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Advanced Biomass Catalytic Conversion

A highly efficient conversion of Kraft lignin to middle distillates by a catalytic hydro-pyrolysis/ hydrotreatment approach

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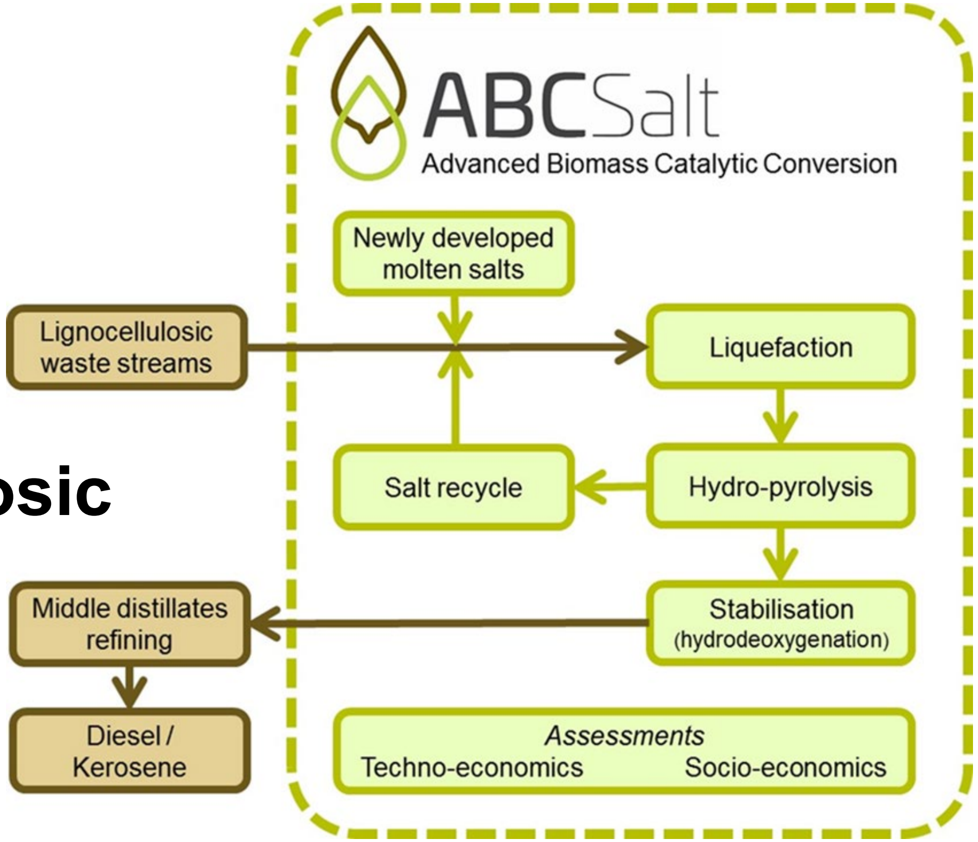
- Introduction
- An integrated concept from lignin to hydrocarbons
  - Catalytic hydropyrolysis of lignin
  - Catalytic hydrotreatment of the intermediate lignin oil
  - Integration
- Conclusions
- Acknowledgment

ABC-Salt project

- **Advanced Biomass Catalytic Conversion to Middle Distillates in Molten Salts** (ABC-Salt)
- A four-year project funded by EU Horizon 2020 to demonstrate a **novel route** to produce **sustainable liquid biofuels** at laboratory scale from **various lignocellulosic waste streams**
- Consortium of **nine** European partners

ABC-Salt concept



Objective and concept

- Demonstrate a **novel route** to produce **sustainable liquid biofuels** from various cheap **lignocellulosic waste streams** for the transportation industry targeting a yield over 35 wt.% to hydrocarbons with 2/3 in the middle distillates range.

- **Concept** – Technical Core.

