Bio4Products

Thermo-chemical fractionation (TCF) of lignocellulosic biomass

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Bio4Products webinar #2 Developing a pyrolysis-based biorefinery

14/11/2019

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 723070.

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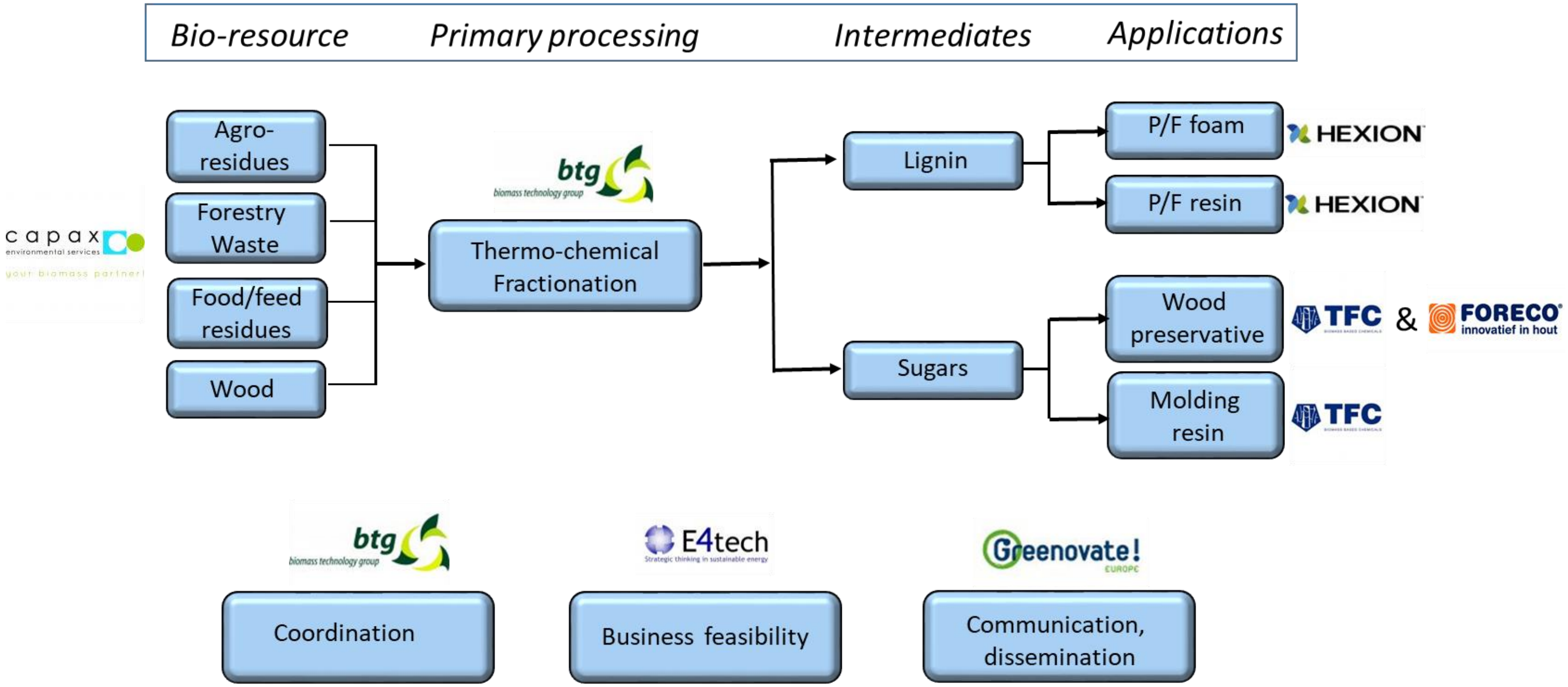
Introduction and objectives of TCF

Specific objectives Bio4Products:



