Fit4Micro

Deliverable 2.1

Production report of 200 L reference-quality HPO

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List of acronyms

Acronym	Full meaning
CHP	Combined Heating Power
DHO	Domestic Heating Oil
FAME	Fatty Acid Methyl Ester is the generic chemical term for biodiesel derived from renewable sources
FPBO	Fast Pyrolysis Bio-Oil
GC-VUV	Gas Chromatography – Vacuum Ultraviolet Spectroscopy
HPO	Hydrotreated Pyrolysis Oil
HVO	Hydrotreated Vegetable Oil
LHV	Lower Heating Value
LPG	Liquefied Petroleum Gas describes two Natural Gas Liquids: propane and butane, or a mix of the two.
PDU	Process Development Unit
PIONA	Paraffin, Isoparaffin, Olefin, Naphthene, Aromatic is a widely used characterization method for petroleum fractions boiling below 200°C.
SPO	Stabilized Pyrolysis Oil

1. Introduction

1.1. Background on biofuels for domestic heat generation

The liquid and liquified fuels currently used for domestic heat generation are almost exclusively derived from crude oil. Crude oil is distilled in refineries to obtain gasoline, kerosine and diesel fractions. The lighter, gaseous, fraction consists of propane (C3) and butane (C4), which is compressed to form LPG. Domestic Heating Oil (DHO) can also be derived, and different qualities are available. However, it typically consists of a mixture of petroleum-derived hydrocarbons in the 14- to 20-carbon atom range that condense between 250 and 350 °C.

Renewable alternatives (biofuels) for these products that have already reached the market are produced from vegetable oils, animal fats or used cooking oils. Transesterification of the triglyceride with methanol yields biodiesel (FAME) and glycerol. FAME biodiesel can be used directly as a fuel but is more commonly blended into fossil-derived diesel at low blends. An alternative to transesterification involves the hydrotreatment of the triglycerides at elevated pressures and temperatures over a catalyst to obtain HVO (Hydrotreated Vegetable Oil). This fuel consists of straight chain alkane hydrocarbons and does not have the fuel limitations of the methyl-esters which make up the biodiesel. Commercially, HVO is produced amongst others by NESTE with facilities in Porvoo (Finland), Singapore and Rotterdam (The Netherlands). One of the by-products from the HVO production is propane, which is sold as bio-LPG. The high quality HVO is typically used in transport applications, as such commercial usage for CHP systems is unlikely.

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1.2. Pyrolysis oil production and upgrading

In Fit4Micro the ambition is to significantly widen the feedstock basis, and use RED-III compliant resources, for biofuel production. To achieve this ambition, feedstocks will be first converted into Fast Pyrolysis Bio-Oil (FPBO), a liquid bioenergy carrier.

The production of FPBO can be done from a wide variety of lignocellulosic biomass resources at relatively small scale, which prevents transport of large quantities of biomass residues. In addition, the conversion by fast pyrolysis is self-sustaining and no external energy input is required. Fast pyrolysis of biomass is a thermochemical conversion technology, where the biomass is rapidly heated in the absence of oxygen to form an organic vapour, non-condensable gas and a solid by-product (char). The organic vapour is rapidly quenched to form the FPBO, the non-condensable gas and char are both combusted in the process to generate the heat for the pyrolysis process as well as a surplus for external usage. Excess heat can be used to dry the biomass before the process and/or be sold as renewable heat or power. FPBO is already produced on a commercial scale in Europe.

FPBO is a liquid bioenergy carrier with properties that differ from conventional fossil fuels. The FPBO is a mixture of hundreds of different organic molecules. The FPBO also contains a significant amount of water (typically 20-30 wt.%) and the oxygen content is high (~50 wt.% on as received basis). As a result, the heating value of FPBO is quite low (LHV ~ 16 MJ/kg) compared to fossil fuels. FPBO may be used for (domestic) heat generation, however the relatively poor combustion properties (such as the low energy density and difficulty to ignite) and incompatibility to conventional boiler materials complicate the technology.

