



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

Production of 300 L SPO



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1. Executive summary

Pyrolysis oils, highly oxygenated and heterogeneous, is catalytically hydrotreated to yield Stabilized Pyrolysis Oil (SPO). The conversion entails the selective hydrogenation ('stabilisation') of the oils at mild temperatures (200 – 250°C) and high pressures (near 200 bar) over a specific Nickel-based catalyst (Picula™).

1.1. Description of the deliverable content and purpose

REFOLUTION aims at the transformation of 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 marine sector. This Deliverable reports the results for the larger scale production of SPO:

1. Production of 300 L stabilised pyrolysis oils (SPO), amongst others for co-processing in FCC.
2. Generate 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
3. Production of an intermediate material as a first step to generate high quality hydroprocessed pyrolysis oils (HPO) for blending purposes

1.2. Deviation from objectives

N/A

1.3. Corrective actions (if relevant)

N/A

2. Introduction

Hydrotreatment is in the petroleum processing industry typically deployed to remove sulphur from petroleum feeds. Temperatures are in between 300 and 500 °C, and hydrogen pressures of 35 to 170 bar. Considering the nature of the pyrolysis liquids, being highly oxygenated and heterogeneous, new innovative catalysts and processes for the pyrolysis treatment had to be developed. These catalysts first included expensive precious metals (typically Ru, Pd and Pt) but these generally seriously deteriorated even after repeated use. The process changes included the development of a two-step processing, 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.

For this first stabilisation step, a specific Nickel-based catalyst (Picula™) was developed. This material shows very high selectivity at low temperatures for hydrogenating aldehydes. The effectiveness of the Picula catalyst is summarised in Table 1 below, summarising the characteristic of the feedstock pyrolysis oil versus the one to be obtained for the SPO. The main differences are listed below:

- Water is reduced from 20-25 wt.% (pyrolysis oil) down to around 5-10 wt.% for the SPO. This reduction is induced by evaporating water from the product yielding the SPO. Evaporation of water is not done for pyrolysis oil as this leads to (very) high viscosities due to polymerisation of the reactive compounds present in the untreated oils.
- The H/C (based on the dry product) is significantly increased, as hydrogen is used to hydrogenate the aldehydes (and to some extent the double bonds).
- The O/C (based on the dry product) is typically constant or reduced, depending on the severity of the reaction. At limited temperatures (200°C) for the stabilisation process, the aldehydes are converted to alcohols, and these are stable at these conditions. However, slightly higher temperatures induce the dehydration of these alcohols, resulting in water formation (and associated higher hydrogen consumption).
- The aldehyde concentration (in mmol carbonyl/g) is significantly reduced with a factor 2 – 4, effectively causing the product to show a lower charring tendency, characterised by the micro carbon residue tests (MCRT):
- Pyrolysis oil with 20 – 25 % water cannot be efficiently distilled and forms 20 – 25 wt.% char (corresponding to around 40-50 % of the carbon of the pyrolysis oil). For SPO with water content the char formation is < 10% (20-25 % of the carbon of the SPO). The char from pyrolysis oil is typical charcoal (formed by reactions), while the one from SPO seems more soot-like (suggesting a non-distillable material).

Some other observations can be made:

- The molecular weight of pyrolysis oils ranges from 100 to 4,000 Da. For SPO this is reduced to 100 – 2000 Da, suggesting some depolymerisation of the heavies take place. Further analysis is ongoing, especially in understanding the relevance of the various parameters than can be derived from these curves. A few parameters do not change dramatically: for example, the acid number of the SPO remains constant, suggesting that at these conditions acids are stable (as known for acetic acid), the liquid density (suggesting limited cracking of the lignin and carbohydrates).
- In the stabilization process a dedicated catalyst – Picula™ - is used. Compared to the precious metal-

based catalyst, Picula shows higher stability and less deactivation. The main reasons for the deactivation are not well understood yet, but reasons include sulphur, nitrogen, alkali and heavy metals, charring and active metal leaching.