- ❑ ***Bio4Products*** is a EU (SPIRE, IA) funded project running from 01/09/2016 until 01/09/2020
- ❑ Design, construct & operate a pyrolysis oil fractionation plant at an input capacity of 3 t/d;
- ❑ Go from TRL 4 →6/7
- ❑ Application of the fractions will be demonstrated in 4 end-products;
  - Replacement of fossil phenol with 30-65 wt% pyrolytic lignin in 2 resins
  - Replacement of f.i. creosote up to 100 wt% by pyrolytic sugars in wood modification
  - Replacement of 30-65 wt% of furan based resins by pyrolytic sugars
- ❑ Techno-economic & environmental assessment of the whole value chain

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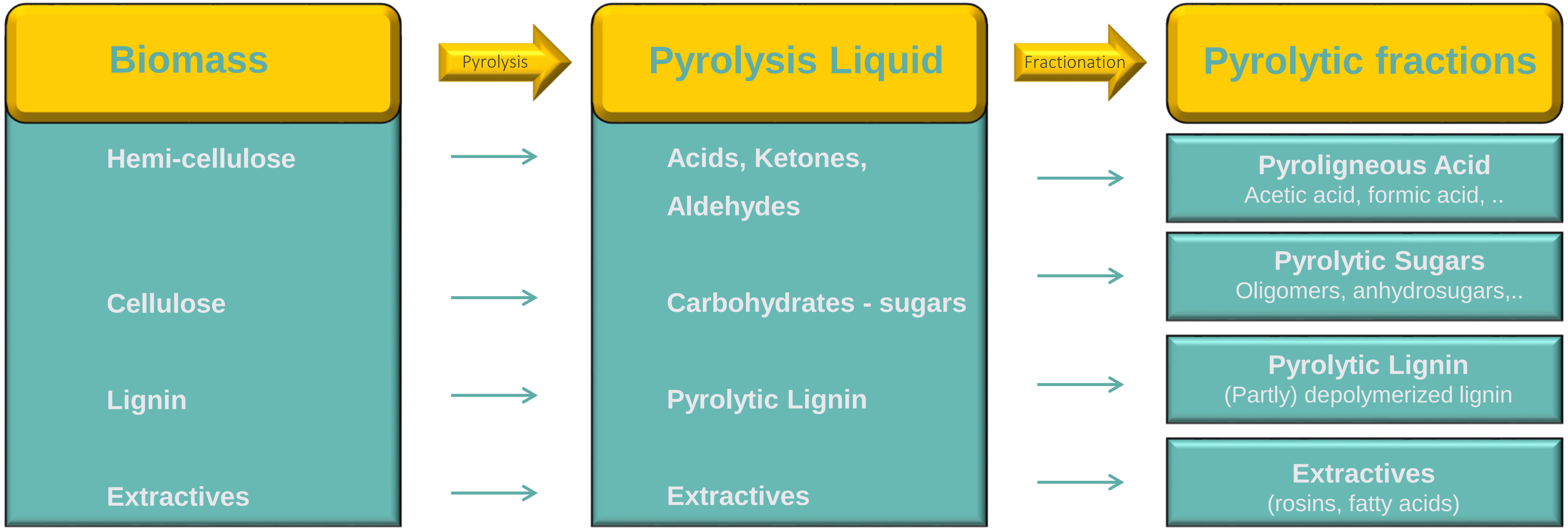
Thermo-chemical fractionation



Thermo-chemical fractionation via Fast Pyrolysis:

- ❑ Key biomass functionalities retained in the pyrolytic fractions;
- ❑ Fractionation process based on liquid-liquid extraction enabling separation on basis of functionality
- ❑ Each fraction is used directly as raw material in bio-based products or a starting point for further dedicated (electro)-chemical, catalytic or biotechnological conversion.
- ❑ No byproducts/waste: Excess fractions can be mixed back in the pyrolysis liquid for fuel application.

