Production of biofuel's precursors from HTL of industrial residues

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RE·CORD

Heat-to-Fuel interfaces to advanced Power-to-Gas and Power-to-Liquids Technologies (e-fuels) workshop

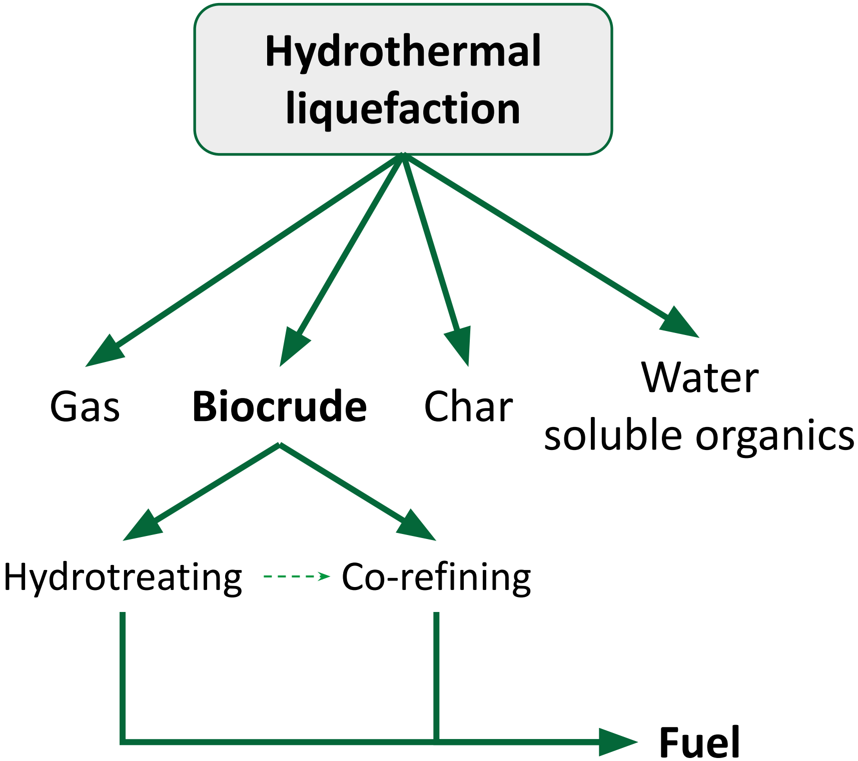
Fuel production session

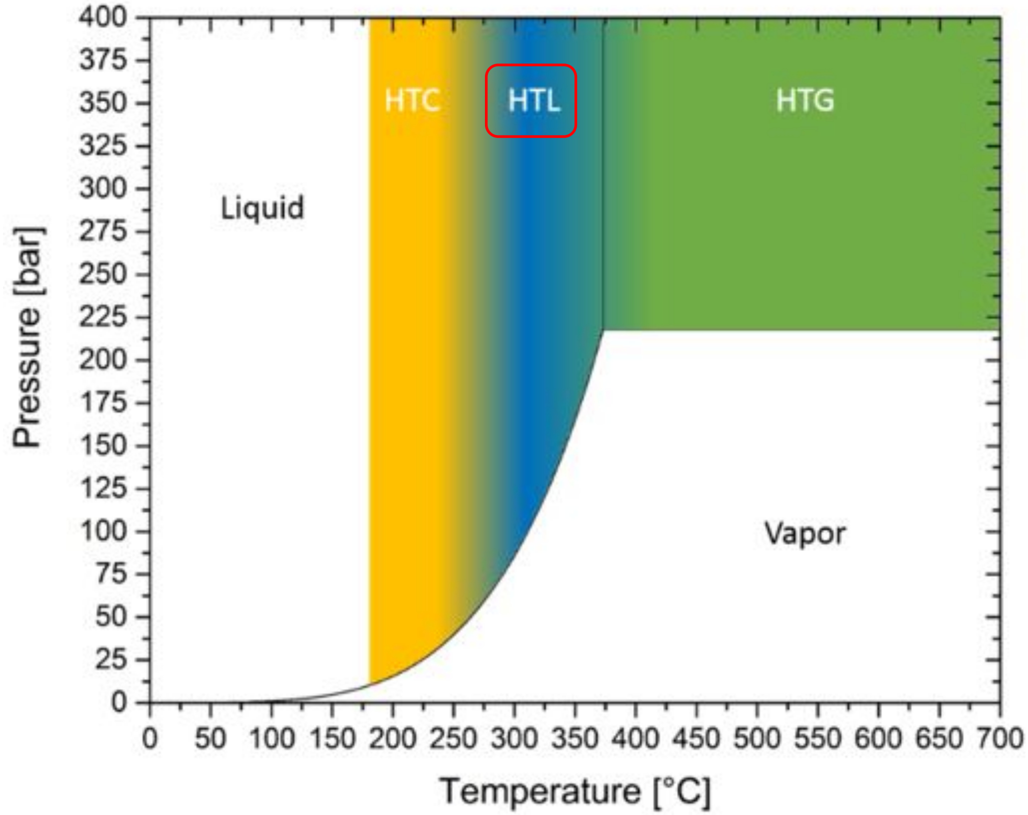
Heat to Fuel

Contents

Hydrothermal liquefaction

- Thermochemical process occurring in sub/supercritical water
- Mimics crude oil formation (high pressure and temperature) in minutes instead of thousands of years