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

Objective of Deliverable 3.3

REFOLUTION aims at the transformation of 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 marine.

This Deliverable report on the specific production of larger amounts of the SPO:

- Production of 300 L stabilised pyrolysis oils (SPO), amongst others for co-processing in FCC and 300 L to produce oxygen lean hydroprocessed pyrolysis oils (HPO) for blending purposes (marine diesel)
- Generate data for the 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.
- Production of high quality hydroprocessed pyrolysis oils (HPO) for blending purposes

BTG has two lab units, each a 1 L/d input, to investigate the SPO production (2 units). Next to this, 2 units are available to deoxygenation the SPO further, and 1 unit to conduct a final refining. A 2 L/h unit is available to produce the larger number of samples, typical in the order of 500 – 1000 L/run.

Table 1. Specific characteristics of pyrolysis oils and stabilised pyrolysis oils

Properties		Pyrolysis oils	Stabilised Pyrolysis Oil SPO
Water content	wt.%	18 - 25	5 - 10
MW	g/mol	200 – 2,000	
MW _{av}	g/mol	600 - 700	
EA (daf)			
C	wt.%	53 - 56	52 – 65
H	wt.%	6.4 - 7.0	8.5 – 9.5
O (by difference)	wt.%	38 - 45	20 - 40
N	wt.%		<0.01
ash	wt.%		0.01 - 0.1
S	wt.%		< 0.01
Kinematic Viscosity	cSt	10 - 100	10 – 100
H/C molar, dry	-	1.4 - 1.6	1.6 - 1.8
O/C molar, dry	-	0.5 – 0.6	0.43 – 0.6
MCRT, a.r.	wt.%	18 - 25	< 10
CAN, a.r. Carbonyl content	mmol/g	3 - 4	1 - 3
TAN, a.r. Total Acid Number	mg _{KOH} /g	60 - 80	60 - 80
pH	-		2.5 – 3.5
Density	kg/m ³	1100 – 1200	1050 – 1200

3. Methodology

To produce the stabilised pyrolysis oil a dedicated system is deployed which includes four staged temperature zones, referred to as hydrotreating reactors (R1 to R4 as indicated below in the simplified diagram in Figure 1). The complete unit, except for the feed and product storage vessels, is placed in a dedicated safe environment (a ‘high-pressure box’ constructed from concrete).

