Demonstration of the fractionation of fast pyrolysis bio-oil by liquid-liquid extraction on pilot scale

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Biomass is a valuable, sustainable feedstock for the production of chemicals and materials. For the optimal utilization of bio-resources, fractionation on the basis of functionalities is often preferred. The approach presented here is applying a two-step, thermochemical fractionation process (TCF). In the first step the biomass feedstock is converted by fast pyrolysis into a liquid product. Fast pyrolysis is characterized by the fast and short heating of the biomass resulting in a partial depolymerisation of the feedstock, but retaining the key chemical functionalities in the liquid. In the second step the liquid is separated at low temperature by a multistep, liquid-liquid extraction process. The fractions - pyrolytic sugars, pyrolytic lignin and extractives- consist of components derived from the de-polymerization of extractives, cellulose, hemicellulose and lignin, see Fig. 1. Subsequently, each of the fractions can be used as a raw-material in bio-based materials or as a feedstock for further (electro-)chemical or biological conversion.

This TCF approach is an alternative to pyrolysis with staged or fractional condensation. In that case the production of the various fractions is an integral part of the pyrolysis process by operating a number of condensers at different temperatures. A separation of components on the basis of boiling point/vapor pressure will be obtained. This is principally different from the TCF process in which a separation on the basis of solubility in specific solvents is achieved, and a better separation on basis of functionalities can be expected in case of TCF.

Pilot plant design & Operation

Prior to designing and building the pilot unit extensive testing was performed on lab- and bench scale. The bench-scale unit has an input capacity of 12.5 kg of FPBO per hour and is operated in continuous flow. All the FPBO fractions produced in this unit were used for initial product development. Furthermore, operation of the unit provided the required data and experience to enable the design of the pilot plant.

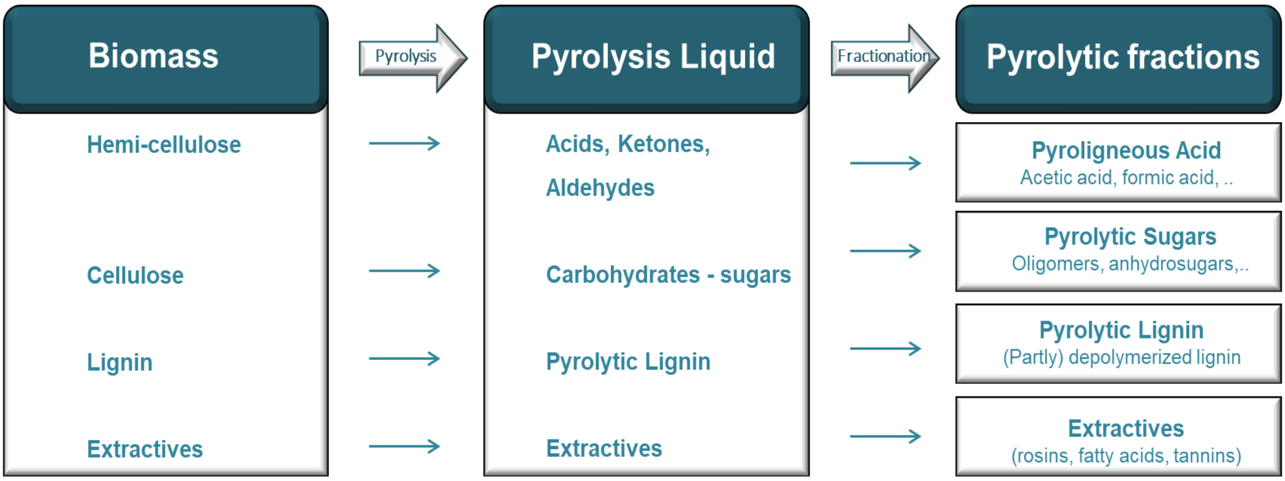

Fig. 1: Illustration of the 2-step Thermo Chemical Fractionation (TCF) concept.

