies at different levels of severities (temperature, hydrogen consumption, carbon yield) for targeting different applications: Fluid Catalytic Cracking (FCC) co-processing for aviation and marine sectors, and co-hydrotreating for the marine sector.

This deliverable report on the specific production of larger amounts (around 200 L) of hydrotreated pyrolysis oils (HPO) for testing in a marine spray chamber, as well as in a single cylinder marine engine (marine diesel).

Table 1. Characteristics of pyrolysis oils and treated oils

Properties		Pyrolysis oils	SPO	HPO
		dark brown	Reddish	Yellowish transparant
Water content	wt.%	18 - 25	5 - 10	<< 0.5
MW	g/mol	100 – 4,000	100 – 2,000	
MW _{av}	g/mol	1000	800	
EA (daf)				
C	wt.%	53 - 56	52 – 65	86 – 88
H	wt.%	6.4 - 7.0	8.5 – 9.5	12
O (difference)	wt.%	38 - 45	20 - 40	< 0.5
N	wt.%	<0.01		
ash	wt.%	0.01 - 0.1		
S	wt.%	< 0.01		
Kinematic Viscosity	cSt	10 - 100	10 – 100	< 5
H/C molar, dry	-	1.4 - 1.6	1.6 - 1.8	> 1.8
O/C molar, dry	-	0.5 – 0.6	0.43 – 0.6	< 0.05
MCRT, a.r.	wt.%	18 - 25	< 10	<< 1
CAN, a.r.	mmol/g	3 - 4	1 - 3	<< 0.1
TAN, a.r.	mg _{KOH} /g	60 - 80	60 - 80	< 0.1
pH	-	2.5 – 3.5		N/A
Density	kg/m ³	1100 – 1200	1100 – 1200	< 900
Heating value	MJ/kg	16 – 18	20 - 25	> 40

3. Methodology

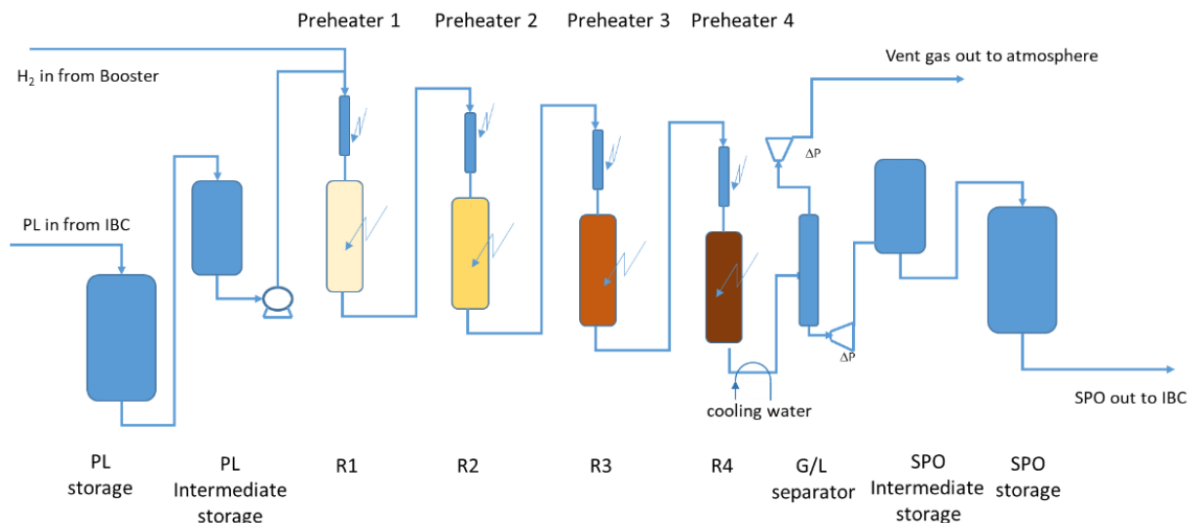
The procedure to produce the HPO is i) preparing stabilised pyrolysis oil over Picula™ catalysts by feeding PO at 200 bar H₂ and a series of the 4 reactors set at temperatures of 80-90/120-140/160-180 and 200-250°C resp., and then evaporating the water down to <10%, ii) produce SDPO over a NiMo catalyst at 120 bar H₂ and temperature 250/350/350/350-370°C, and separate the water, and iii) feed the SDPO again, at similar conditions, to remove all remaining oxygen.