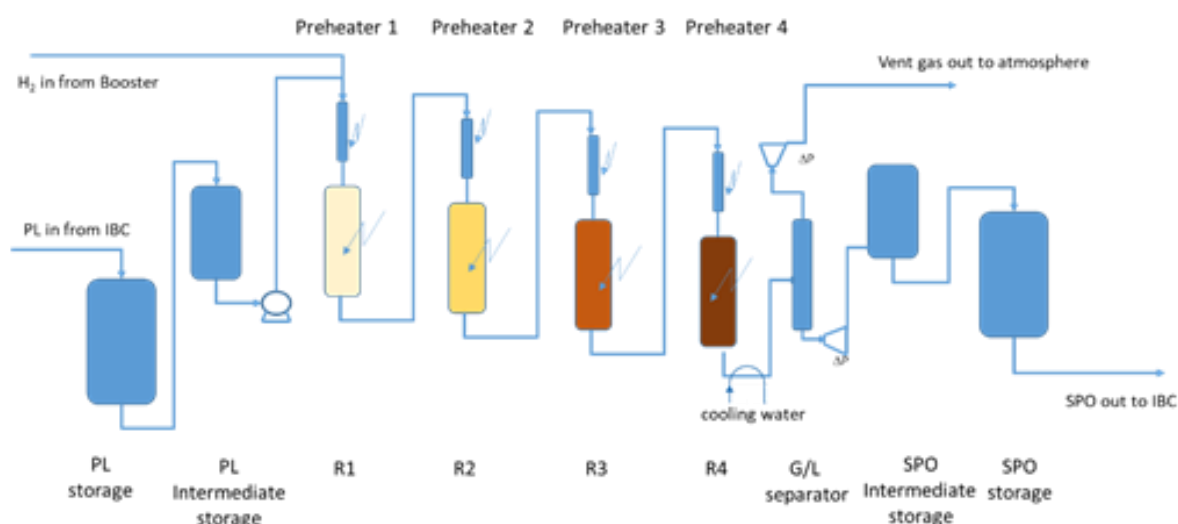


Figure 2. Schematic representation of the stabilisation unit.

The pyrolysis oil is fed from a storage area outside the high-pressure box into an intermediate storage vessel in the high-pressure box. From there the oil is pumped into the reactor section, where right before it enters the reactor, it is mixed with hydrogen. The storage vessel is continuously weighted to monitor the liquid flow rate. The hydrogen required is taken from a series of hydrogen bottles connected to a commercial “Booster” system; recently a dedicated electrolyser is added to deliver ‘green hydrogen’. The hydrogen flow is controlled using mass flow controllers. All reactors are filled with Picula catalyst, and the oil is treated in each subsequent reactor at slightly higher temperatures. Typical temperatures in the four sequential beds are 80, 120, 160 and 200°C resp. Before oil enter any of the reactor it is preheated to the temperature of the specific reactor segment. The reactor exit stream, a mixture of gas and liquid, is cooled down to room temperature through a water-cooler, and the mixture is then fed into a G/L separator, where gas is allowed to leave at the top and the liquid at the bottom. The gas depressurized to atmospheric pressure by a dedicated pressure reducing system, directed into an intermediate vessel, and can be further cooled. A gas flow meter records the flow of gas. The gas is vented after passing an online gas analyser.

The liquid is depressurized to atmospheric pressure, and then directed to a product collection vessel. The weight of the vessel is monitored constantly by a weighing scale. From here the liquid product can be pumped out of the setup after manually activating a drain pump. Pictures of the unit are shown below.

Recycle of treated product has been demonstrated to be a very effective tool to avoid any temperature excursions. Approx 400 L ‘recycle SPO’ was prepared prior to the actual production runs reviewed below. The recycle product was prepared at similar conditions as run 2 listed below, however, after its production, water was evaporated in a standard evaporator to obtain a remaining water content close to 8 wt.%.

Two production runs were carried out, using a single batch of 4.6 kg Picula catalyst:

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

The runs lasted around 527 h, 385 h in Run 1 and 142 h in Run 2, with a total of 225 h stop time (due to stops required in the weekends). They were stopped after emptying the IBC containing the pyrolysis oil.

Typical process conditions:

	A
Pressure (bar)	200
Temperature (°C)	80 - 300
Reactors	4
Catalyst	Picula™
WHSV	0.2 – 0.5



Figure 3. Photograph of the stabilisation unit.

A schematic representation of the runs to produce the amount of SPO are summarised below.

- One batch 4.6 kg Picula catalyst
- Initial batch SPO (BTG) used as recycle (~400 kg)



Run 1: 385 hr

Run 2: 142 hr

Figure 4. Runs carried out to produce the SPO for further use in REFOLUTION.