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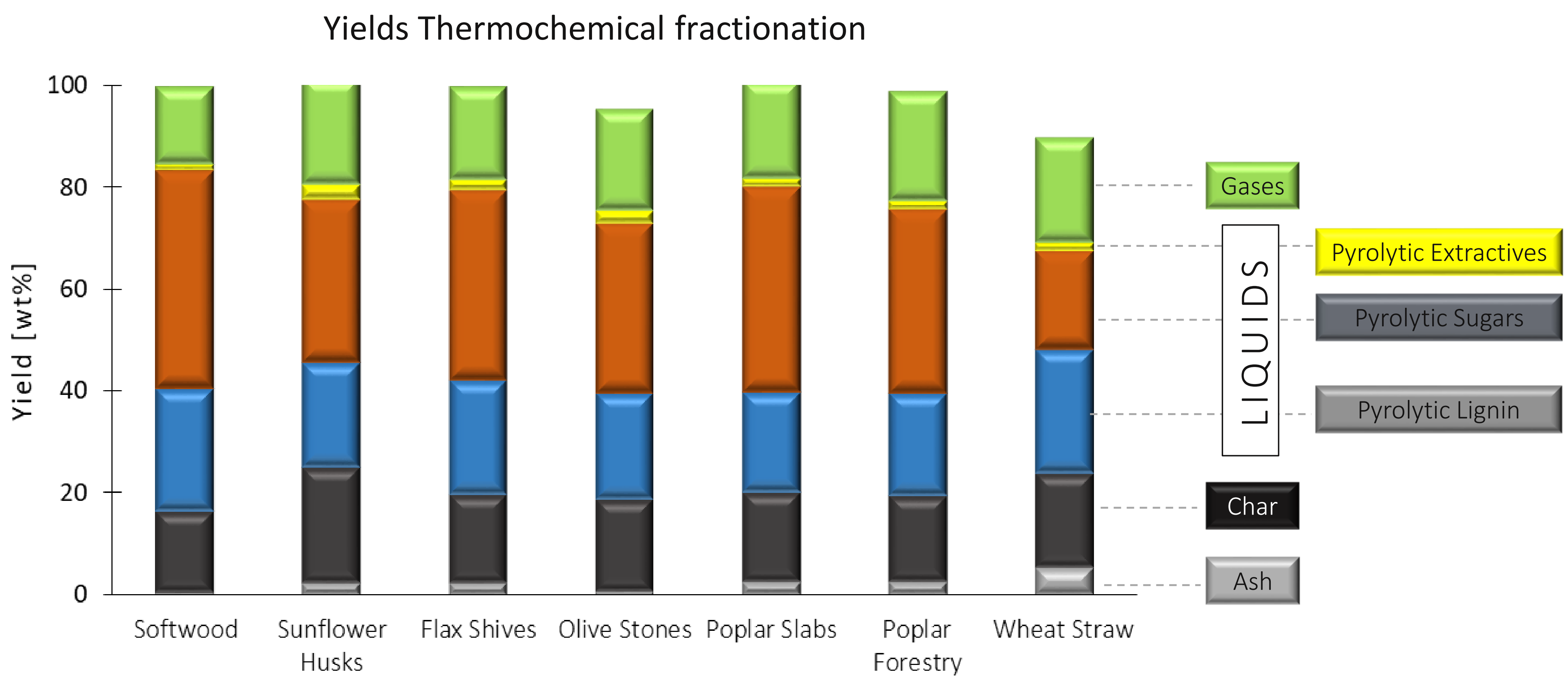
Thermo-chemical fractionation of selected biomass feedstocks



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Fraction 1: Extractives

- ❑ Extractives originating from the resin- , terpene- and fatty acid components
- ❑ Extractives are tall oil like
- ❑ Further quantitative analysis required
- ❑ Possible applications:
  - Specialty chemicals
  - Co-feed in HDO to produces diesel

(Fraction: max.3 wt% of FPBO)

