Main results of the hydrothermal liquefaction of cellulosic ethanol lignin

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This project has received funding from European Union's Horizon 2020 research and innovation programme under grant agreement n° 764675

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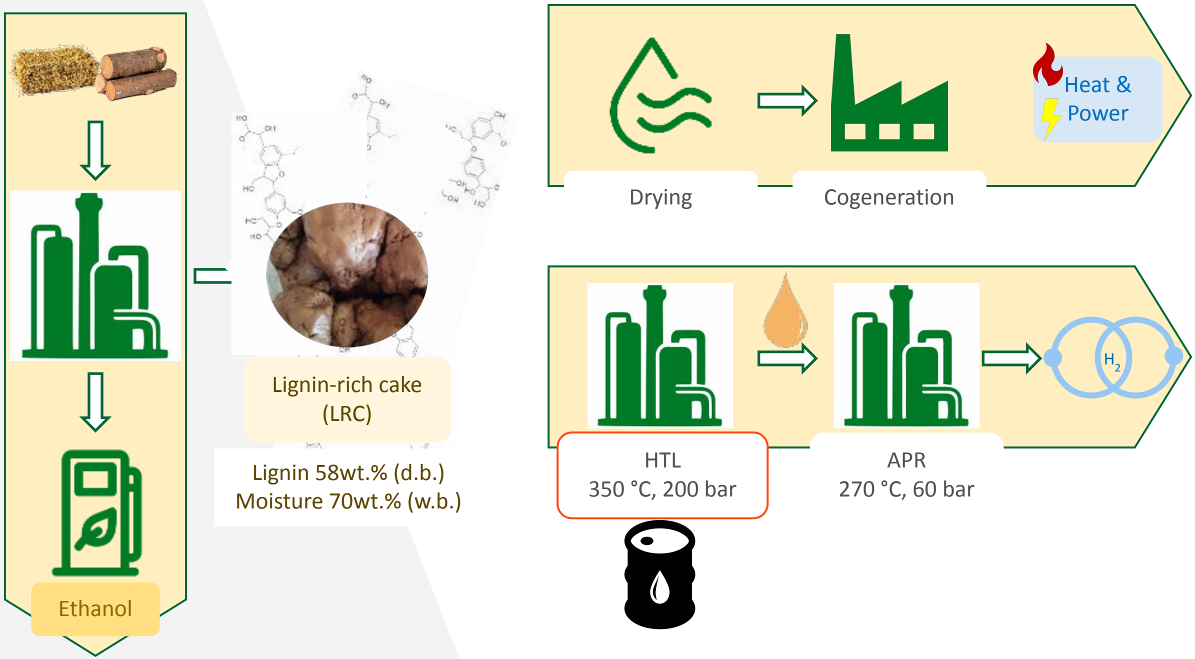
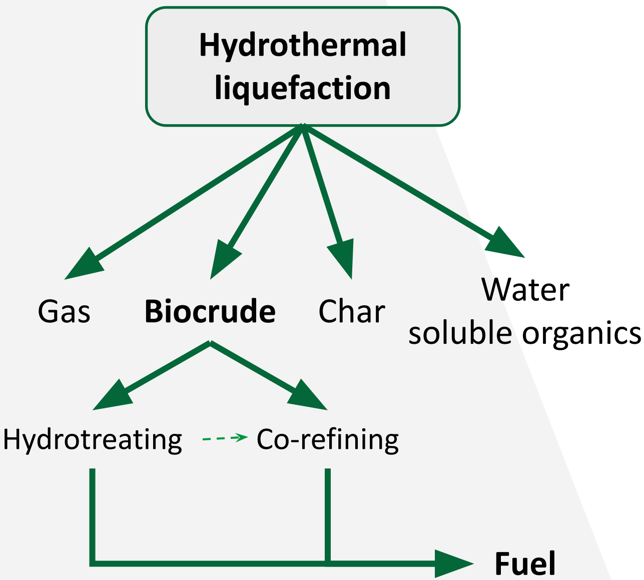
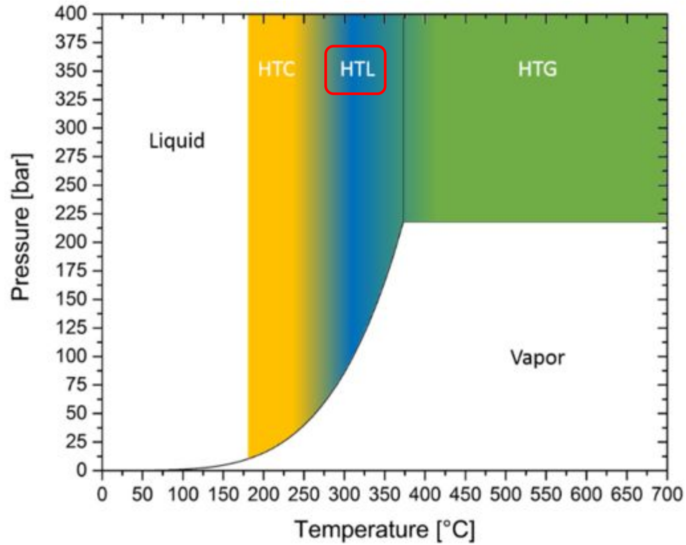
HTL in the HTF framework