4. Results

4.1 Results from production runs

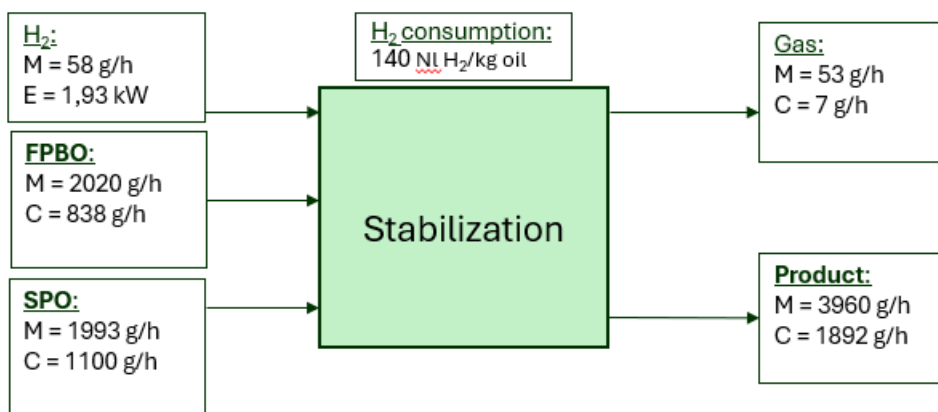
The two runs were conducted in a once-through mode using a recycle. The mass balances for both, run 1 and run 2, are summarised in Figures 5 and 6 below.

Some general remarks are summarised here:

- The results from both runs are similar, despite the different nature of the recycle streams (with or without excess water).
- In both runs all overall balances were very good, typically close to 100%, for mass as well as for the carbon, hydrogen and oxygen balances.
- Nearly all carbon from the pyrolysis oils end up in the SPO, 98 % and 104% for run 1 and 2 resp. Negligible amounts are transferred into the gaseous products, typically < 0.5 % of the carbon in the pyrolysis oils are seen as CO₂ and CH₄. Only traces of CO can be found in the hydrogen rich gas (< 0.1 vol.%).
- The amount of product collected incl. 400 L feed) was approx. 950 L (averaged feed 1.8 kg/h PO), which was further treated in an evaporator to yield ≈ 800 kg SPO and ≈ 150 kg of an aqueous phase (Figure 6). Typically, the product is evaporated in a conventional vacuum evaporator to avoid high temperatures (0.01 bar and 60 - 70°C). Water and some light organic components (methanol, ethanol, and minor amounts of acids) are distilled off, causing a minor loss in carbon yield of pyrolysis oil to the SPO (around 3 wt.%).

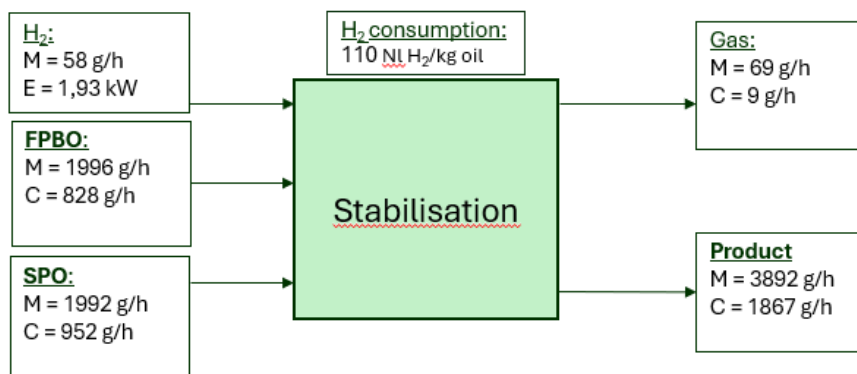
The main characteristics of the SPO and distillate fraction produced from these two runs are summarised in Table 2. All parameters for SPO align with the requirements summarised in Table 1.

R1	R2	R3	R4
80 °C	120 °C	160 °C	200 °C



Mass balance: $\underline{M}_{in} = 4.1 \text{ kg/h}$ $M_{out} = 4.0 \text{ kg/h}$ Balance = 98,6 %

R1	R2	R3	R4
80 °C	120 °C	160 °C	200 °C



Mass balance: $\underline{M}_{in} = 4.0 \text{ kg/h}$ $M_{out} = 4.0 \text{ kg/h}$ Balance = 97,9 %

Figure 5. Overview of the runs (top run 1 and bottom run 2).