Sample	Olive stone	Sunflower husks	Wheat straw	Pine wood
Group	Conc. (wt%)	Conc. (wt%)	Conc. (wt%)	Conc. (wt%)
Aromatics	1.2	0.4	1.4	1.0
Cycloalkanes	2.2	3.2	3.4	3.2
Dihydroxybenzen	2.3	1.3	1.9	2.0
Fatty acid methyl ester	0.2	0.3	0.1	0.2
Free fatty acids	4.2	7.5	1.8	2.8
Hydrocarbons	6.8	4.3	3.0	0.3
Ketones	1.1	0.9	0.9	1.3
long-chain aliphatic ketones	0.3	0.1	0.4	0.1
Methoxyphenols	10.5	8.7	8.7	18.4
Naphthalenes	2.0	0.7	2.1	1.5
Phenols	6.3	4.2	6.4	5.9
Volatile fatty acids	4.5	4.1	4.2	5.9
Volatile fraction of oil	**41.4**	**35.7**	**34.2**	**42.5**

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Fraction 2: Pyrolytic sugars

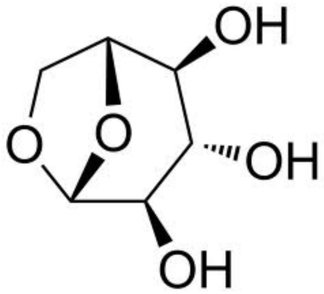
- In pyrolysis cellulose and hemicellulose polymers are cracked into:
    - Sugar monomers (e.g. levoglucosan)
    - Sugar oligomers (e.g. cellobiosan)
    - Sugar polymers

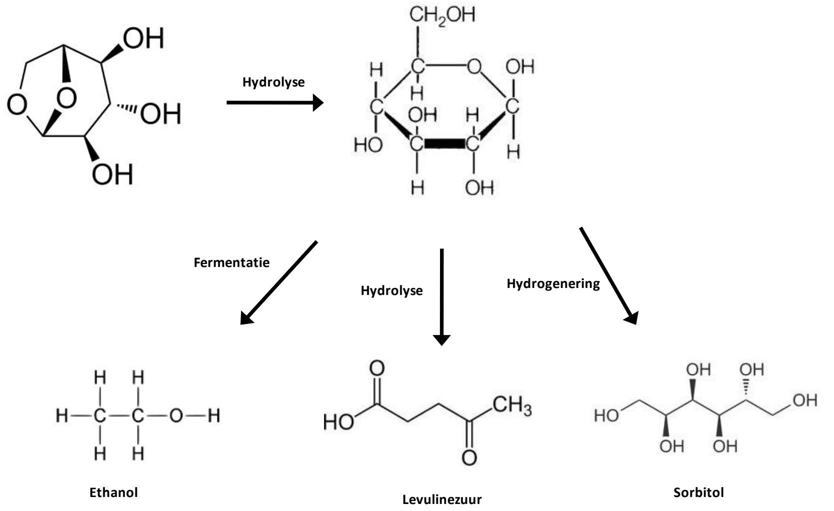
- Pyrolytic sugar used as aqueous solution (incl. acid, ketones etc) or further concentrated to a syrup.

- Properties
    - Water content 4 – 65 wt%
    - Mineral free

(Fraction: max. 40 wt% of FPBO)

Levoglucosan from FPBO





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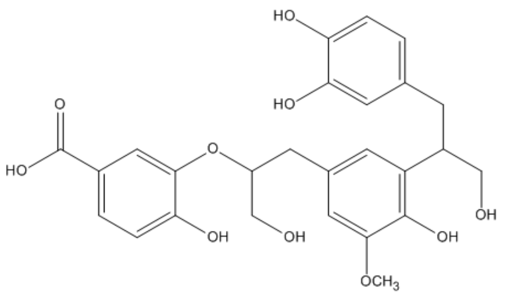
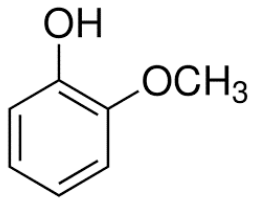
Fraction 3: Pyrolytic lignin

In pyrolysis the long lignin polymers are cracked (partly depolymerized) into:

- ❑ Phenolic monomers
- ❑ Phenolic oligomers
- ❑ Phenolic polymers





- The pyrolytic lignin is a highly viscous liquid
- Mineral free
- Relative low Mw
- Soluble in many solvents
- More reactive than other lignin's (natural, kraft, etc.), but less reactive than phenol

(Fraction: max. 30 wt% of FPBO)

	Pyrolytic Lignin	Solid Pyrolytic Lignin
C(wt%) H (wt%) N (wt%)	53.9 7.2 0.5	68.4 6.2 0
H_2O (wt%)	10-15	-
TCN (mg BuO/g)[1]	8.8	-
TAN (mg KOH/g)[2]	25.5	-
CR (wt%)[3]	30.1	37.8
SP (°C) MP (°C)	- -	130 160
Mw (g/mole)	837[4]	1309[4]

[1]: TCN = Total Carbonyl Number, calculated in mg butanone/g sample. [2]: TAN = Total Acid Number, calculated in mg KOH/g sample. [3]: CR = Carbon Residue. [4]: Mw Kraft lignin = 1000-8000 g/mole.

Monomeric PL mainly: Guaiacols, alkylphenols, cyclohexanols, etc.

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Fractionation on bench-scale

- Continuous unit with input capacity: 12,5 kg/h
- 2 liquid-liquid extraction units
- Primarily, fractionation into extractives, aqueous sugars and liquid lignin;
- Operational since 2011;
- Ambient pressure, temperatures up to 70 – 80 °C;
- Pyrolysis oil produced from different biomass feedstock in bench-scale and pilot-scale fast pyrolysis units;
- Initiated development bio-based products
- Design basis for pilot plant

btg
biomass technology group

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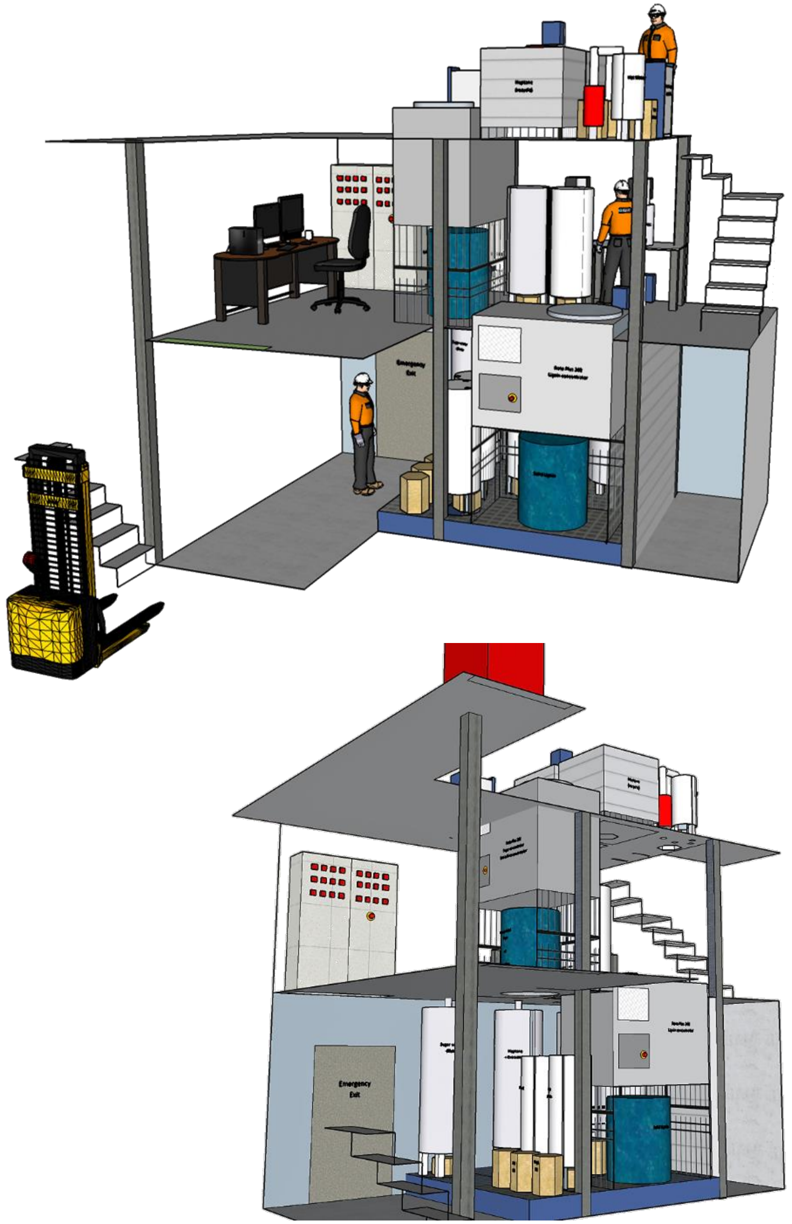
Fractionation Pilot Plant