These processes were developed in BTG's smaller scale (1 L/d) and scaled up in a 2 L/h unit. Typical conditions used in the production runs are provided in Table 2 below.

Table 2. Process conditions in the SPO/ SDPO / HPO production runs.

	Reactor Temperature [°C]				P [bar]	Average liquid flow [g/h]	H ₂ /feed [Nm ³ /h/(kg _{feed} /h)]
	1	2	3	4			
SPO	80	120	160	200	200	1,000	500 – 1,000
SDPO	250	350	350	350	120		
HPO	350	350	350	350	120		

In these runs, a dedicated system is deployed in a four staged temperature reactor system (R1 to R4 as indicated below in the simplified diagram in Figure 2).



Figure

2. Schematic representation of the stabilisation unit.

A feed is pumped into the reactor section, where it is mixed with hydrogen. All reactors are filled with Picula catalyst, and the oil is treated in each subsequent reactor at slightly higher temperatures. The exit stream is first cooled down to room temperature, and the mixture is then fed into a G/L separator. The gas is depressurized to atmospheric pressure before finally vented. The liquid is depressurized to atmospheric pressure, and collected in a product collection vessel.

4. HPO Production

HPO is prepared by i) producing stabilised pyrolysis oil over Picula™ catalysts by feeding PO at 200 bar H₂ and a series of the 4 reactors set at temperatures of 80-90/120-140/160-180 and 200-250°C resp., and then evaporating the water down to <10%, ii) get the SDPO over a NiMo catalyst at 120 bar H₂ and temperature 250/350/350/350-370°C, and separate the water, and iii) feeding the SDPO again at similar conditions to remove all remaining oxygen. Details are provided below.

SPO:

Typical temperatures in the four sequential beds for the SPO are 80, 120, 160 and 200°C resp., but these temperatures were adjusted to ensure MCRT values of the final product below 10 wt.% (@10 wt.% water). The liquid from the reactor, after depressurization to atmospheric pressure, is taken into a vacuum rotary evaporator to reduce the water content (0.01 bar and 60 - 70°C). To avoid temperature excursions, a recycle of SPO is deployed: this 'recycle SPO' is prepared prior to the actual production runs at similar conditions. Two production runs for the SPO were carried out:

- Run 1: Fresh pyrolysis oils with the previously produced SPO as recycle, and
- Run 2: Fresh pyrolysis oil with the non-evaporated product from run 1 as recycle.

The amount of product collected ≈ 800 kg SPO and ≈ 150 kg aqueous phase:

- 300 L stabilised pyrolysis oils (SPO), amongst others for co-processing in FCC.
- Data for a further modification of the existing hydrotreating plant (~ 1 - 2 kg/h feed) into a prototype scale unit to be operated in an intended environment close to expected performance, and
- Production of an intermediate material as a first step to generate high quality hydroprocessed pyrolysis oil (HPO) for blending purposes

SDPO

The similar set-up as described above has been used for the SDPO, but with a different set of four reactors (smaller, total 4 L) for the SDPO process. Each of these four reactors is again operated at different temperatures, but now at elevated temperatures of 250, 350, 350 and 350°C resp., while a different catalyst (commercial NiMo) was used. The process operates at slightly lower pressures, at BTG typically 120 bar¹ and a weight hourly space velocities WHSV around 0.5 kg_{SPO}/(kg_{cat}h).

The SDPO run started in a once-through mode feeding just SPO, but once sufficient product was prepared, this was used as a recycle to suppress temperature excursions due to the strong exothermic reactions. In contrast with SPO, where water is to be evaporated to obtain water < 10 wt.%, in the SDPO the water is spontaneously separated, yielding materials < 1 wt.% residual water. A total of around 250 kg SDPO was prepared. This SDPO shows a significant reduction in oxygen content. Oxygen is removed as water and as gaseous CO_x.

The characteristics of the SDPO product appear much closer to a crude fossil oil, with a molar ratio H/C in the range of 1.7 - 1.8, oxygen content typically well below 10 wt.%. This leaves a product with a MCRT < 1 wt.% (almost fully distillable), and densities typically in the range of 900 to 950 kg/m³.

