Thermo-Chemical Fractionation, a unique technology to unlock biomass

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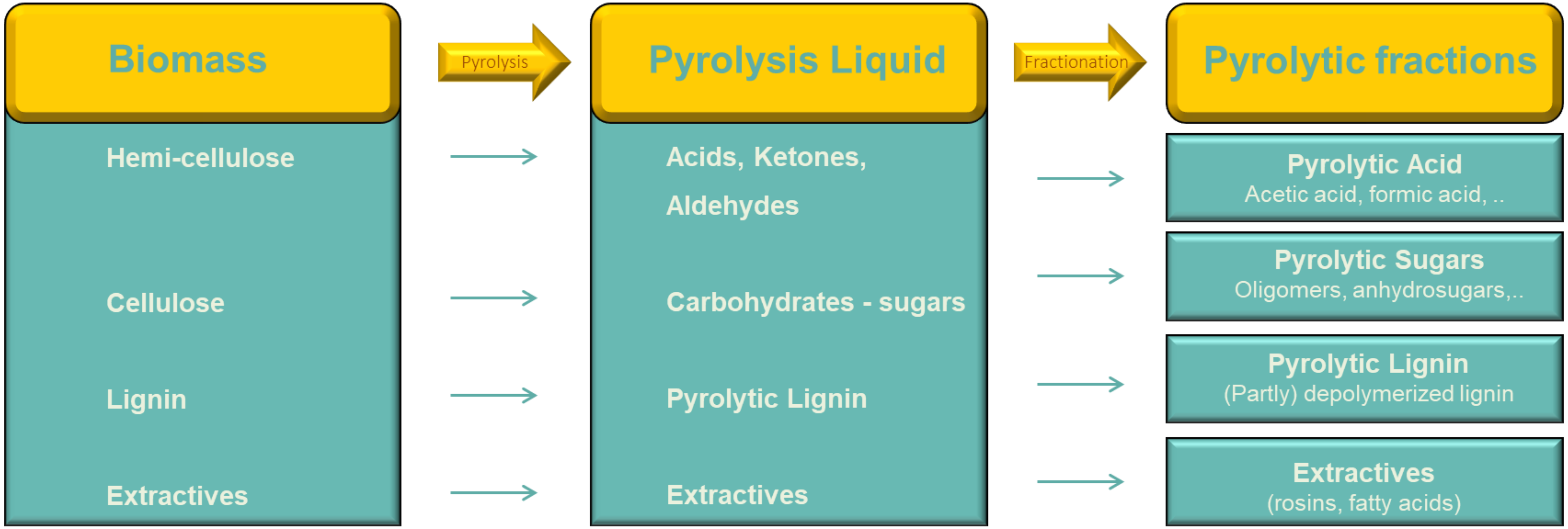
Content

Content:

- Thermo-Chemical Fractionation (TCF)
  - The process
  - Properties of fractions
- The Bio4Products project (finalised)
  - Examples of the use of fractions in products
- The NewWave project
  - Introduction
  - Manufacturing lines
  - Production of polyols

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.