- In: 960,8 kg
- Uit: 802,6 kg **84,2%**
- Distillate: 150,3 kg **15,8%**

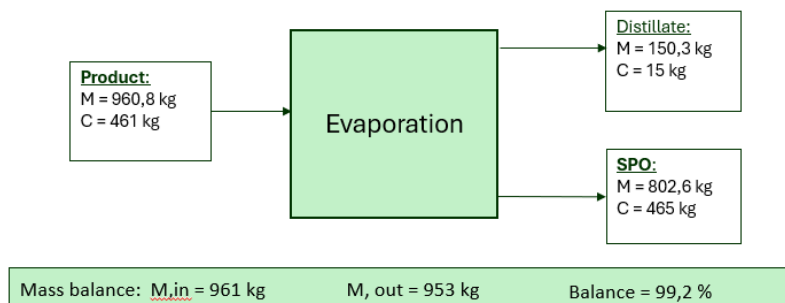


Figure 6. Distillation of the product to yield SPO and a distillate phase.

Table 2. Properties of the final products, SPO and distillate fraction

Parameter	SPO	Destillate	Unit
Moisture content	8.2	80,6	wt.%
Solid content	0.01		wt.%
Density	1138		kg/l
Kinematic Viscosity (40°C)	106		cSt
Acid number	47.3		mg KOH/g
Carbonyl content	2.7		mmol/g
MCRT	8.0	-	wt.%
EA (as received)			
C	57.8	9.8	wt.%
H	9.3	11.2	wt.%
N	0.13	0	wt.%
O (by difference)	32.8	79.0	wt.%
Higher Heating Value*	27.7	5.4	MJ/kg
Lower Heating Value*	25.7	2.9	MJ/kg
H/C (dry basis)	1.73		mole/mole
O/C (dry basis)	0.33		mole/mole

4.2. Consolidation of SPO production data

The main objectives to produce SPO is to obtain data and information for a further commercial implementation of the concept in the pyrolysis oil production pathways. Data from runs 1 and 2, together with information from years of small-scale experiments can be consolidated. Here below two representations for the consolidation approach are summarised:

- 1) A full mass and energy balance for the process (Figure 7): > 90% carbon is transferred from pyrolysis oil to SPO. The loss in carbon is mainly related to the evaporation of water, for which an optimisation can be done. The carbon in the aqueous phase is available as valuable materials as methanol, ethanol

and acids (incl. acetic acid). Importantly, the data are consistent with results from earlier tests, both in lab and pilot scale.

- 2) A simplified overall carbon balance starting from pyrolysis of a woody biomass (Figure 8). Overall, a carbon yield from biomass to SPO is 55 to 68%, depending on actual process conditions of both, the pyrolysis process and the SPO production (and on type of feedstock). The largest 'loss' in carbon is in the pyrolysis process.