Hydrothermal liquefaction

- Thermochemical process occurring in **sub/supercritical water**
- Mimics crude oil formation (high pressure and temperature) in minutes instead of thousands of years
- **Wide range** of operating conditions **(250-450°C / 80-350 bar)**
- Reaction medium is water □ indicated to treat **wet biomass (algae, sludge, lignin-rich stream)**





Modified from Peterson et al. Energy Environ. Sci. 1 (2008) 32–65. doi:10.1039/b810100k

Shift towards residual feedstocks

- From early studies with wood (late 70s) and the boom of microalgae (from 2008), now academia and industry are focusing on **waste and industrial residue**:

Sewage sludge

Genifuel

Forest residue

Steeper Energy

OFMSW

ENI

End-of-life plastic

Mura Technology

Lignin/Black liquor

Heat to Fuel

BL2F

Batch experimental campaign

Batch experimental campaign

- Batch experiments for preliminary screening and aqueous phase production for APR

  - Custom tubular reactor in hot fluidized bed and autoclave

Two-step solvent extraction

Solids

AP

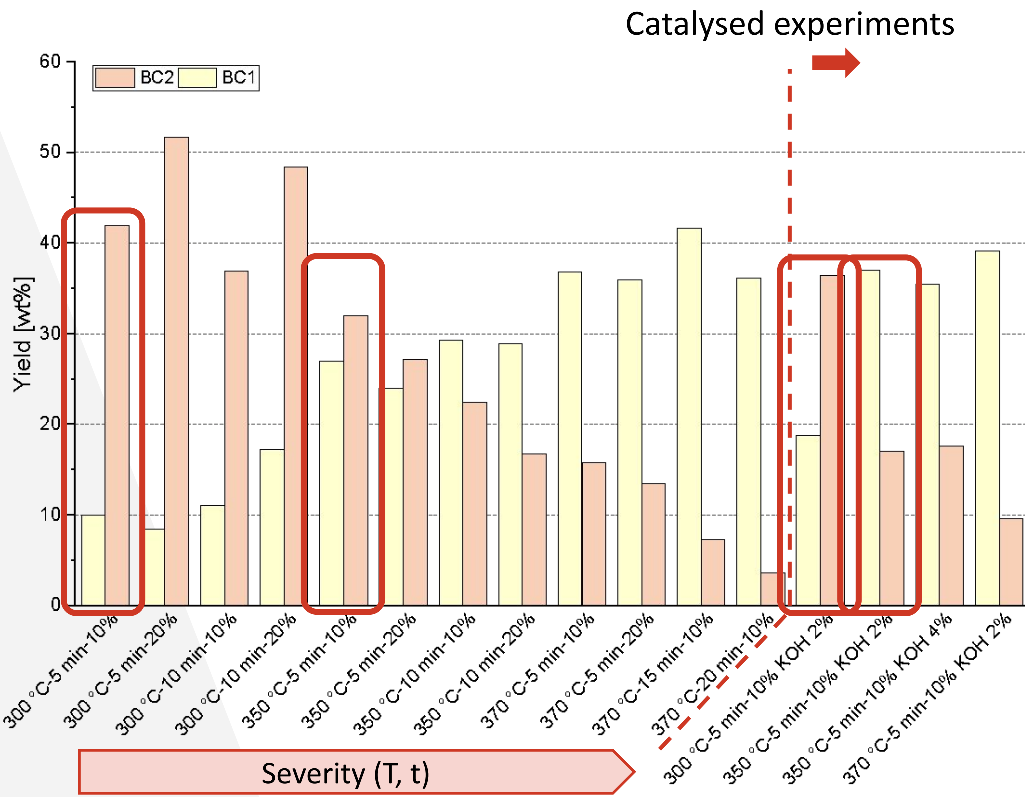
Light BC

Heavy BC

Biocrude yield

- Light fraction (BC1) increased with severity
- Heavy fraction (BC2) decreased
- Temperature depolymerization enhanced by KOH:

  ↑ Relative abundance of lighter fraction
  ↓ Relative amount of heavier fraction

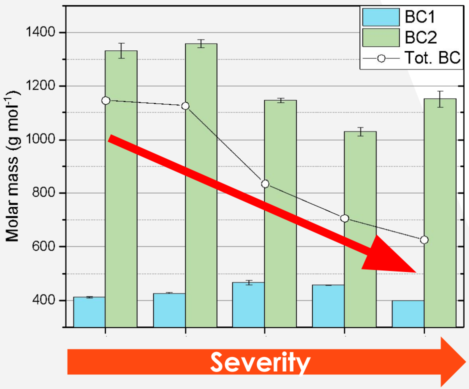


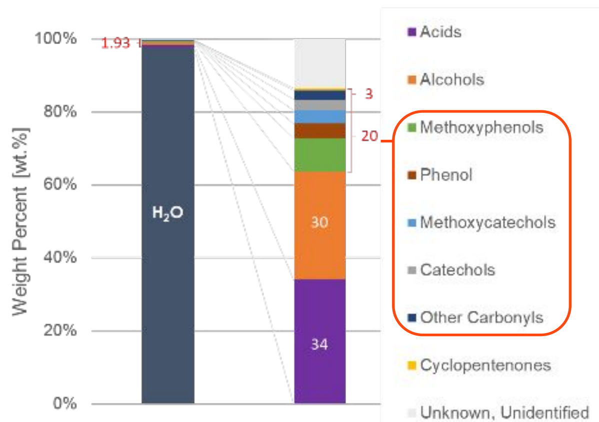
Products characterization


- Elemental analysis
- GC-MS
- GPC
- FT-IR
- ^{1}H NMR

- HPLC
- ICP
- GC-MS
- KF titration
- TOC
- pH

BC1 400 – 470 g mol^{-1} **BC2** 1030 – 1360 g mol^{-1}





- Mainly composed by complex <u>oxygenated aromatic compounds</u>, originating from lignin depolymerization
- Solid below 70 °C