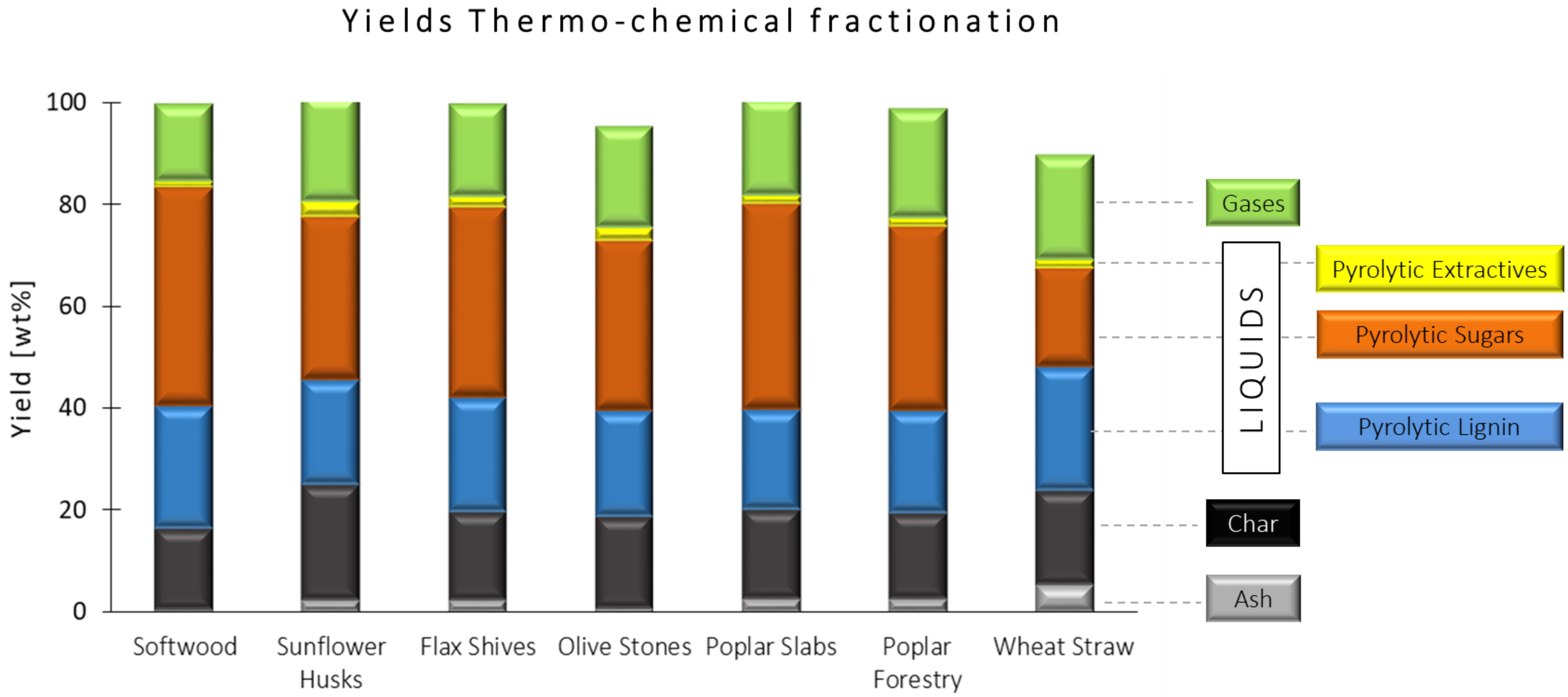
Thermo-chemical fractionation

Fractionation of pyrolysis oil, how does this work?

- Pyrolysis oil: Acidic emulsion of depolymerized biomass
  - H_2O content of ~23 wt.%
- Separation of pyrolysis oil by extraction into :
  - *Extractives, depending on BM used*
  - *Liquid pyrolytic lignin (25-30 wt.%)*
  - *Pyrolytic sugar solution (30-40 wt.%)*
- Further processing yields:
  - *Pyrolytic sugar syrup*
  - *Solid pyrolytic lignin*
- At BTG the fractionation of pyrolysis oil is performed on pilot-scale
  - Developed/built in Bio4Products
  - Commissioned in Q4, 2018
  - Capacity: 3 t/d of oil processing

Thermo-chemical fractionation

Fractionation of pyrolysis oil; some yields:

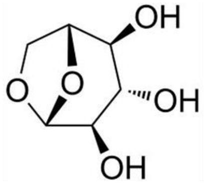


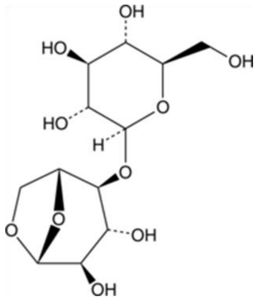
Thermo-chemical fractionation

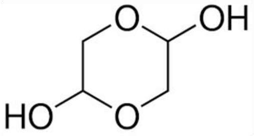
Fractionation of pyrolysis oil; sugars:

- Pyrolytic sugar contains:
  - Sugar monomers (e.g. levoglucosan) → ~ 28,3%
  - Sugar oligomers (e.g. cellobiosan) → ~ 40,2%
  - Sugar polymers → ~ 13,9%
  - Glycoaldehyde → ~ 12,6%
  - Small amounts of phenols, acids and ketones → ~ 5%
  - Sugars are mainly cellulose (C6) derived

(Fraction: max. 40 wt.% of FPBO)







Composition of pyrolytic sugar syrup:

Levoglucosan (wt%)[1]	18,6
Glycoaldehyde (wt%)[1]	12,6
Organic acids (wt%)[1]	2,9
Ketones (wt%)[1]	1,6
Phenols (wt%)[1]	0,47
Other mono-saccharides and their anhydro-form (wt%)[1]	9,7
Di-saccharides and their anhydro-form (wt%)[1]	16,6
Tri-saccharides and their anhydro-form (wt%)[1]	14,8
Tetra-saccharides and their anhydro-form (wt%)[1]	8,8
Higher oligo-saccharides and their anhydro-form (wt%)[1]	13,9
Formaldehyde	< 0,01
Acetaldehyde	< 0,01
C/H/N	46,3/6,9/0,1
Karl Fischer H_2O (wt%)	8,3
Carbon residue (wt%)	22,8
Acid no. (mg KOH/g)	60,0

[1]: On dry base

PS (UVCB):

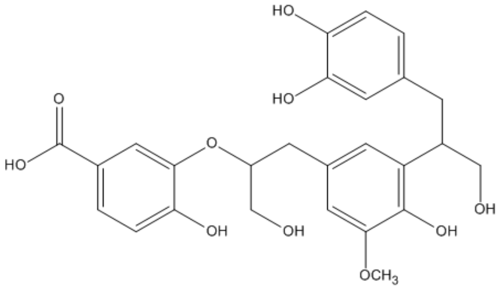
- PPORD submitted January 2020
- CAS number PS: 2414605-13-1
- REACH number PS: 01-2120886739-29-0000
- Dossier submitted in June 2021 (1-10 t/y):

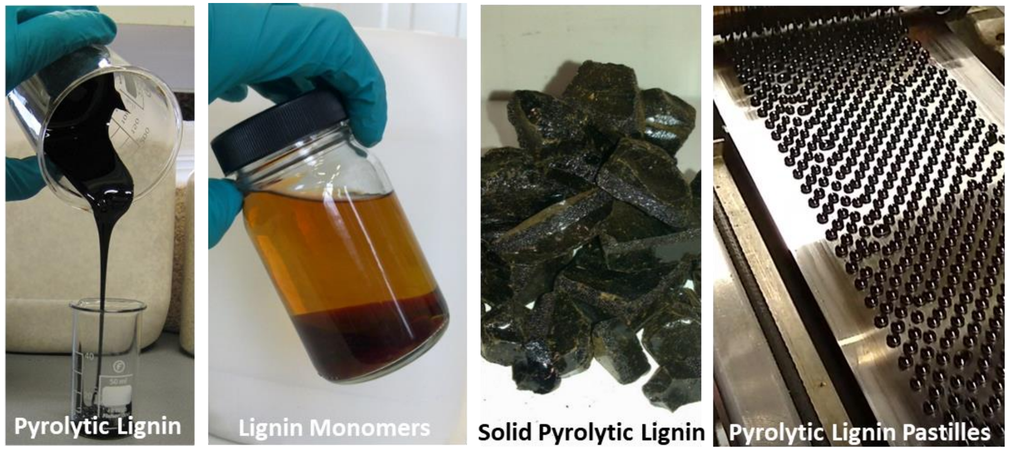
UVCB: Substances of unknown or variable composition, complex reaction products, or biological material

Thermo-chemical fractionation

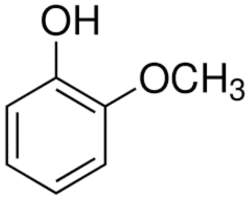
Fractionation of pyrolysis oil; lignin:

- 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



(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.