In particular, for small scale heat and power generation, improving the FPBO fuel properties before usage is desirable. Various options to improve the fuel properties have been investigated, both by BTG and other companies and institutes. One of the most promising ways to improve the fuel property is through hydrotreatment. By hydrotreating the FPBO, oxygen is removed from the fuel, increasing the heating value and ultimately a hydrocarbon fuel chemically similar to conventional fossil fuels can be obtained.

1.3. Hydrotreatment of FPBO

The hydrotreatment of FPBO involves reacting the FPBO with hydrogen gas at high pressure, elevated temperature and in the presence of a catalyst. The hydrotreatment technology is already applied in fossil fuel refineries, where hydrotreatment primarily aims to remove heteroatoms such as nitrogen and sulfur from the oil. Hydrotreatment of FPBO requires some adjustments as the FPBO is very reactive due to the large number of chemical components. Over the last twenty years BTG established an efficient upgrading process which involves two stages, an initial stabilization of the FPBO, followed by hydrotreatment.

During the stabilization process the most reactive components in the FPBO are converted first while suppressing polymerization and cracking reactions. The liquid product is referred to as Stabilized Pyrolysis Oil (SPO). For the production of SPO, BTG developed a proprietary catalyst “Picula™”. In the second stage, the SPO is reacted over a conventional hydrotreatment catalyst such as CoMo or NiMo, the product from this stage is referred to as Hydrotreated Pyrolysis oil (HPO). HPO is a mixture of hydrocarbons, HPO can be used ‘as such’ as a fuel, or it can be separated by distillation to obtain various fuel qualities. If desired a low boiling fraction referred to as ‘HPO-Naphtha’ or ‘lights’ can be separated from the HPO. This can be done for example to increase the flashpoint of the other fraction ‘HPO-Diesel’ in order to comply with existing fuel (safety) standards.

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The product properties of HPO can be controlled by adjusting the process conditions (severity) in the hydrogenation stage. A schematic representation of the upgrading process is presented in Fig. 1. Here, HPO^- denotes a 'less severely' treated product, HPO is the 'conventional, or reference, quality' and HPO^+ involves more severe hydrotreatment.

