Advanced Biofuels from fast pyrolysis bio-oil

An urgent demand exists to decarbonize the transport sector and to reduce its dependency of fossil fuels. To achieve this goal advanced biofuels will certainly play a substantial important role in the aviation and marine sector, and likely in long-haul road-transport. Fast pyrolysis followed by chemical upgrading is a high potential route to sustainable, advanced biofuels. This paper provides an overview of the *BTG-neXt* process.

Fast Pyrolysis

In the biomass fast pyrolysis process organic materials are rapidly heated to 450 - 600 °C in absence of air. Under these conditions, organic vapours, permanent gases and charcoal are produced. The vapours are condensed to the primary product *Fast Pyrolysis Bio-Oil* (FPBO), typically in an amount of 50 to 75 wt% of the feedstock. The FPBO can be used to produce sustainable energy and chemicals. Its volumetric energy density is typically five times higher than the original solid material, offering important logistic advantages. The pyrolysis process is maturing with commercials plants in operation in the Netherlands, Finland, and Sweden. The technology is provided by BTG Bioliquids (www.btg-bioliquids.com).

Advanced biofuels from pyrolysis oil

FPBO as such is not suitable for direct use as transportation fuel and further chemical upgrading is required. Different approaches can be followed like co-FCC, (co-) hydrotreating or combinations thereof as summarized in Fig. 1.

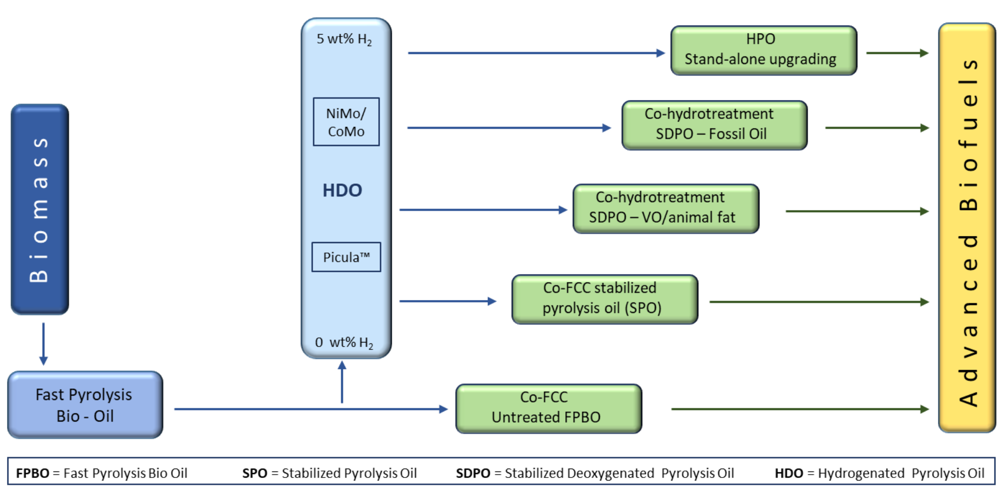

Fig. 1: Biofuels from fast pyrolysis oil

Co-feeding of untreated pyrolysis liquids is very well possible, but the co-feed ratio is limited to 5 or maybe 10 wt% depending on the FCC configuration, operation and VGO used. The chain has been successfully demonstrated by Petrobras (Brazil) on pilot scale, and Swedish oil company Preem has implemented this value chain on full industrial scale at their oil refinery in Lysekil (S).

Further increasing the FCC co-feeding rate, enabling co-hydrotreating or even stand-alone upgrading to a transportation fuel will need chemical upgrading of the FPBO. To design the upgrading process it is important to realize that FPBO is not really an oil, but an aqueous sugar syrup containing emulsified lignin fragments. Consequently, a standard hydrotreatment process and catalyst does not work properly. Instead, upgrading of FPBO starts with a so-called stabilization step. In this first step the main objective is to improve the quality of the liquids not by removing the oxygen per se, but by de-functionalising the oxygen present in the carbohydrates and to transform them –preferentially- to alcohols. Once these reactive aldehydes/ketones are removed, the liquid – called SPO- can be fed to catalytic reactors containing standard commercial catalysts. Depending on conditions, dehydration- and hydrogenation- reactions are allowed to happen, resulting in hydrodeoxygenation of the liquid. An illustration of the effect of the stabilisation and hydrogenation on the composition is shown in Fig. 2.