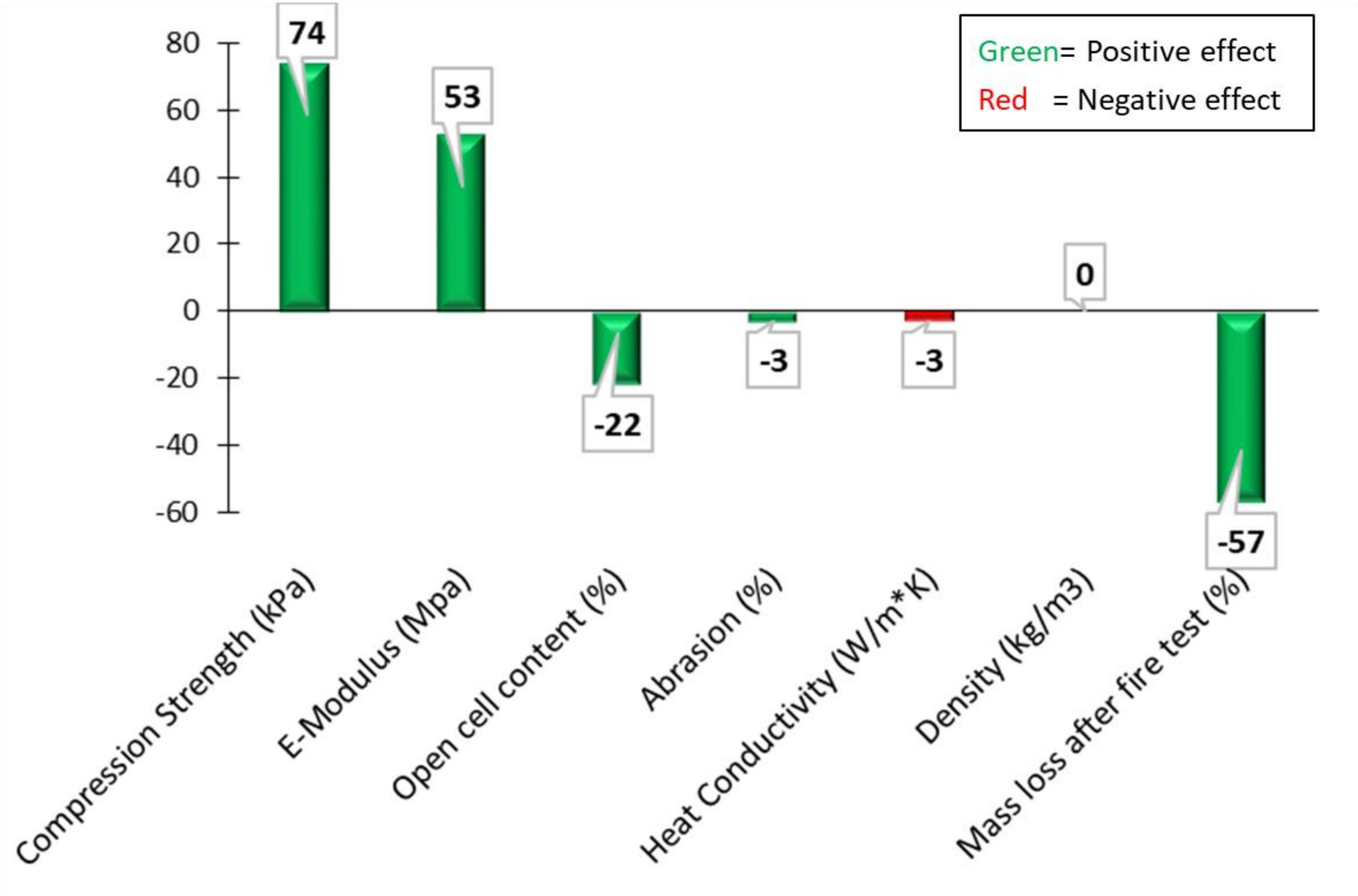
PL (UVCB):

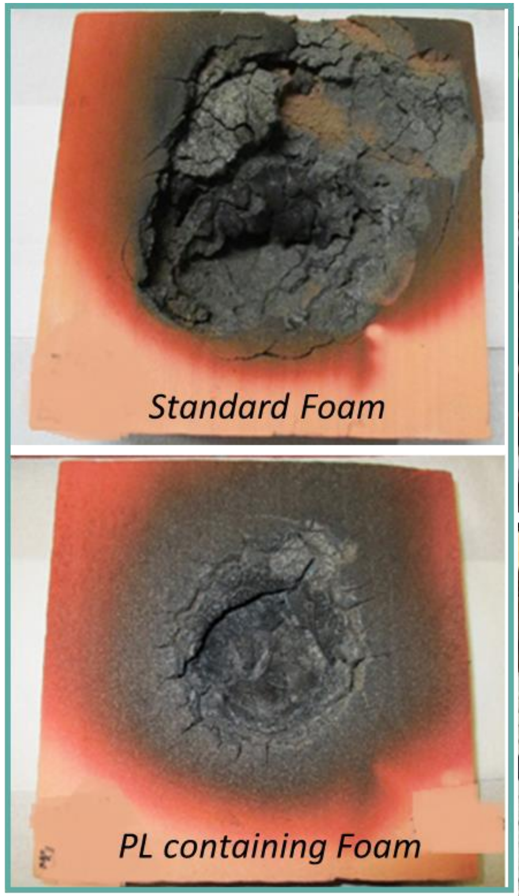
- PPORD submitted January 2020
- CAS number PL: 2411004-28-7
- CAS number SPL: 2411004-20-9
- REACH number PL: 01-2120886738-31-0000
- Dossier submitted in June 2021 (1-10 t/y):