- Reaction medium is water □ indicated to treat wet biomass (algae, sewage sludge, lignin-stream, etc.)

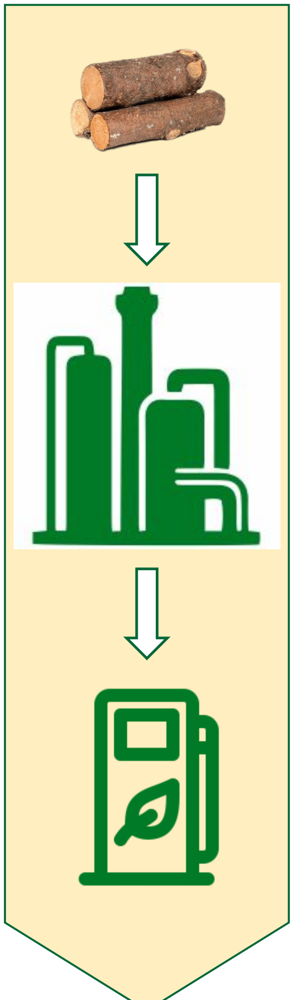




Modified from Peterson et al. Energy Environ. Sci. 1 (2008) 32–65. doi:10.1039/b810100k

Heat to Fuel

Project focus on lignin-rich cake from cellulosic ethanol



Lignocellulosic biomass

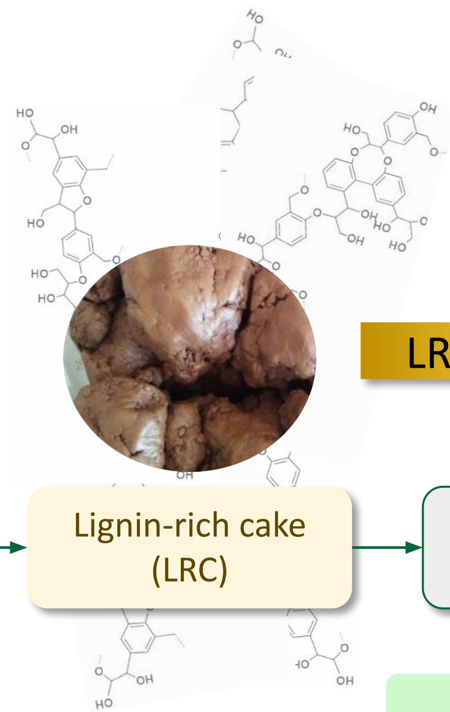
Pretreatment (e.g. steam explosion)

Enzymatic hydrolysis

Fermentation

Ethanol separation

Ethanol



Lignin-rich cake (LRC)