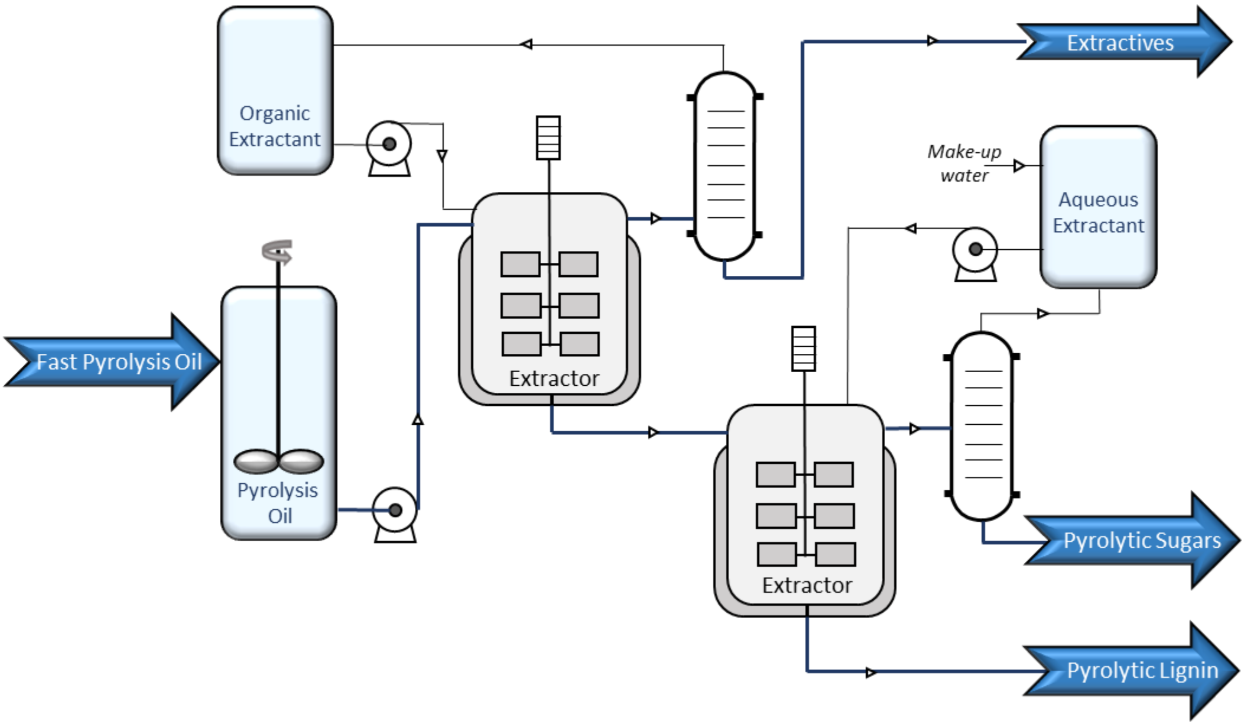

Fig. 2: Simplified process flow diagram of the TCF process

The design capacity of the pilot unit equals 3 ton of FPBO input per day, which is roughly a ten-fold scale-up of the bench-scale unit. It includes two extraction units; the first one to remove extractives from the oil, the second one to separate the pyrolysis oil in a lignin and sugar fraction. Extractants (both organic and water) can be recovered and eventually recycled to the process. The sugar fraction can be further concentrated, and the liquid lignin can be divided in a sold lignin and a phenolic fraction. A simplified process flow diagram is shown in Fig. 2; a photo of the unit in Fig. 3.

The pilot plant was commissioned by the end of 2018, and several campaigns were conducted in 2019-2021. Normally, only one or two unit operations are operated simultaneously, and recovery of extractives is only performed if needed for the specific FPBO (i.e. rich in extractives). Currently, actual capacity achieved for the lignin/sugar separation is 120 kg/h which is very close to the design capacity. The products obtained in the pilot plant show very similar properties compared to those from the bench scale unit.

Product properties
Table 1 shows typical properties of the products obtained by the fractionation of the FPBO. Primary products are aqueous sugars, liquid lignin and extractives; concentrated sugars, solid lignin and phenolics are only obtained by aftertreatment of the primary products.

Applications
The fractions produced in TCF can be used in a range of applications and dedicated development work was performed within the *Bio4Products* project. Inhere, the fractions were a.o. used to partly replace fossil based raw-materials in various phenol-based resins, and as an active component in formulations for wood modification and in foundry resins. Recently, the *NewWave* project has started; in this project the fractions are used as sustainable raw materials in four existing manufacturing lines, largely replacing fossil based raw materials and substituting toxic chemicals like formaldehyde and creosote. The manufacturing lines will produce engineered wood panels, furan base-

Table 1: Indicative properties of the products obtained by the fractionation of FPBO

			CAS: 2414605-13-1		CAS: 2411004-28-7 / 2411004-20-9			
			Aqueous	Concentrated	Liquid	Solid	Phenolics	
C	wt%	44	18	49	54	71	63	76
H	wt%	7	10	7	7	6	8	10
Carbon residue	wt%	17	5	22	30	36	5	2
Water content	wt%	23	63	5	13	<1	2	<1
MW	g/mol	-	-	-	~850	~1300	-	-
LHV	MJ/kg	16				28	26	35

chemicals, polyols and polyurethanes, and modified/engineered wood with the goal to enhance the sustainability of building materials in the construction industry. The four manufacturing are interlinked, and output from one line will further improve the sustainability of the other. Besides the production of sustainable products, water re-use, end-of-life recycling options and efficient use of byproducts are an integral part of the project and will result in an almost zero-waste approach.

To enable or simplify product research and development at reasonable scale, REACH (1-10 t/y) and PPORD registrations have been filed for the lignin and sugar fractions. Product research on extractives have been limited so far and only tests at labscale have been carried out.

Fig 3: Photo of the FPBO fractionation pilot plant at BTG.

Acknowledgement
The Bio4Products project received funding from the European Union's Horizon 2020 Research and Innovation programme under Grant agreement No. 723070. The NewWave project receives funding from the European Union's Horizon Europe Research and Innovation programme under Grant agreement No. 101058369.

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