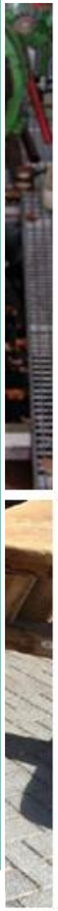
UVCB: Substances of unknown or variable composition, complex reaction products, or biological material

Bio4Products applications

Applications



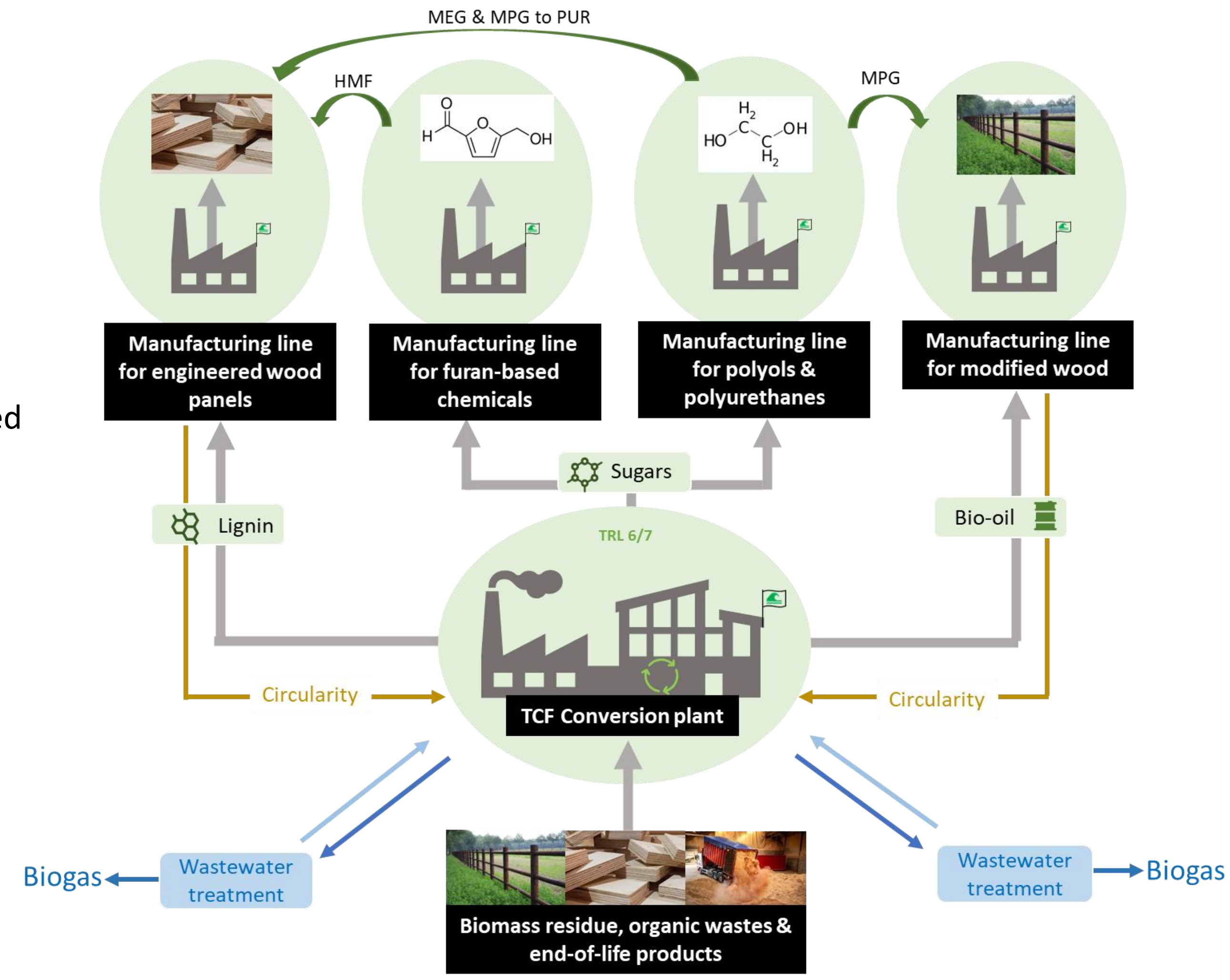




NewWave introduction

NewWave introduction

- NewWave is a Horizon Europe funded project
  - Started in April 2022, running for 4y
  - NewWave will introduce sustainable raw materials in four different manufacturing lines, replacing toxic chemicals, and lowering the environmental footprint of the products
  - The products produced in the manufacturing lines will be used to enhance the sustainability in the construction industry



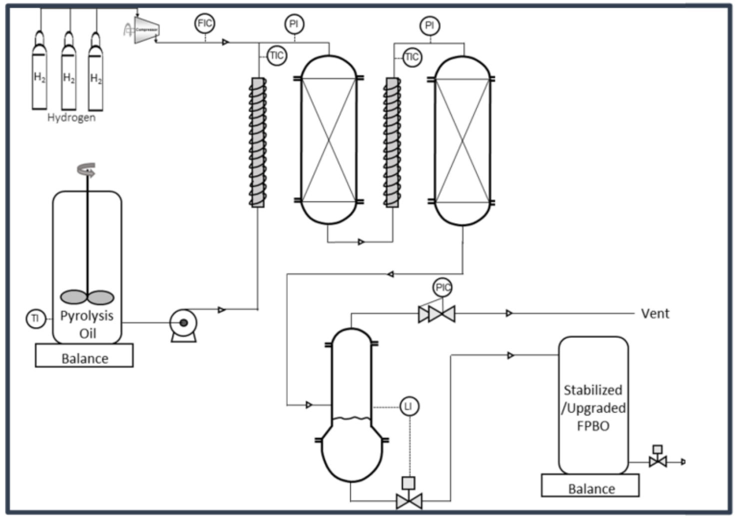
NewWave process scheme

- TCF → Thermo-Chemical Fractionation (TRL: 6/7)
  - Fast pyrolysis + fractionation of pyrolysis oil into:
    - Lignin & Sugars