Hydrothermal liquefaction

Biofuel precursor

LRC properties

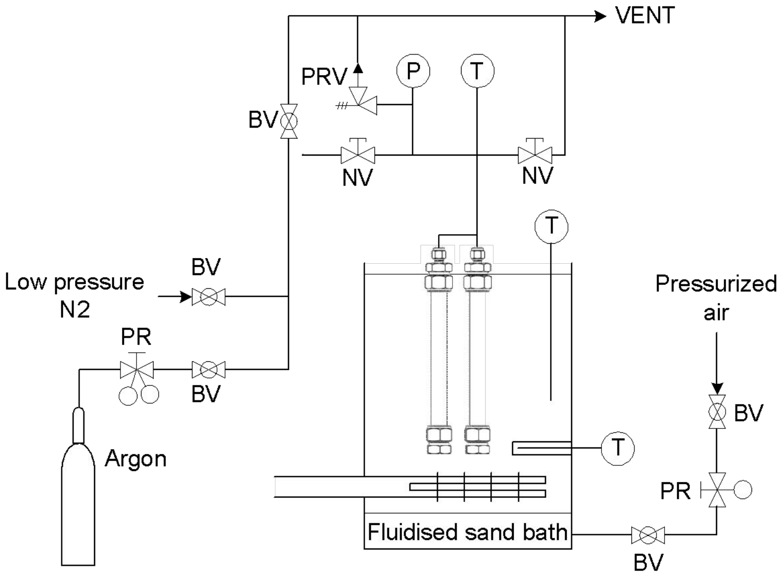
Parameter	Value	Unit
Total lignin	57.8	wt.% daf
Structural sugars	35.5	wt.% daf
Moisture	69.7	wt.% wb
Volatile matter	71.0	wt.% db
Ash	2.6	wt.% db
Fixed carbon	26.4	wt.% db
C	54.2	wt.% db
H	5.9	wt.% db
N	1.0	wt.% db
S	0.2	wt.% db
O	36.1	wt.% db

BATCH EXPERIMENTS

Experimental setup

Custom tubular reactor in hot fluidized sand bed

- Biomass-water ratio: 10-20 wt% (d.b.)
- Reaction temperatures: 300 – 370°C
- Residence time: 5-20 min
- Heating rate: 37 – 41°C min^{-1}



BV: ball valve; NV: needle valve;
PR: pressure regulator; PRV: pressure relief valve

- Two-step solvent extraction:
  - Light and heavy biocrude fraction

Biocrude yield

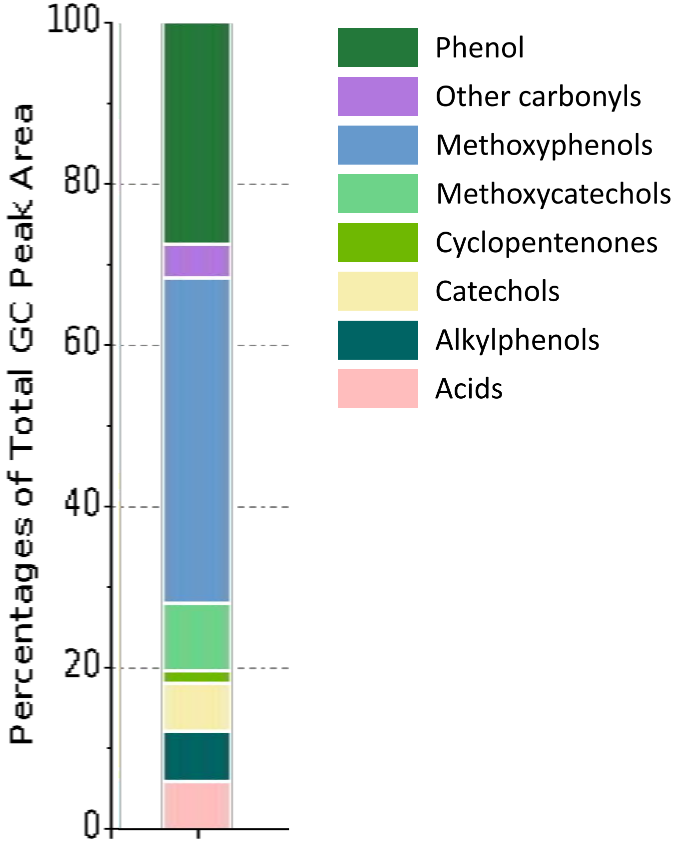
- **Total biocrude** yield from **44.1** to **65.7** wt% (d.b.)
- Light fraction (BC1) increased with severity
- Heavy fraction decreased
- Temperature depolymerization enhanced by KOH:

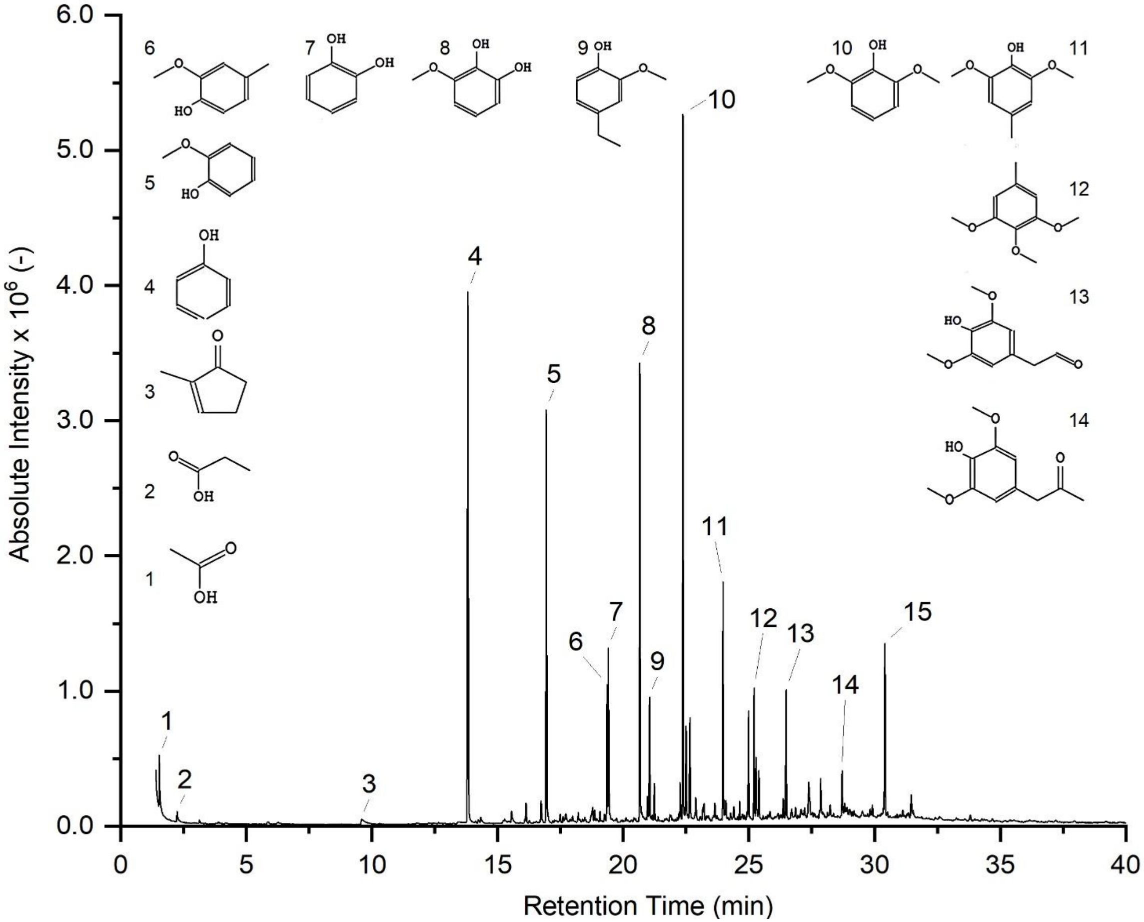
↑ Relative abundance of lighter fraction
↓ Relative amount of heavier fraction

Biocrude characterization

Chromatogram of a typical light biocrude

- Mainly oxygenated aromatics
- Only **20 wt%** of the light fraction can be analyzed via GC-MS, the remaining fraction is constituted by lignin oligomers