3D model of Bio4Products Fractionation Pilot Unit - 3 t/d FPBO input (made in Sketchup))

- ❑ Need for large amounts of raw-material = pilot plant
- ❑ Scale up from continues bench-scale (12.5 kg/h) to pilot-scale (125 kg/h)
- ❑ Heart of the pilot-plant: 2 liquid-liquid extractors
- ❑ Multiple concentrators for the recovery and/or recycling of the extractants
- ❑ Additionally; treatement to produce the solid lignin
- ❑ Placed next to pyrolysis pilot plant
- ❑ Input fractionation pilot plant is output pyrolysis pilot plant
- ❑ A compact 3 level design was made

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Fractionation Pilot Plant

- Input capacity: 3 t FPBO/d (10-fold scale-up)
- Production
  - ***extractives***,
  - ***pyrolytic lignin (S/L)***,
  - ***pyrolytic sugars***
- Construction completed in summer 2018
- Commissioning pilot plant in Q4-2018
- Proven input capacity ~105 kg/h (~ 84% of design)
- Product properties & yields (lignin & sugars) similar to bench-scale testing

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Fractionation Pilot Plant

Fractionation plant consists of 5 separated processes:

1. Section 100: FPBO extraction (removal extractives)
2. Section 200: FPBO fractionation
3. Section 300: Sugar & extractives processing
4. Section 400: Lignin processing
5. Section 800: Liquid handling; Add FPBO’s etc., and retrieve products

❑ Pilot plant is controlled by a dedicated data acquisition and control system. Each section has a separate control system

❑ Other auxiliary systems used:
- Cooling and heating
- Afterburner
- Clean in place system

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Fractionation Pilot Plant

Since commissioning (Q4 2018)

- ❑ 4.0 t of FPBO fractionated producing:
  - ❑ 4.7 t PS aq
  - ❑ 324 kg PS syrup
  - ❑ 1.0 t of PL
  - ❑ 750 kg SPL
  - ❑ 16 kg extractives

- ❑ Fractions (lignin & sugar) will be used for demonstration activities in the coming months
  - Molding resins
  - Foam resins
  - Foundry resins
  - Formulations for wood modification

In the next webinars presentations will be given on the application of the fractions and product development

- ❑ Activities with respect to REACH registration of the fractions have now been started to allow the delivery of extended quantities
- ❑ Fractions can be purchased for testing

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Summary

- TCF is a flexible innovative two-step conversion process to transform different bio-resources into raw-materials for renewable chemicals and products
- TCF uses as short thermal treatement (fast pyrolysis) followed by low temperature fractionation of the mineral free liquid product, that keeps the key chemical functionalities intact in separate liquid, depolymerized fractions
- In TCF the minerals are recovered, and excess fractions can mixed back in the pyrolysis oil used for fuel applications
- TCF enables the development of a new range of bio based products. Promising results have been obtained for e.g.:
  - Molding resins
  - Foam resins
  - Wood modification
  - Foundry resins
- The FPBO fractionation process has been scale-up to a capacity of 3 t/d to enable product testing at industrial relevant scale

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Thank you for your attention

Questions?

Please visit us at:
www.Bio4Products.eu

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