- 4 Manufacturing lines
- Interlinked manufacturing lines
- Circularity of final products
- Wastewater treatment

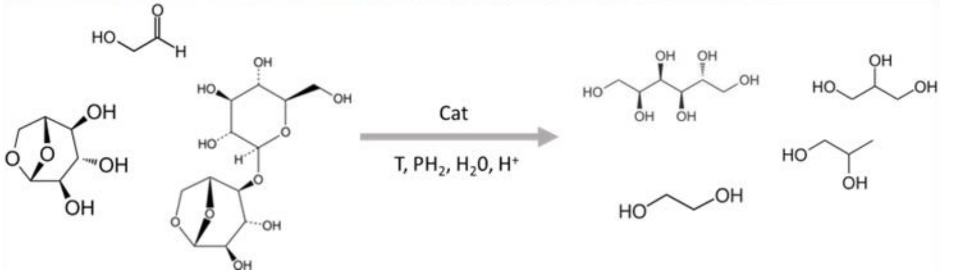
NewWave polyols

How are the polyols produced?

- Hydrogenation performed in dedicated set-ups
  - Lab-scale hydrotreater (continuous)
  - Pilot-scale hydrotreater (continuous)
- Production of polyol’s performed by applying:
  - PICULA™ catalyst
  - Elevated temperature
  - Elevated H_2 pressure
- Hydrogenation of pyrolysis oil and/or pyrolytic sugars
- Prepare samples from SPO/SPS:
  - By fractionation (to remove lignin)
  - By distillation (to remove small polyols)
- Perform analysis to determine composition
- Test polyols in PUR applications (AEP Polymers)



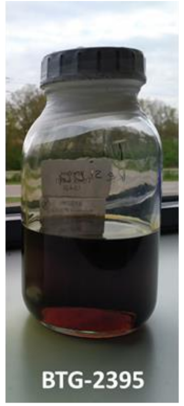
Capacity ~ 50 l/d
Max. T: 450 °C
Max P: 200 bar



NewWave polyols

How are the polyols produced?