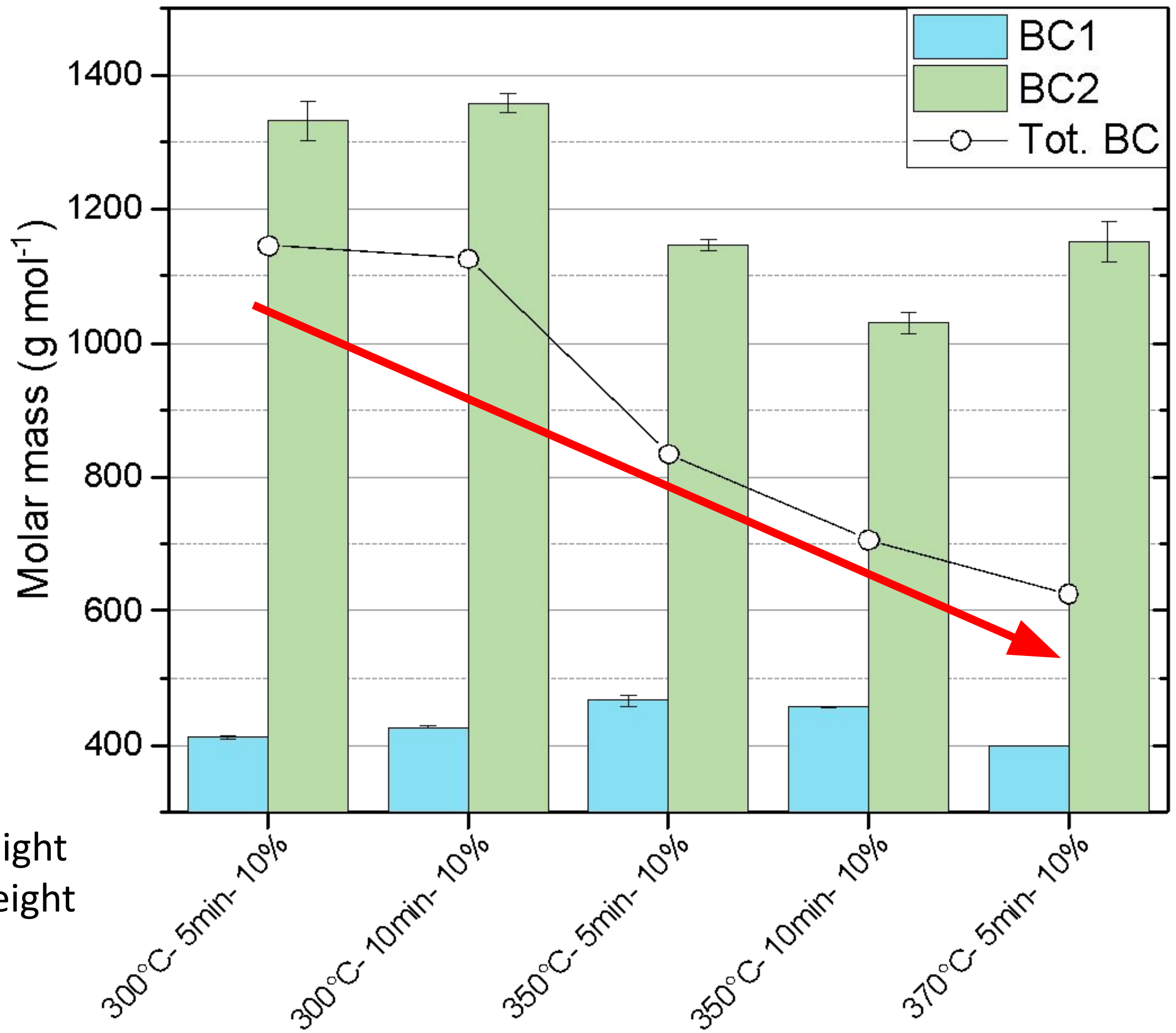


Biocrude characterization

Molecular weight

- Confirmed temperature depolymerization effect

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