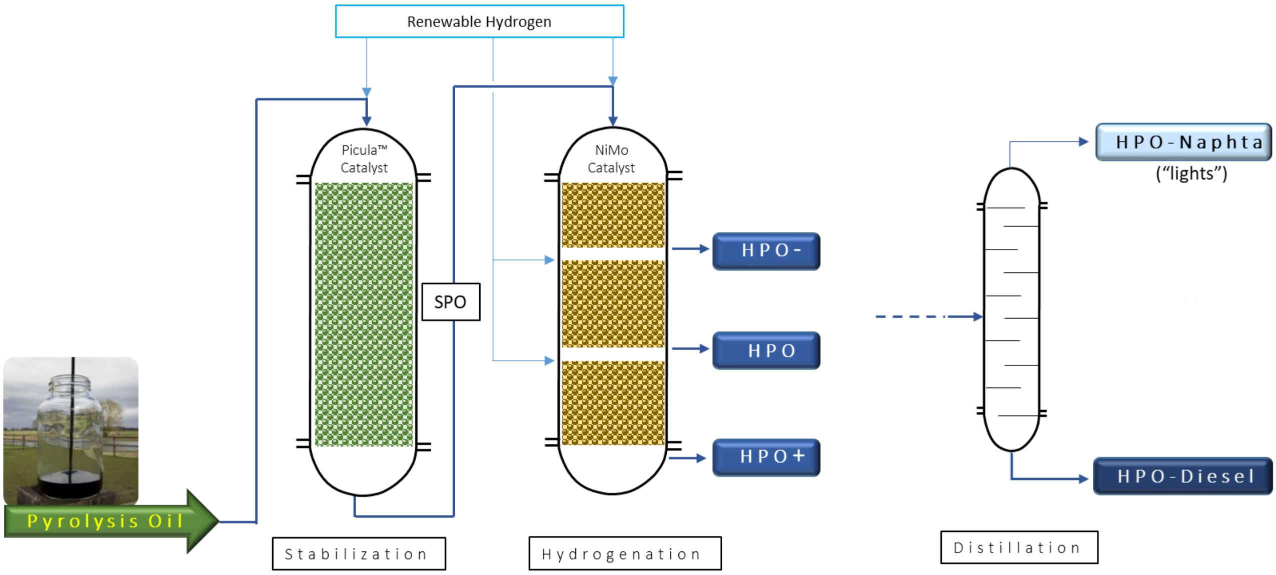

Figure 1: Schematic representation of the hydrotreatment process

2. Materials and methods

The HPO production initially targeted in Fit4Micro is the 'reference' quality. This quality is expected to be of sufficient quality for combustion in the micro turbine. It was decided to supply a few samples of smaller volume for initial testing to increase the confidence level that the large batch will be suitable. The volumes were agreed upon with partner OWI and MITIS and were chosen in such a way that sufficient material was available for analysis and the atomization tests described. In this chapter the materials and methods used to produce the samples are presented first, in the next chapter the results of the production are presented.

2.1. Materials

For the production of the HPO, typically FPBO from one of the commercial scale pyrolysis plants using BTG Bioliquids' fast pyrolysis technology is used. In this particular case, a FPBO batch from the Pyrocell plant was used. The Pyrocell plant is located next to Setra's Kastet Sawmill, located in Gävle (Sweden). Relatively clean wood residues (sawdust) from the sawmill are used to produce the FPBO. Detailed analysis results for the FPBO are presented in Table 1.

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Table 1: Properties of the FPBO used for the HPO production.

Parameter	FPBO	Unit
Moisture content	27.3	wt.%
Ash content	0	wt.%
Solid content	0	wt.%
Density	1.18	kg/l
Viscosity (40°C)	15.2	cSt
Acid number		mg KOH/g
Carbonyl content	4.2	mmol/g
MCRT	14.7	wt.%
Carbon content	40.5	wt.%
Hydrogen content	7.6	wt.%
Nitrogen content	0.1	wt.%
Oxygen (by difference)	51.8	wt.%
Higher Heating Value*	16.6	MJ/kg
Lower Heating Value*	14.9	MJ/kg
H/C (dry basis)	1.36	mole/mole
O/C (dry basis)	0.51	mole/mole

2.2. Methods

Within BTG several setups are available for the hydrotreating of FPBO. Five bench scale units, each with a capacity of around 0.5-1.5 kg FPBO input per day, are used to investigate the influence of process conditions and catalyst properties on the process performance. The bench-scale units run unattended on a continuous (24/7) basis. A photograph of one of the bench-scale units is presented in Figure 2. In the upgrading process the Picula^{TM} and NiMo catalysts are used. For larger quantities of HPO, a process development unit (PDU) or pilot scale unit is available. The PDU operates at a feed capacity of 20-50 kg/day. Photographs of the PDU are presented in Figure 3 (pressurized section) and Figure 4 (feed and control section).

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Figure 2: Photograph of the bench-scale hydrotreatment setup

Figure 3: Photograph of the pilot-scale hydrotreatment setup

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Figure 4: Photograph of the feed & control section of the pilot-scale hydrotreatment setup

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3. Results of the HPO production in Fit4Micro

Various qualities of HPO were produced in the bench-scale systems to increase the confidence level that the ‘reference-HPO’ would be of sufficient quality to be used in the microturbine. The production of these samples is presented in section 3.1, while the results of the pilot scale production are presented in section 3.2.

3.1. Production of various qualities HPO on bench scale

During a trilateral meeting between MITIS, OWI and BTG it was decided to start with two samples, standard HPO and the ‘HPO-Naphtha’ fraction as preliminary test by MITIS were very positive with this sample. In total BTG produced 2x 0.9 L of HPO. In addition, 2x 0.7 L of ‘HPO-Naphtha’ were produced. These samples were sent to OWI in February 2023.