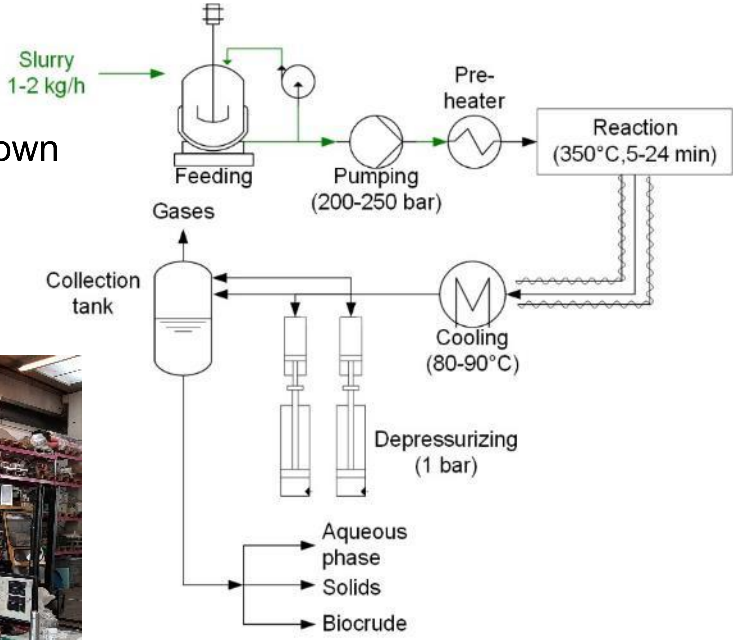
- WSO in aqueous phase mass balance closure □ **83-86 %**
  - S content <u>60 ppm</u>

Continuous experimental campaign

HTL continuous unit

- Up to 2 kg/h
- High pressure piston pump (250 bar)
- Tubular reactor (350°C - 5-20 min)
- Double-piston system for pressure letdown
- Technically challenging

  Solids handling in pumping, heating, filtering, depressurizing, etc.



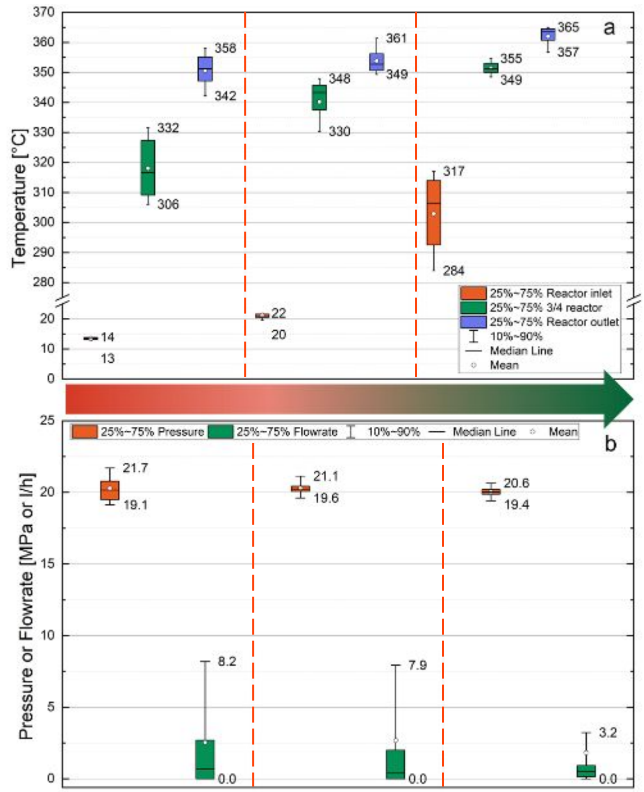
Main challenges in continuous operation

Issues

- Pressure and flow rate oscillation
- Blockage in reactor, cooling and pressure let-down system
- Low residence time and heating rate

Solutions

- Flow rate-driven PID control of backpressure system
- Improving temperature management
- Stepwise heating