BIOMASS →(1) Liquefaction in Molten Salts →(2) (Catalytic) Hydro-Pyrolysis →(3) (Catalytic) Hydro-Deoxygenation

Step 1: Biomass dissolution in molten salt media at ambient pressure and low temperature

Step 2: Biomass vaporisation at elevated pressure (H_2) and temperature

Step 3: Vapour-phase hydro-deoxygenation to produce middle distillates

Biomass to Middle Distillates via Thermochemical Conversion

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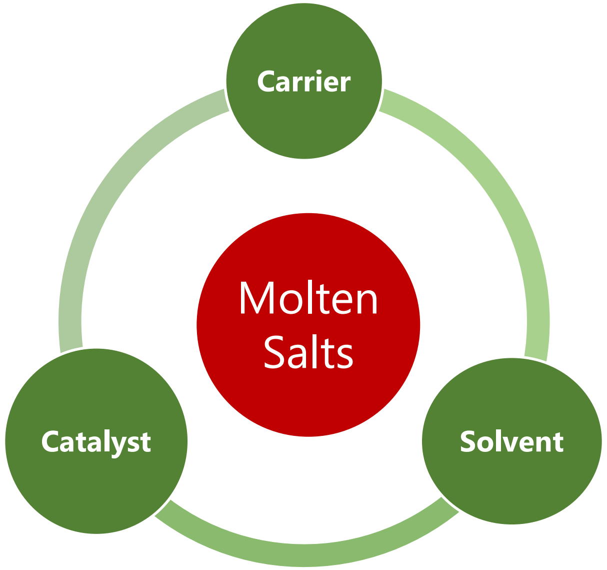
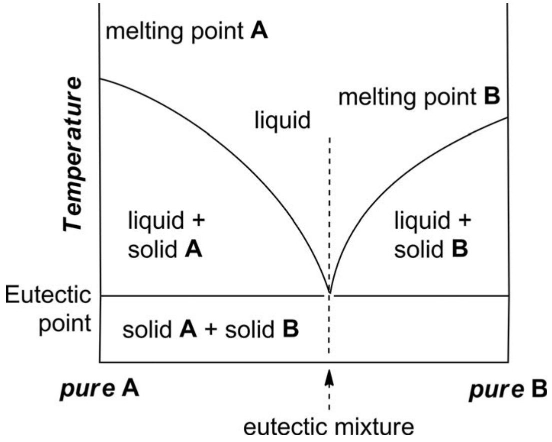
- **Integrated hydro-pyrolysis/catalytic hydro-treatment (IH2®)**
  - Developed by Gas Technology Institute
  - 15-35 bar H_2, 340-470 ^oC, 370-400 ^oC
  - 25-28% liquid yields, 2/3 gasoline and 1/3 in the MD range
- **Catalytic pyrolysis followed by catalytic hydro-treatment**
  - Scaled-up by KiOR: Khosla Ventures and BIOeCON
  - 10 wt.% yield, most in the gasoline range
- **Fast pyrolysis followed by a catalytic liquid-phase hydro-deoxygenation**
  - BTG and PNNL
  - 24-30% yield; 2/3 in MD range

https://www.osti.gov/scitech/biblio/1059031/
Environ. Prog. Sustainable Energy **2012**, *31*, 191

What are Molten Salts?

- Solid at STP but melt at elevated temperatures
- Baths for alloy heat treatments, heat transfer fluids, thermal storage etc.
- Eutectic salt mixtures of chlorides, fluorides, hydroxides, carbonates, nitrates – e.g.: $NaNO_3$:KNO_3 (60:40) and $ZnCl_2$:KCl (70:30): ~260 ^oC





Lovering, D. G. *Molten Salt Technology;* Plenum Press: New York, **1982**
J. Sol. Energy Eng. **2004**, 126, 850-857

Why Molten Salts?

Major issues
in (Hydro)-pyrolysis

1. Feeding of solid biomass to a pressurized reactor especially for lignin-rich feeds.
2. Requirement for rapid heating of biomass particles to optimise vapour yield and minimize char and gas formation.