HPO:

To obtain a fully deoxygenated oil, a further hydrodeoxygenation / refining step (HPO) is done, using similar pressures and temperatures and similar catalysts and conditions as used in the SDPO step. The full deoxygenation step was done on the SDPO, at temperatures slightly above those for the SDPO (effectively

extending the WHSV). A total of around 150 kg HPO was produced in the run from about 200 L SDPO. The overall mass balance for this run is specified in Figure 3 below. In this HPO step, less than 5% 'losses' are seen in the carbon, and this is transformed into light gases. The HPO contains practically no oxygen (see Table 1). All characteristics are in the ranges for the various crude oil derivatives.

HPO run

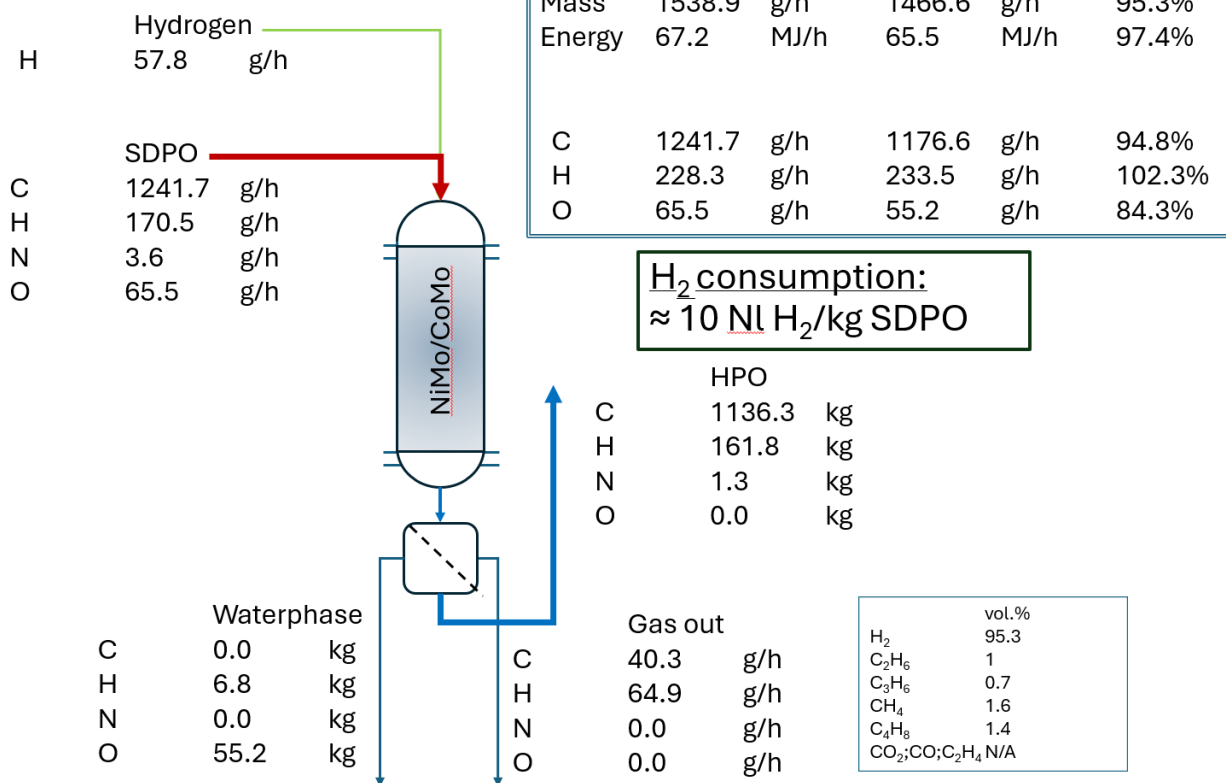


Figure 3. Mass balance HPO run

A balance for the transformation of the SPO into HPO is summarised in Figure 4 below. While operating conditions will determine the exact values, ranges are provided for the different parameters. Relevant observations are summarised here:

- Noticing the process can be further optimized in terms of yields, qualities and aspects related to catalyst vs reaction mechanisms, all steps are reproducible / repeatable, and consistent with lab scale experiments.
- 'Losses' of carbon, around 20 %, are mainly in carbon transformed into permanent gases in the SDPO production, but are negligible in the HPO step. The main gas formed are ethane and propane, contributing to around 70% of the carbon present in the gases (C₄⁺ components are absent). Less than 25 % of this carbon goes to CO_x, suggesting that main oxygen removal takes place through production of water. It should be mentioned that the carbon containing gases are products of reasonable to high value in conventional refining processes. For the HPO, < 5 % 'loss' in carbon is transferred into gas phase, and from this approx. 50 % of the gaseous carbon is converted into butane, whereas methane, ethane and propane typically contribute 15 - 20% each.