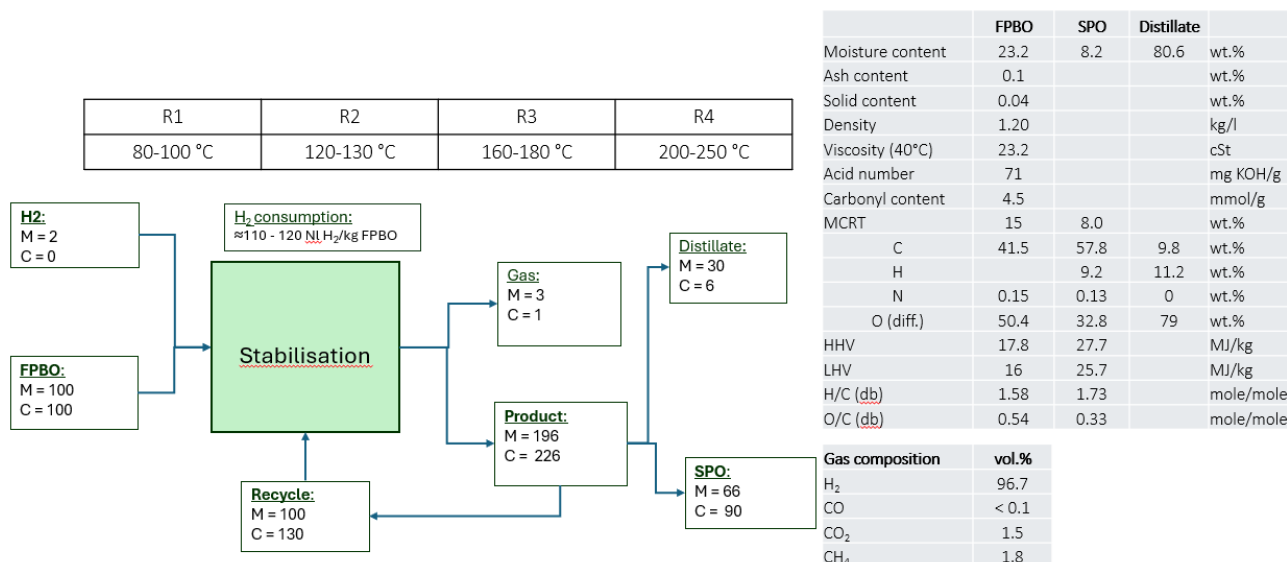


Figure 7. Overall mass balance for the SPO production over a Picula catalyst (excluding hydrogen recycle)

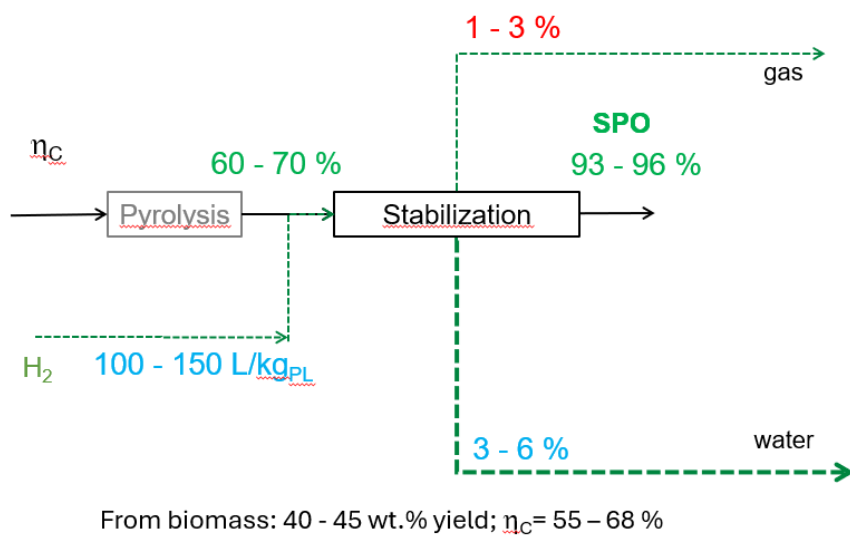


Figure 8. Simplified carbon balance for the SPO production from biomass over a Picula catalyst

In a next step further modifications are planned:

- Recycling the unconverted hydrogen, to reduce the overall hydrogen demand to the unit. As of date the hydrogen is used once through, and excess hydrogen is vented. In a further optimisation step, the hydrogen-rich gas, after a first depressurisation step, will be recycled and only a fraction of the gas vented.

- In run 1 a priorly produced SPO was used as recycle and in run 2 the product as derived from the process. In a further step, a semi-batch / semi-continuous evaporator will be used to ensure the recycling of the SPO.

5. Conclusions

Hydrotreatment is in the petroleum processing industry typically deployed to remove sulphur from petroleum feeds. For pyrolysis liquids, highly oxygenated and heterogeneous, new innovative catalysts and processes for the pyrolysis treatment are developed. The process changes included the development of a two-step processing, 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 – 100 bar) to remove the oxygen.

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This Deliverable reports the successful larger scale production of SPO:

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