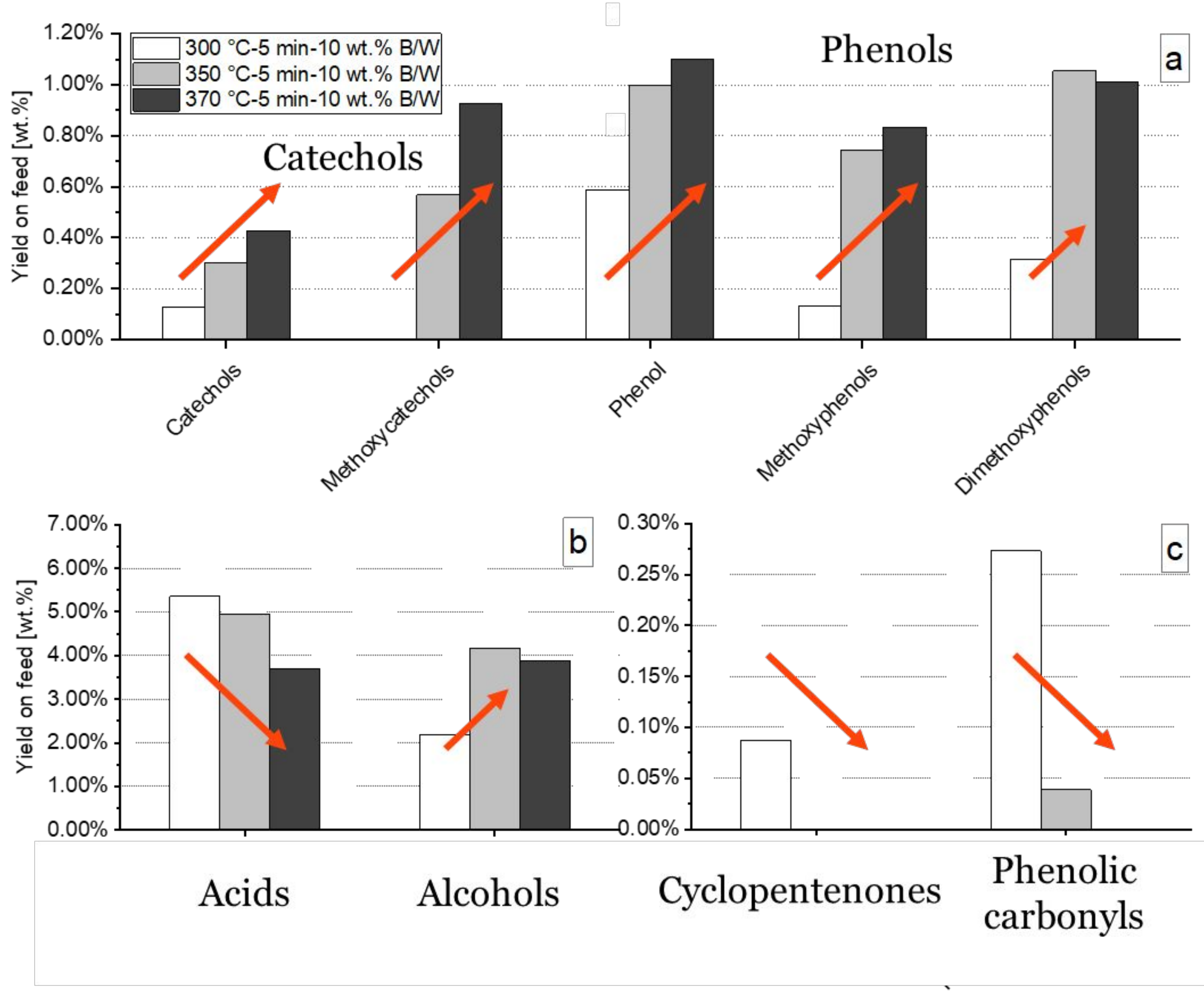
- M_W = Weight-average molecular weight
- M_n = Number-average molecular weight
- PDI = Polydispersity index, M_W / M_n