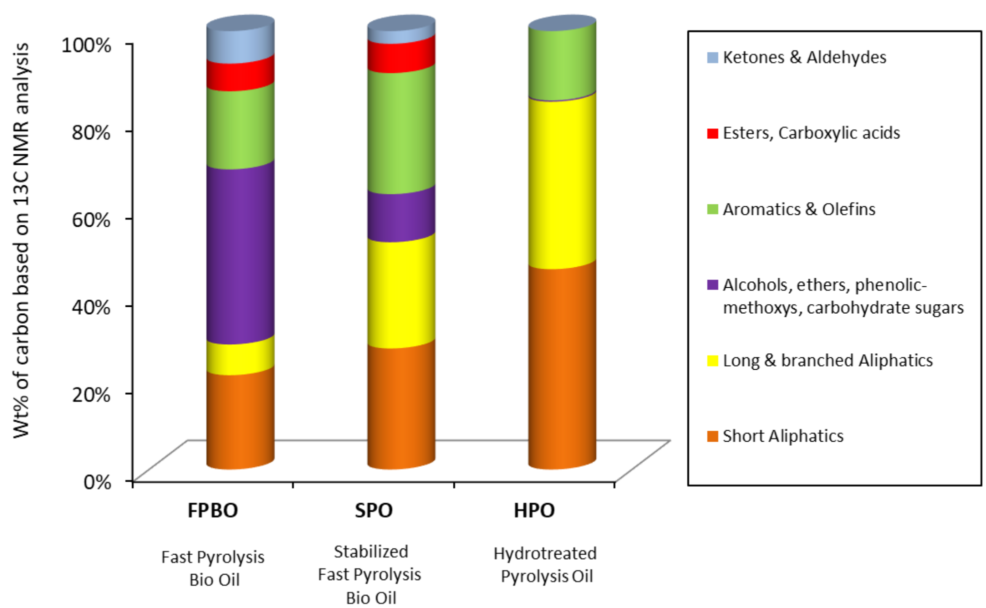

Fig. 2: Carbon based composition of crude pyrolysis oil (FPBO), stabilized oil (SPO) and fully deoxygenated oil (here denoted by PMTF); Samples produced by BTG and analysed by SASOL [ref]

Picula™ - BTG-neXt proprietary catalyst

The critical step in the upgrading process is the stabilisation of FPBO, and in particular the catalyst. A dedicated Ni-Cu based catalyst called Picula™ was developed by BTG and partners, and patents have been granted in several countries around the world. The stabilization process takes place at 200 bar pressure in a hydrogen atmosphere. The initial temperature is around 100 °C and can be stepwise increased to 250 – 300 °C depending on the required treatment severity. The product of this first stage is called stabilized pyrolysis oil (SPO). It can either be used as improved feedstock in co-FCC or as a starting material for further upgrading.

Co-FCC of stabilized oil

Co-feeding of SPOs works better than of the untreated liquids. RTD work was done in several EC-funded projects, and in addition BTG performed an experimental campaign with a Chinese University on co-FCC of SPO in a continuous DCR like pilot unit, see [1]. Overall, the observation is that stabilization of pyrolysis oil improves the performance of co-FCC and higher co-feeding ratios can be achieved (i.e. > 10 wt%). However, it must be realized that actual performance will depend on the operation of a specific FCC like catalysts used, operating mode, and type of VGO.

Stand-alone hydrotreating

The SPO can be a feedstock for further upgrading to a "drop-in' biofuel. After stabilization a conventional HDO-NiMo or CoMo catalyst can applied. This 2nd step has also been tested at BTG, and fuels of different qualities can be produced ranging from SDPO to HPO. Typically, the pressure of the 2nd step is somewhat lower (~ 130 bar) than for the 1st step. In cooperation with the Technical University of Eindhoven combustion testing of the HPO was carried out showing positive results [5]. The stand-alone upgrading process is summarized in Fig. 3.