Larger volumes (2x 4.5L) of reference HPO and HPO$^+$ (a more severely treated product) were supplied to OWI for further combustion tests in task 3.3. These samples (see Figure 5) were sent in March 2023.

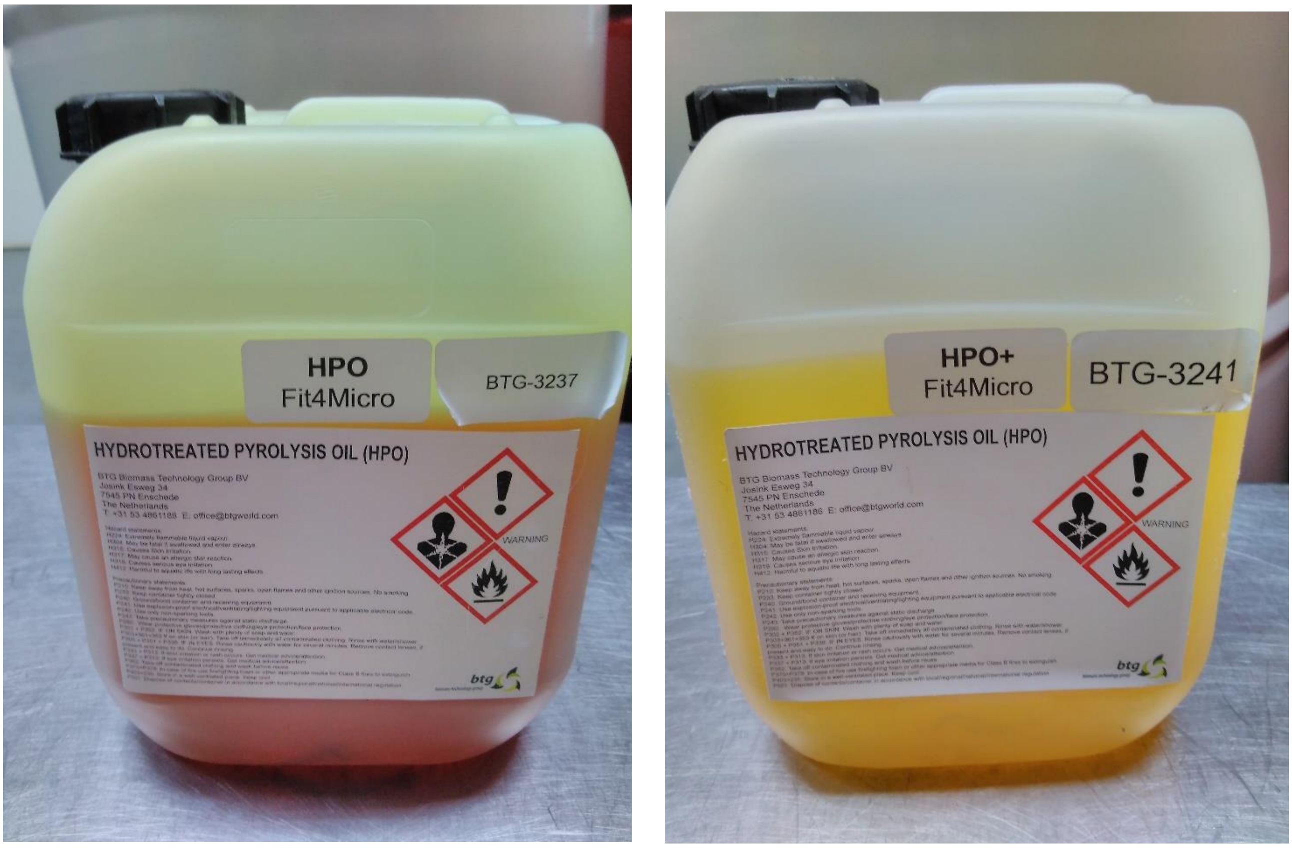

Figure 5: Photograph of the HPO samples sent to OWI, reference HPO on the left, HPO$^+$ on the right side.