Reaction mechanism

Influence of Temperature on monomers yield in **biocrude** and **aqueous phase**

Main influencing parameter

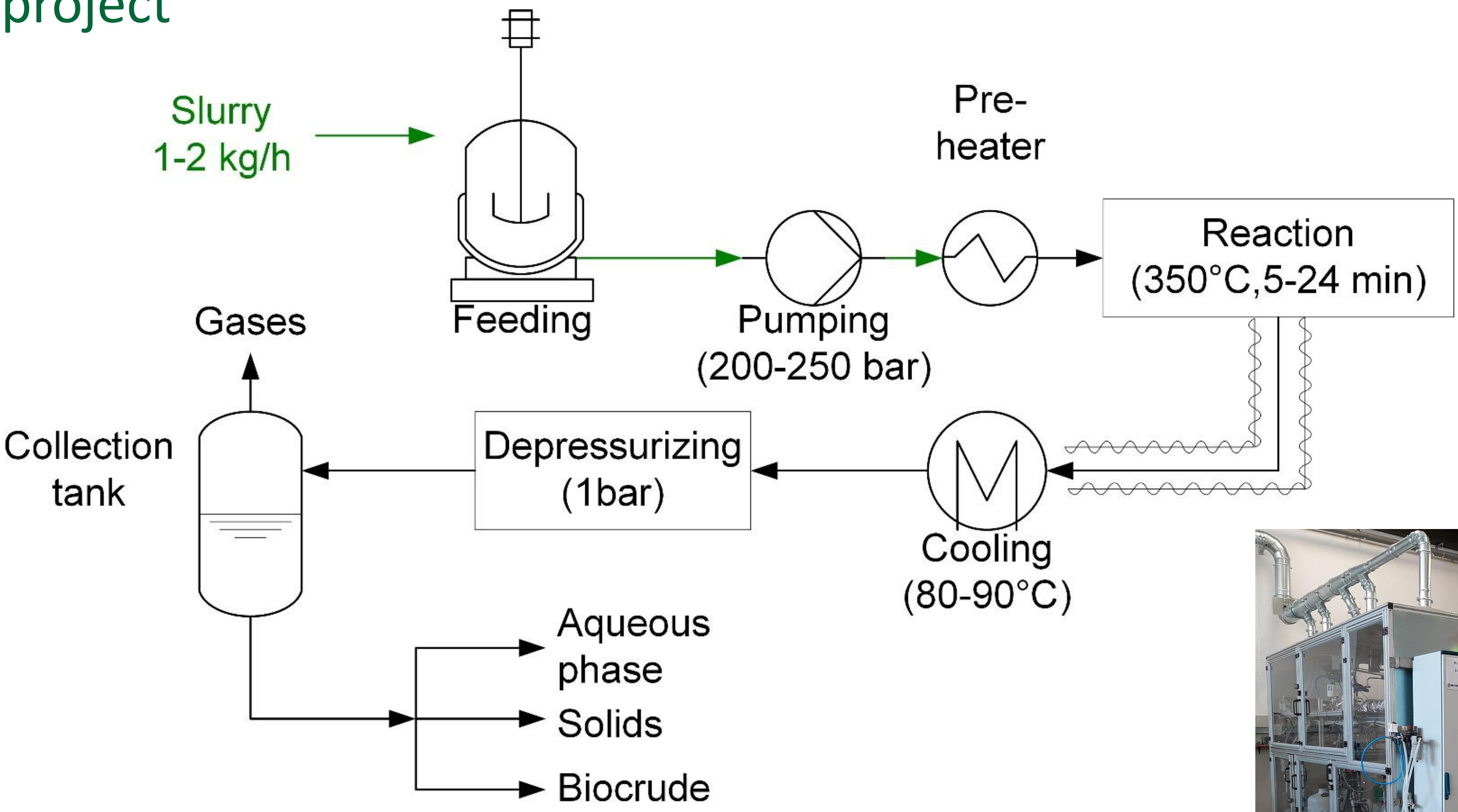
- **Increase of aromatic monomers**
- **Depolymerization** confirmed by **methanol** increase via **demethylation/demethoxylation** of the methoxyaromatic compounds
- **Cracking of acids** (lactic)
- High reactivity of carbonyls and cyclopentenones (c)



CONTINUOUS EXPERIMENTS

Experimental setup

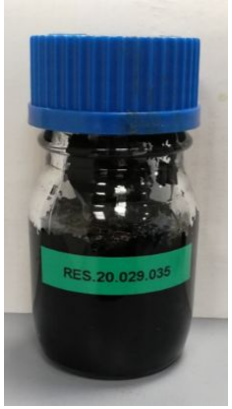
Continuous pilot unit designed and operated within the Heat to Fuel project



Experimental campaign

Continuous experiments with lignin from cellulosic ethanol

- with Na_2CO_3 as alkaline additive
- with NaOH as alkaline additive
- without additive
    - Better performances with NaOH in terms of plant operability



Total processing time: 18 h

Main challenges in continuous operation

- Presence of solids (biomass) in the process stream:
  - Equipment with small orifices (e.g. pump and valves) must be avoided
  - Risk of settling Plugging. A suitable velocity must be maintained
  - Alkaline additives (Na or K carbonates or hydroxides) can help to form a stable slurry with lignocellulosic feedstock

- High pressure (> 200 bar) and moderately high temperature (> 300°C) and presence of chemicals (biocrude, water-soluble organics, alkaline solution):
  - Special materials for tubing and gaskets

- Lignin fragments polymerize during heating:
  - Rapid heating rate is required to avoid blockage

- Biocrude (from lignin) is solid below 70-80°C:
  - The pipeline after the cooler must be heat-traced

