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

The REFOLUTION project is dedicated to transforming raw pyrolysis oils into advanced biofuels. The core strategy involves refinery integration, scale-up and certification to produce biofuels specifically targeting the aviation and marine sectors. Since pyrolysis oils are highly oxygenated and heterogeneous, new innovative catalysts and processes were necessary for their successful treatment.

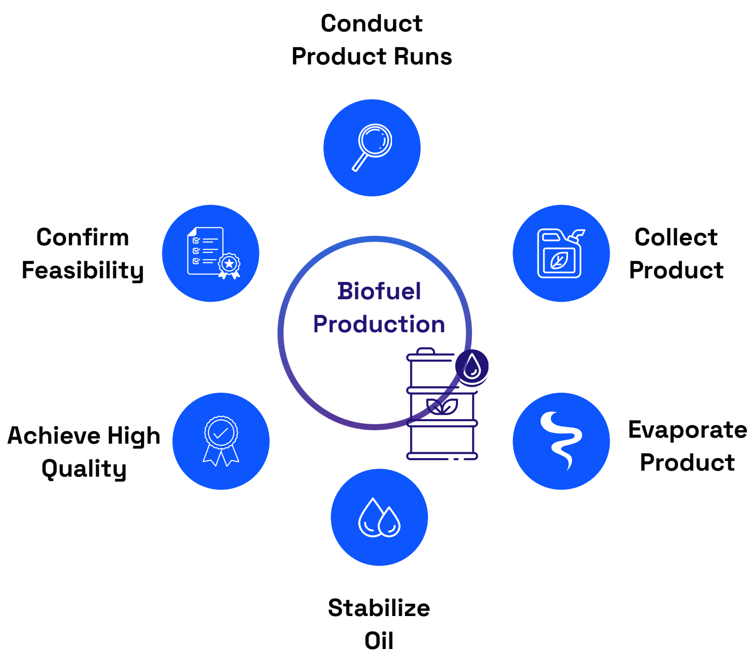
This transformation relies on intermediate processes, such as fractionation and stabilization, combined with downstream co-processing technologies. Targeted applications include Fluid Catalytic Cracking (FCC) co-processing for the aviation and marine sectors, and co-hydrotreating for the marine sector.

The challenge: treating pyrolysis oils

Hydrotreatment in the traditional petroleum industry is typically used to remove sulfur at temperatures between 300 and 500 °C and pressures between 35 and 170 bar. However, pyrolysis oils are inherently highly oxygenated and heterogeneous, necessitating the development of new, innovative catalysts and processes for their treatment. Historically, expensive precious metals (such as Ru, Pd, and Pt) were initially used, but these often suffered severe deterioration even after repeated use.

To overcome these difficulties, the process developed in the project employs a two-step processing method:

1. Stabilization: Selective hydrogenation at mild temperatures to reduce the 'carbohydrate' content.
2. Full Deoxygenation: Subsequent processing at high temperatures (350–400 °C) and mild pressures (typically 60–120 bar) to fully remove oxygen.



The stabilization technology (SPO)

The stabilization process converts pyrolysis oils into **SPO** via catalytic hydrotreatment. This conversion occurs under specific operating conditions:

- **Mild Temperatures: 200 – 250°C**
- **High Pressures: Near 200 bar**

The specific catalyst used is Nickel-based, named **Picula**™. This material was specially developed and demonstrates very high selectivity for hydrogenating aldehydes at low temperatures. Furthermore, compared to precious metal-based catalysts, Picula™ exhibits higher stability and less deactivation.

The stabilization unit utilizes a dedicated system comprising four sequential hydrotreating reactors with a typical temperature profile over the four from 80 to 200°C.
To prevent temperature excursions during the process, recycling of the treated product (SPO) was demonstrated to be highly effective. Approximately 400 L of "recycle SPO" was prepared prior to the main production campaigns.

Operational results and product quality

Deliverable D3.3 achieved the large-scale production objective, successfully reporting the production of 300 L of stabilized pyrolysis oil.
Various production campaigns were carried out using a single batch of 4.6 kg of Picula™ catalyst for over 500 hours and a capacity of around 2 L/h PL.

The water in the product was subsequently evaporated to yield the SPO and aqueous phases.
Overall balances for mass, carbon, hydrogen, and oxygen were very good, typically close to 100%.

• **Carbon Yield:** Nearly all carbon (93–96%) from the pyrolysis oils is transferred into the SPO. For the two runs, the carbon balance closure was near 100%.

• **Losses:** Minor carbon loss is associated with the evaporation of water and light organic components (such as methanol, ethanol, and minor amounts of acids), which are distilled off in the aqueous phase.

• **Gaseous Products:** Negligible amounts of carbon (typically < 0.5%) are converted into gaseous products like CO_2 and CH_4.

Stabilization significantly improves the oil properties (based on typical characteristics in Table 1)

Property (Based on 'as received' characteristics)	Pyrolysis Oil	Stabilized Pyrolysis Oil (SPO)
Water Content (wt.%)	18 – 25	5 – 10
H/C Ratio (molar, dry basis)	1.4 – 1.6	1.6 – 1.8
Carbonyl Content (Aldehydes) (mmol/g)	3 – 4	1 – 3 (Reduced by a factor of 2–4)
Micro Carbon Residue (MCRT) (wt.%)	18 – 25	< 10 (Reduced charring tendency)
Total Acid Number (TAN) (mgKOH/g)	60 - 80	60 - 80 (Remains constant)
Higher Heating Value (HHV) (MJ/kg)	17, 8	27, 7
Density (kg/m³)	1100 – 1200	1050 – 1200

The selective hydrogenation significantly reduces the aldehyde concentration, enhancing the product stability. Water removal (5 -10 wt.%) is a crucial step to further improve the SPO quality, a method difficult to do for the untreated PL while it leads to a very high viscosity and risks of polymerization.

Future applications and developments

SPO is seen first as an intermediate material for a further processing. It can be co-fed in FCC units, but clearly it can also be fully deoxygenated. This can be done over commercial CoMo or NiMo catalysts, yielding Hydroprocessed Pyrolysis Oil (HPO): this is a mixture of components with boiling point range of gasoline (15%), kerosene (35-50%) and diesel (35-50%).

Detailed production data has been collected and used to improve the existing hydrotreating plant (~ 1 - 2 kg/h feed) into a prototype scale unit, intended to operate in an environment reflecting expected performance.

Process optimisation options included:

1. Hydrogen Recycling: In past experiments, unconverted hydrogen is vented. In this optimization phase, the hydrogen-rich gas, after a first depressurization step, is recycled to reduce the unit's overall hydrogen consumption.

2. Stable SPO Recycling: A semi-batch or semi-continuous evaporator is implemented to ensure the continuous recycling of SPO, proven effective in process control and monitoring.

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This factsheet is based on D3.3 Production of 300 L SPO of BTG.