In addition to the supplied samples, a few more products were produced by BTG to further investigate the ‘extremes’. A low severity sample (HPO$^-$) and a very high severity sample (HPO^{++}) were produced in small quantities for analysis only. In addition, three separate HPO-Naphtha qualities were produced.

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Results of the chemical analysis of the various products are presented in Table 2.

Table 2: Analysis results of the various HPO samples.

Parameter	Unit	HPO^+	HPO	HPO^+	HPO^{++}	HPO^-
BTG-Analysis No.		3201	3237	3241	3245	3689
Water content*	wt.%	0	0.0055	0.01	0.01	0.5
Density (T=20 °C)	kg/l	0.82	0.843	0.83	0.84	0.88
Viscosity (20°C)	cSt	2.2	2.4	2.9	2.9	10
Acid number	mg KOH/g	-	0.08	<0.01	<0.01	0.66
Carbonyl content	mmol/g	0	0	0	0	
MCRT	wt.%	0	0	0	0.1	0.5
Flash point	°C	14.3	-6	11	19	-18
Flash Point (OWI)	°C	< 23	<23	<23		
DCN/ICN	-	41.3	35	43.5	48.5	
CP - Cloud Point (OWI)	°C	-12/-24	-5	-6		
CCFPP - loud Filter Plug Point (OWI)	°C	-41	-35	-35		
Carbon	wt.%	85.9	86.1	86.7	86.6	83.8
Hydrogen	wt.%	14.7	12.8	13.5	13.6	12.5
Nitrogen	ppm		<5	<5	<5	1,120
Sulfur	ppm	7.6	4.7	1.1	1.2	< 5
Chlorine	ppm	<10				< 10
Oxygen (by diff.)	wt.%	0	1.1	0	0	4.4
Higher Heating Value (calc)	MJ/kg	48.4	46.2	47.3	47.4	43.2
Lower Heating Value (calc)	MJ/kg	45.2	43.4	44.4	44.5	40.7
Net Heat of combustion (meas.)	MJ/kg	43.2	42.1	42.5	42.9	39.6
IBP Simdis (D86)	°C		105.7	85	114.5	
FBP	°C		398.3	413.2	398.6	

Generally, the different samples complied with the KPI's set in the project for the quality of the fuel. The nitrogen content should be below 100 ppm and the heating value above 40 MJ/kg. The HPO^- sample was the only sample not achieving these targets.

Based on the physical/chemical properties, and the initial combustion and atomization test results it was concluded the reference HPO is likely of suitable quality for the microturbine. For the pilot scale a quality similar to sample HPO-ref (3237) was targeted.

3.2. HPO composition

To get a better insight in the composition of HPOs a PIONA analysis was carried out on two HPO samples by GC-VUV. In Figure 6 the results are shown for a HPO and HPO^+. Major components are the iso- and cycloalkanes, small amounts of paraffinic alkanes, and depending on the severity of the hydrotreatment a variable amount of olefins and aromatics.