- These issues are worsened in lab-scale plants due to the small size

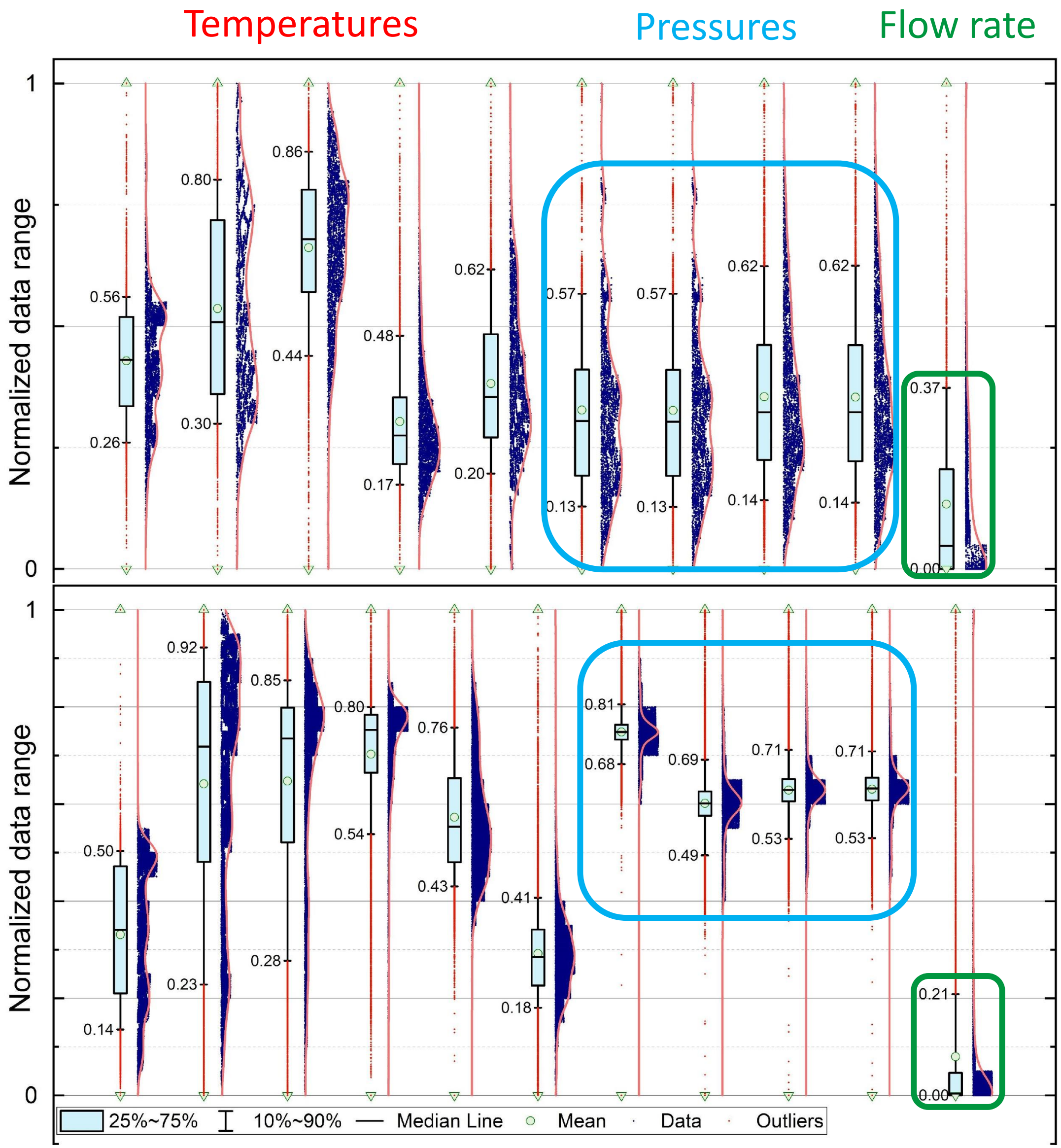
Main challenges in continuous operation

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 valve
- Improving temperature management
- Stepwise heating



Biocrude characterization

- Relatively low water content
- Low ash
- Good higher heating value
- High O_2 content
- High molecular weight
- Solid at ambient temperature

Upgrading needed

Parameter	Continuous	U.M.
Water content	1.2	wt% w.b.
Ash	0.1	wt% d.b.
HHV	30.3	MJ/kg d.b.
C	69.3	wt% d.b.
H	6.8	wt% d.b.
N	0.9	wt% d.b.
S	0.2	wt% d.b.
O	21.6	wt% d.b.
Mw	900	g mol^{-1}

Conclusion

- Hydrothermal liquefaction is a technology indicated to process wet biomass
- Lignin cake from cellulosic ethanol produces a high molecular weight biocrude rich in aromatics
- Harsh process conditions and presence of dispersed solids challenge lab-scale continuous operation
- Further hydrotreatment or co-refining is needed to obtain a transport fuel