SDPO production

120 bar, 250/350/350/350 °C

HPO production

120 bar, 350/350/370/370 °C

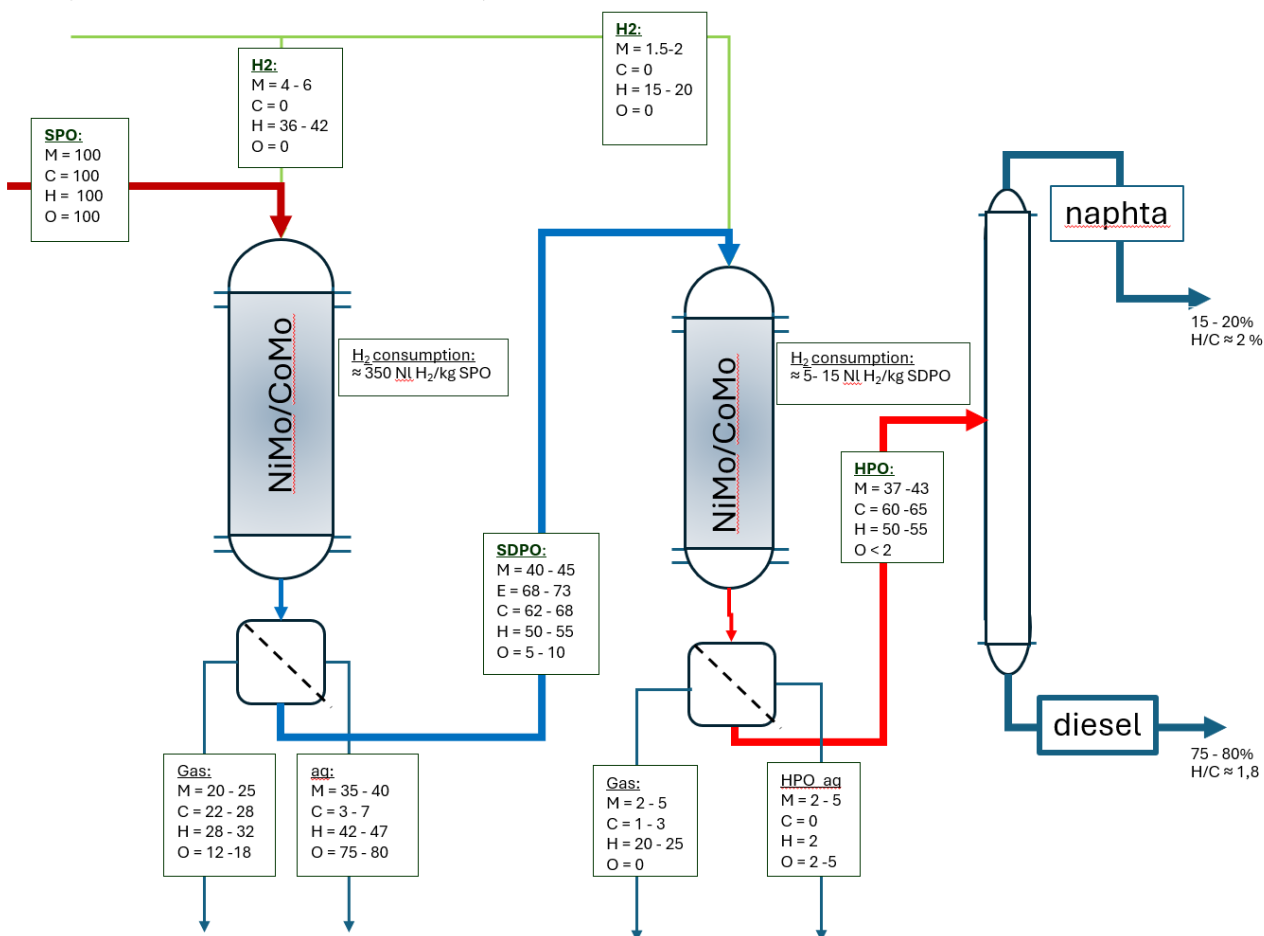
DESTILLATION


Figure 4. Ranges for the overall mass balances for the process of the conversion of SPO to HPO