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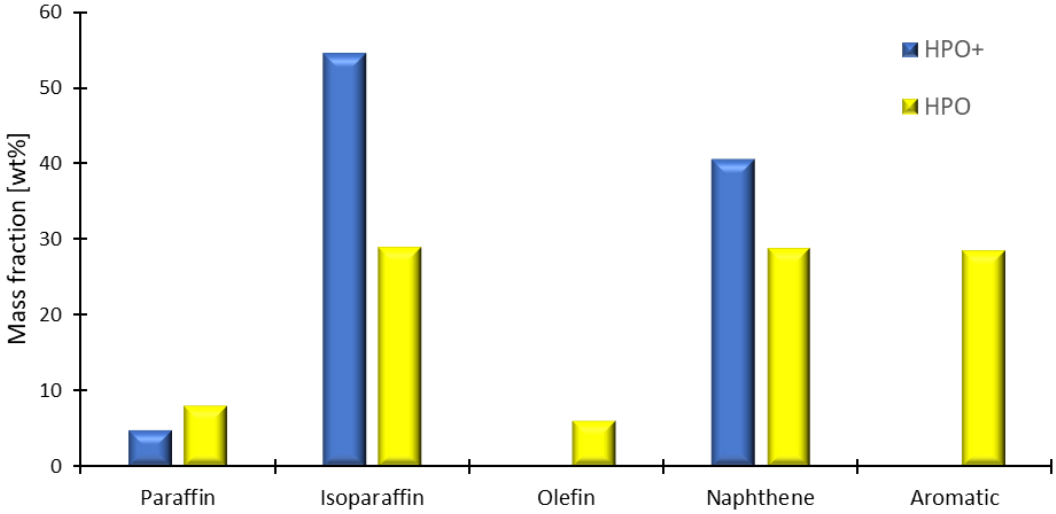

Figure 6: PIONA composition of a HPO and a HPO^+ sample. Method based on GC-VUV.

In Figure 7 also the carbon number distributions for the HPO and the HPO^+ sample are shown, which are rather similar for both samples.

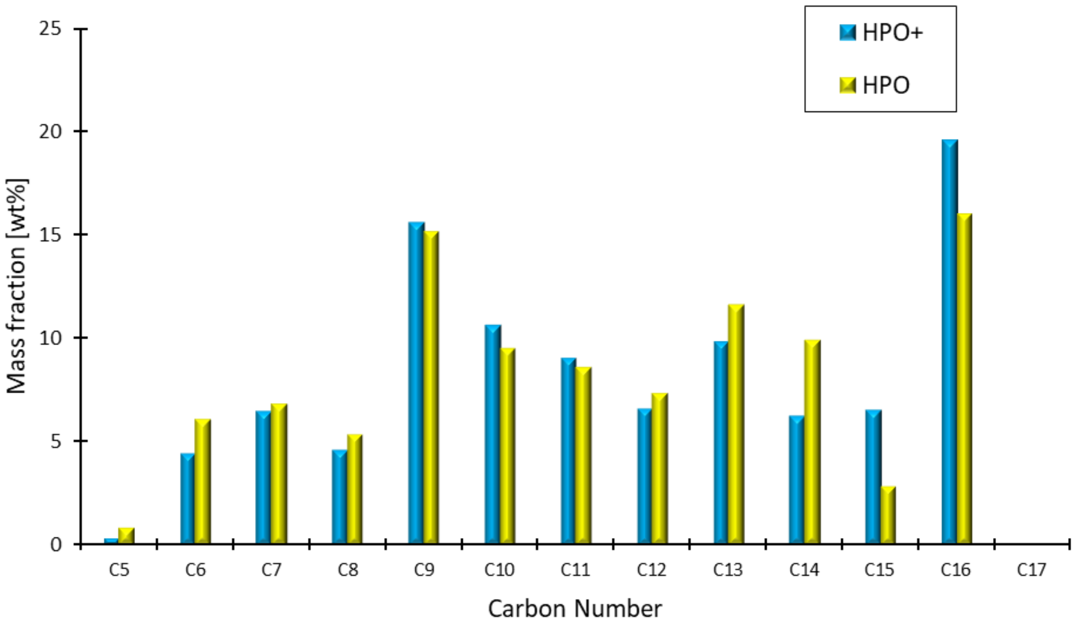

Figure 7: Carbon number distribution for a HPO and a HPO+ sample

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3.3. Production of reference HPO on pilot scale

According to the grant agreement, up to 200 L of reference HPO will be produced for combustion test at OWI. After discussing the planned activities, it was decided that 100 L would be sufficient for the test program at OWI, the remaining HPO will be used at BTG for further upgrading and characterization work. The HPO is produce in the pilot scale hydrotreater (see Figure 3) aiming to achieve similar product properties as HPO sample BTG.3237.