Late 2019, BTG-neXt (www.BTG-next.com) was established with the aim to further demonstrate and commercialize the FPBO upgrading process. A demonstration plant is foreseen with an output capacity of 3-4 barrels per day. Both SPO and HPO can be delivered as a product.

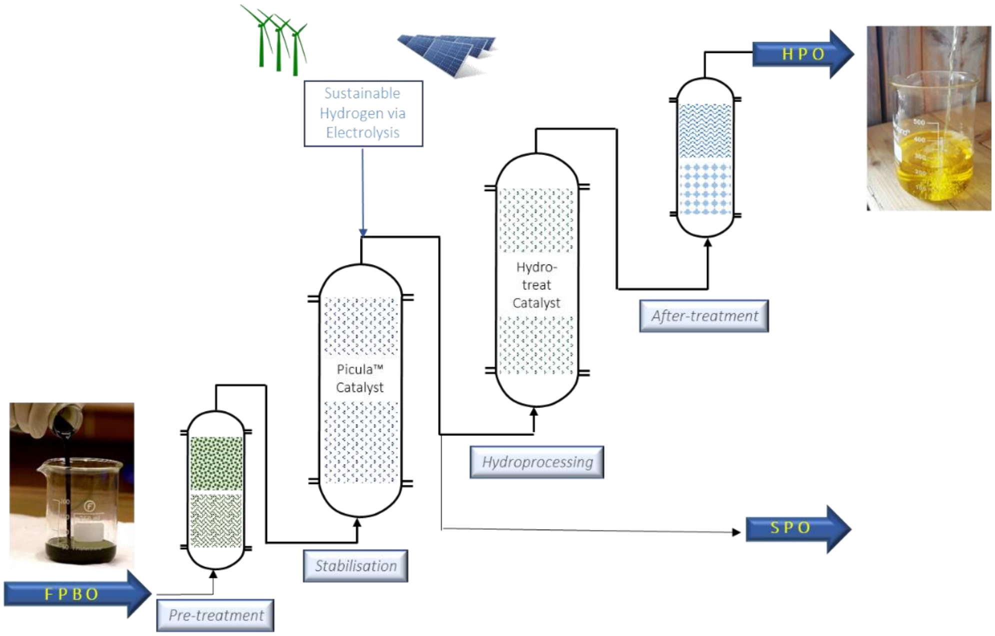

Fig. 3: Hydrotreatment of FPBO

Abbreviations

FCC	Fluid Cat Cracking
FPBO	Fast Pyrolysis Bio Oil
HPO	Hydrotreated Pyrolysis Oil
SDPO	Stabilized Deoxygenated Pyrolysis Oil
SPO	Stabilized Pyrolysis Oil
VGO	Vacuum Gas Oil
VO	Vegetable Oil

Selected references

1. *Co-processing of crude and hydrotreated pyrolysis liquids and VGO in a pilot scale FCC riser setup,* Wang C., Venderbosch R.H., Fang Y., Fuel Processing Technology, 2018, 1811, pp. 157-165
2. *Recent developments in the catalytic hydrotreatment of pyrolysis liquids,* Yin W., Venderbosch R. H., Heeres H. J., chapter 8:, Direct Thermochemical Liquefaction for Energy Applications, 2018, pp. 249-292
3. *Optimizing the bio-gasoline quantity and quality in fluid catalytic cracking co-refining*, Gueudre, Laurent; Chapon, Florian; Mirodatos, Claude; Schuurman, Yves; Venderbosch, Robbie; Jordan, Edgar; Wellach, Stephan; Gutierrez, Ruben Miravalles, Fuel (2017), 192, 60-70.
4. *Biomass pyrolysis oil as a renewable feedstock for bio-jet fuel,* Mariam Ajam, Chris Woolard, Carl Viljoen, IASH 2013, 13th international conference on stability, handling and use of liquid fuels, Greece.
5. *HPO combustion Ignition and combustion characteristics of hydrotreated pyrolysis oil in a combustion research unit*, Jinlin Han, Yu Wang, L.M.T. Somers, Bert van de Beld, Fuel 316 (2022) 123419.