- Separation by extraction and distillation:
  - Mixed polyols (all water-soluble polyols in SPO)
    - Dark red liquid BTG-2395
    - ~30-40 wt.% of SPO (db)
  - Large/heavy polyols
    - Thick black liquid: BTG-2410
    - Yield: ~ 65-75 wt.% after distillation
  - Light polyols
    - Light yellow liquid BTG-2479
    - Yield: ~ 25-35 wt.% after distillation



Distillation unit

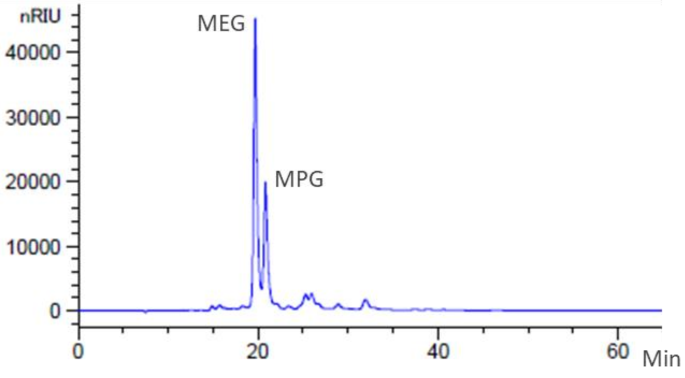
NewWave polyols

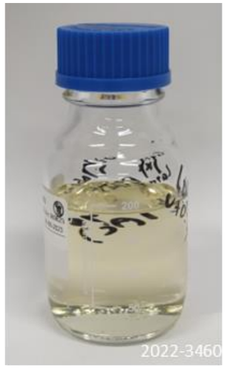
Analysis of polyol samples

	BTG-2410	BTG-2479	BTG-2395
HPLC[1]			
MEG (wt.%)	ND	55,3	28,2
MPG (wt.%)	ND	23,3	12,8
Standard analysis			
C/H/N (wt.%)	63,1/7,8/,0,0	44,8/10,0/,0,1	46,2/8,9/0,3
Karl Fischer H_2O (wt.%)	0,6	1,2	1,1
TAN (mg KOH/g)[2]	11,6	11,9	19,5
CAN (mmol/g)[3]	1,9	0,6	1,6
pH	4,5	4,4	4,1
CR (wt.%)[4]	15,6	0,0	3,8

[1]: HPLC analysis: MEG = Mono ethylene glycol, MPG = Mono propylene glycol. [2]: Total acid number. [3]: Carbonyl number. [4]: Carbon residue.

MEG + MPG: 78,6 wt.% !





- Various analysis performed
- Still some unknowns on “other” polyols
  - Additional analysis required → Qualification & quantification
  - Further purification required
- Simple one-step purification was applied to increases MEG & MPG conc.
  - Recovery cleaned: 55 wt.% (db) → should be increased

- Increase yield of smaller polyols by:
  - Testing of alternative in-house catalysts
  - Optimization of process conditions
- Pilot-plant runs to produce large quantities (with most promising system)
- Test polyols (all) in PUR applications (AEP polymers)

Summary

- Fast Pyrolysis is a suitable process to convert a variety of biomasses into a liquid (FPBO);
- FPBO can be an excellent raw material for developing a so-called Bio-liquids refinery covering Bioenergy, Biofuels and Bio-based products & chemicals;
- FPBO contains similar chemical functionalities as the original biomass;
- Fractionation of FPBO by liquid-liquid extraction yields a.o.:
  - Pyrolytic lignin
  - Pyrolytic sugars
- Fractions can be applied directly as raw material in biobased products or as raw-material in chemical processing:
  - Pyrolytic lignin in molding resins, insulation foams & wood panels
  - Pyrolytic sugars in wood modification, foundry resins, and in the production of polyols and furan-based chemicals
- Further product development ongoing in the NewWave project, please visit: https://www.newwave-horizon.eu/

Acknowledgement

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BIO4 PRODUCTS
Creating sustainable resources for process industry

NewWave – Grant agreement 101058369 (Horizon EU)

NewWave

Questions?

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