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1. Ensure pumping of molten salts with the liquefied biomass.
2. Prepare of solubilized biomass source with excellent heat transfer medium.
3. Dilution of the reactive compound

Set-up for hydropyrolysis

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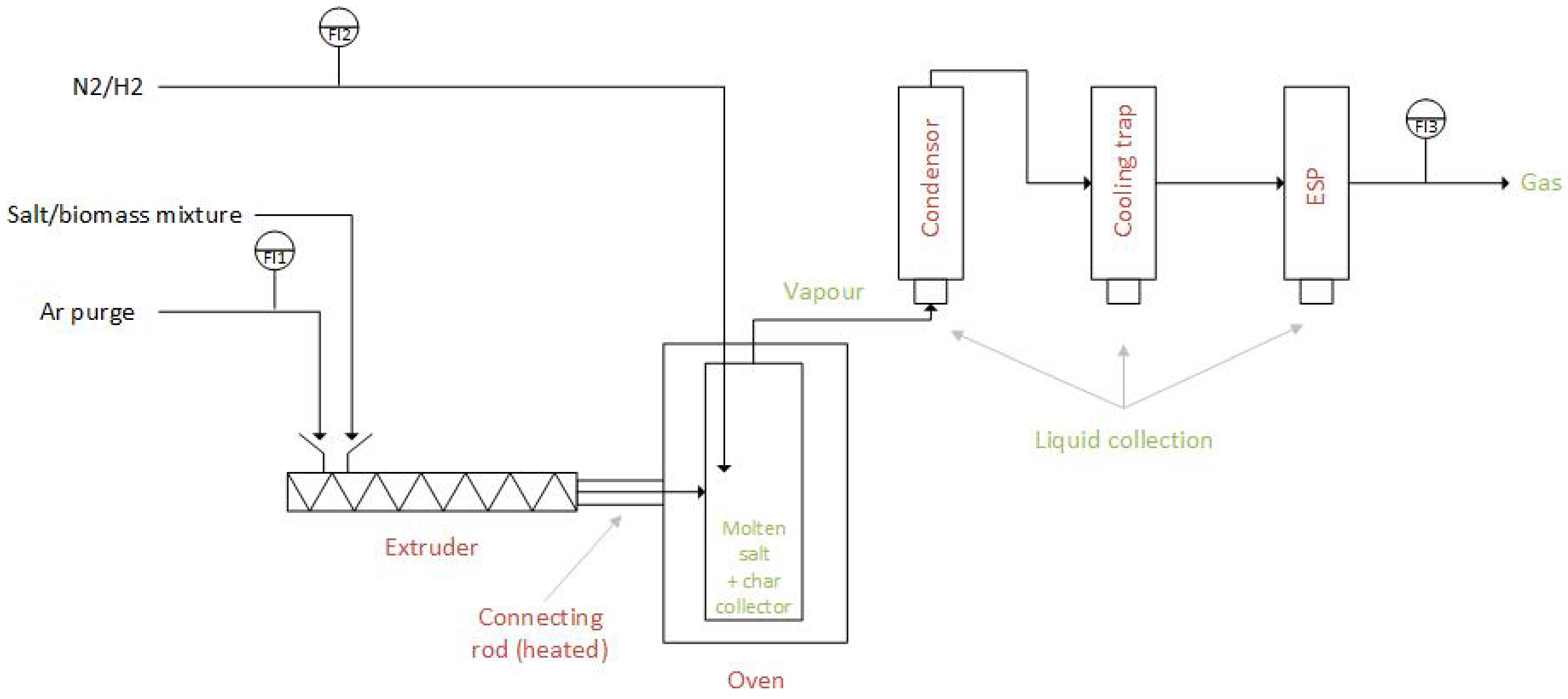
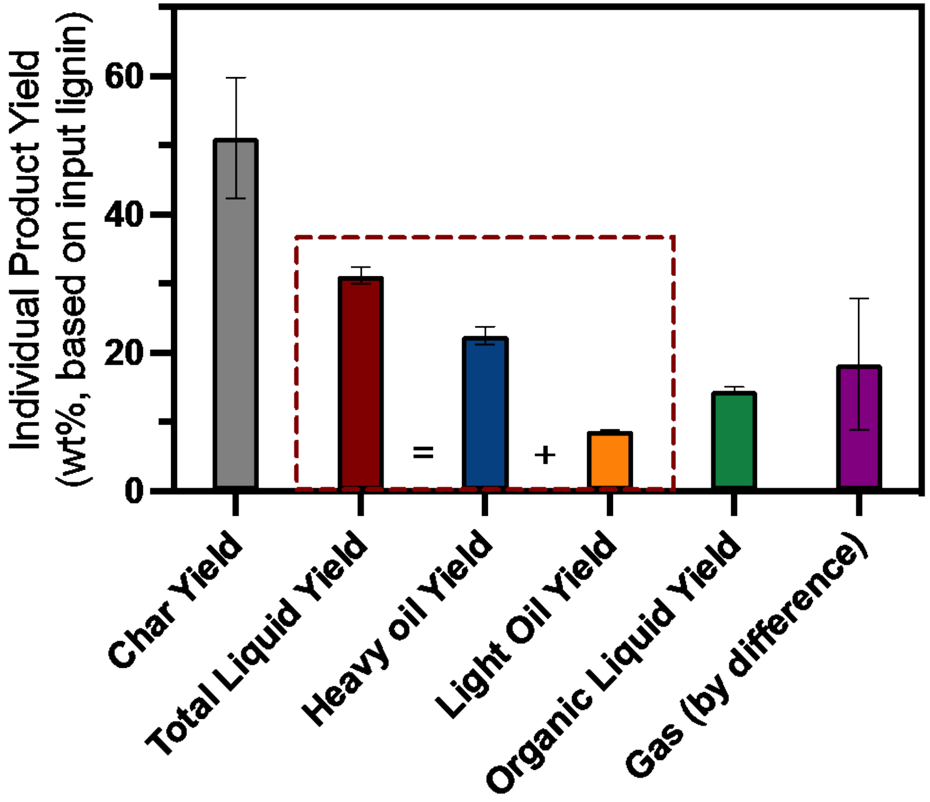