Table 3. Relevant process characteristics

		SPO	SDPO	HPO
H₂ consumption	NL H ₂ /kg _{feed}	120 - 160	325 - 375	5 - 15
Yield	kg _{Product} /kg _{feed}	0.67 - 0.72	0.40 - 0.45	0.90 - 0.95
Overall H₂ consumption	NL H ₂ /kg _{P0}	350 - 400		

Samples of several liters were distilled and sent to UROS for specific analysis and blending tests, and fuel quality assessment (DIN EN ISO 8217). For this, two samples were taken from lab scale runs and two from the larger PDU run). A typical characterization based on a series of samples is presented in Table 4.

Table 4. HPO - Product characteristics

parameters	Unit	HPO sent to UROS
Density	kg/m ³	880 - 910
Kin. Viscosity at 40°C	mm ² /s	3.99 - 4. 72
Kin. Viscosity at 50°C	mm ² /s	3.26 - 3.72
Water content	mg/kg	16 - 31
Total acid number	mg _{KOH} /g	0.05 - 0.08
Flash Point	°C	61 - 82

Cloud Point	°C	(-34.5) - (-21.4)
Pour Point	°C	(-36) - (-21)
Sulphur content	mg/kg	<1

These values comply with the standard (ISO 8217) and with the limit value for the flash point, and exhibit excellent cold behaviour (cloud and pour point). Importantly, a suitable fuel fraction could be obtained from hydrogenated pyrolysis oil in accordance with the standard. From FT-ICR-MS approx. 1000 components can be detected in the samples, among them, mainly CH species, but in some cases also oxygen-containing molecules (up to 7 oxygen atoms per sum formula) as well as nitrogen-containing sum formulae have been identified. In more details, mainly single oxygenated species ('O1') are present, and identified molecules have carbon numbers of up to approx. 35. They also exhibit high aromaticity, which indicates the presence of polynuclear aromatics. Pre-blending tests are carried out by UROS with a series of solvents (marine diesel fuel, FAME, HVO and methanol) in different ratios. The distilled fraction of the HPO has a good miscibility with all, except for methanol (as expected), for which a low miscibility can be seen. Stability of the blends were followed by using accelerated aging test (ASTM D4625) and the results for the distilled HPO used in this case were well in line with the limits set in ISO 8217. During the accelerated aging test, no changes in viscosity or density values were observed, indicating good stability of the blends. Some variation in water content and acid number was observed, especially in those blends that contained FAME.

It can be concluded that a suitable fuel fraction can be obtained from HPO, in line with the marine fuel standards. 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.

5. Discussion and further work

Qualities of SDPO and HPO will vary depending on operating conditions, such as temperature, WHSV and catalyst. Figure 5 below shows a photo of a set of HPO with an increase in process severity.



Figure 5. Different qualities of HPO produced; hydrotreatment severity increases from left to right.

The samples produced so far are of appropriate quality, and a smaller batch of around 20 – 30 kg is available for test work at UROS. Transformation of SDPO into HPO requires very low amounts of hydrogen but improves the product quality substantially, suggesting the relevance of HPO samples while distributing separate large

amounts of SDPO samples offers few advantages.

For this reason, it was agreed upon by BTG and UROS to prepare fresh amounts of HPO for the next test runs, viz for use in the spray chamber

- Shipment to UROS of around 15 L HPO product of proper quality ($< 925 \text{ kg/m}^3$) in Oct 2025.
- Shipment of around 10-20 L SDPO product (possibly part of it will be distilled to accommodate the flash point) in Oct 2025. This will be used both as a pure fuel, as well as ignition fuel in methanol blends.

For the larger test in a single cylinder marine engine:

- Preparation of a new batch of around 200 L HPO product (after distillation of the light to meet the flash point requirement resulting in around 150 L HPO final product) in Feb 2026 to conclude the experimental work for high fidelity assessment for marine fuels.