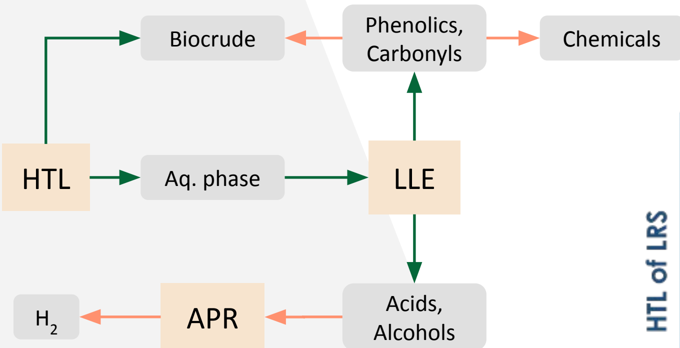
Biocrude characterization

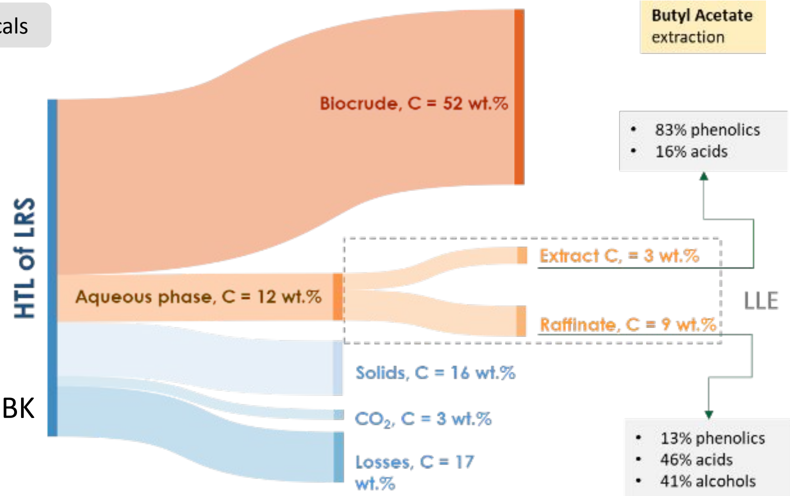
Parameter	Lignin-rich cake	Batch biocrude	Continuous biocrude	U.M.
Water content	69.7	n.d.	5.6	wt% w.b.
Ash	2.6	0.1	0.3	wt% d.b.
HHV	22.9	30.6	29.3	MJ/kg d.b.
C	54.2	72.4	67.9 (0.21)	wt% d.b.
H	5.9	6.3	6.8 (0.23)	wt% d.b.
N	1.0	1.1	1.3 (0.06)	wt% d.b.
S	0.2	0.1	0.2 (0.01)	wt% d.b.
O	36.1	20.0	23.7	wt% d.b.
Mw	n.d.	800	900	g/mol

Abs. std. dev. reported in brackets

Aqueous phase treatment

Aqueous phase treatment





- Liquid-Liquid Extraction (LLE)
  Investigated solvents: DEE, EtAc, BuAc and MIBK
  - Biocrude yield enhancement
  - Bio-based chemicals precursors

    1,2 benzenediol, *1,4-Benzenediol, 2-methoxy-*, *Phenol, 2,6-dimethoxy-*, *Phenol, 2-methoxy-*
  - Expensive, due to the high amount of AP to be treated
- Alternative: cleaning with activated carbon
  - Cheaper than LLE (no solvent make-up, no distillation); Regeneration of spent AC is possible

Conclusion

- Batch experimental campaign
  - T most influencing parameter
  - High biocrude Mw solid below 70°C
  - Phenolics and S in AP hinder APR
- Continuous experimental campaign
  - >11 h time on stream
  - Lower depolymerization than batch, but comparable properties
- Aqueous phase treatment
  - LLE selectively removes phenolics, potential increase of BC yield
  - AC treatment (alternative)

Open access publications

1. Miliotti, E et al., Lignocellulosic Ethanol Biorefinery: Valorization of Lignin-Rich Stream through Hydrothermal Liquefaction. *Energies* **2019**, *12*, 723.

2. Dell'Orco, S. et al., Hydrothermal Depolymerization of Biorefinery Lignin-Rich Streams: Influence of Reaction Conditions and Catalytic Additives on the Organic Monomers Yields in Biocrude and Aqueous Phase. *Energies* **2020**, *13*, 1241.

3. Rizzo A.M. et al., Design, Commissioning and Start-up of a New Hydrothermal Liquefaction Continuous Pilot Unit. Chemical Engineering Transactions, **2020**, 80, 367-372.

4. Di Fraia, et al., Coupling hydrothermal liquefaction and aqueous phase reforming for integrated production of biocrude and renewable H_2. *AIChE J*. **2022**, 1–14.

THANK YOU