In a first stage, SPO is produced by reacting the FPBO with hydrogen at 200 bar over the Picula^{TM} catalyst. The temperature is increased to 80 °C in the first section of the process and increases up to 200 °C at the outlet of the process. Besides SPO, a waterphase product is also formed in the stabilization process.

A surplus of hydrogen gas is supplied to the reactor to improve the conversion, about half the hydrogen is consumed within the process, the other half leaves the reactor together with minor quantities of produced CO_2. For full scale operation gas cleaning and recycle should be included to improve the overall hydrogen usage. The actual hydrogen consumption in the stabilization stage is about 10% on energy basis, most of which is recovered in the SPO. The properties of the SPO intermediate product are listed in Table 3.

Table 3: Analysis results of the SPO intermediate product

Parameter	SPO	Unit
Moisture content	9.9	wt.%
Ash content	< 0.01	wt.%
Solid content	< 0.01	wt.%
Density	1.12	kg/l
Viscosity (40°C)	67	cSt
Acid number	57	mg KOH/g
MCRT	8.5	wt.%
Carbon content	53.2	wt.%
Hydrogen content	8.5	wt.%
Nitrogen content	0.2	wt.%
Oxygen (by difference)	38.1	wt.%
Higher Heating Value*	24.3	MJ/kg
Lower Heating Value*	22.5	MJ/kg
H/C (dry basis)	1.66	mole/mole
O/C (dry basis)	0.41	mole/mole

The FPBO feed to the hydrotreater is 2.005 kg/h, containing 40.5 wt.% carbon (see Table 1) for a total of 0.812 kg Carbon/h. The SPO product leaving the hydrotreater is 1.385 kg/h with 53.2 wt.% carbon (see Table 3) for a total of 0.737 kg carbon/h, giving a carbon efficiency of 91%.

The SPO intermediate product obtained after stabilization was hydrotreated using 120 bar of hydrogen pressure over a NiMo catalyst at a temperature gradient from 250 to 350 °C. The product obtained from the process did not fully achieve the desired HPO properties and it was decided to re-process the liquid once more with the same catalyst and hydrogen pressure, but at a temperature gradient from 350 to 425 °C.

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The product properties obtained after the hydrotreatment are listed in Table 4

Table 4: Analysis results of the HPO products

Parameter	HPO	Unit
Moisture content	< 0.1	wt.%
Ash content	n.a.	wt.%
Solid content	n.a.	wt.%
Density	0.85	kg/l
Viscosity (40°C)	2.1	cSt
Acid number	< 0.01	mg KOH/g
Carbonyl content	0	mmol/g
MCRT	0	wt.%
Flashpoint	5.0	ºC
Carbon content	87.8	wt.%
Hydrogen content	12.5	wt.%
Nitrogen content	16	ppm
Oxygen (by difference)	0	wt.%
Chlorine	< 10	ppm
Sulfur	< 5	ppm
Higher Heating Value*	46.3	MJ/kg
Lower Heating Value*	43.6	MJ/kg
Net Heat of Combustion	42.2	MJ/kg
H/C (dry basis)	1.71	mole/mole
O/C (dry basis)	0	mole/mole

Some photographs of the liquid product are included below. Drums containing the HPO product are presented in Figure 8. A sample of the liquid product after the hydrotreatment, before water separation, is presented in Figure 9.

Figure 8: Drums containing the HPO products.

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Figure 9: part of the liquid after the second hydrotreatment, HPO on top with a small amount of water at the bottom

4. Conclusion

Reference-quality HPO was produced in the pilot scale hydrotreater in a sufficient quantity for the combustion work planned in WP3. At least 100 L is available for testing, which will be shipped in several batches according to the test demands and schedule to avoid storage of large quantities of HPO at OWI. The remaining amount of HPO will be used by BTG in the project for further upgrading and characterization work.

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