pyrolysis temperature of 375 °C, salt to lignin ratio of 1:5, rotational speed 80 rpm and a gas flow rate of 500 mL/min

Results hydropyrolysis



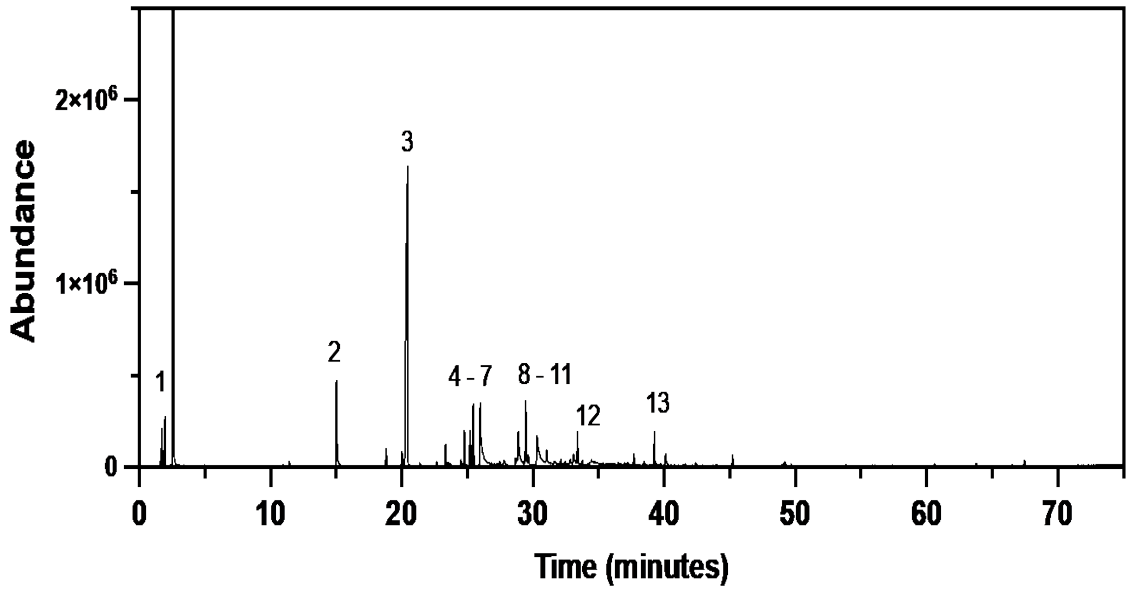
Significant amounts of char

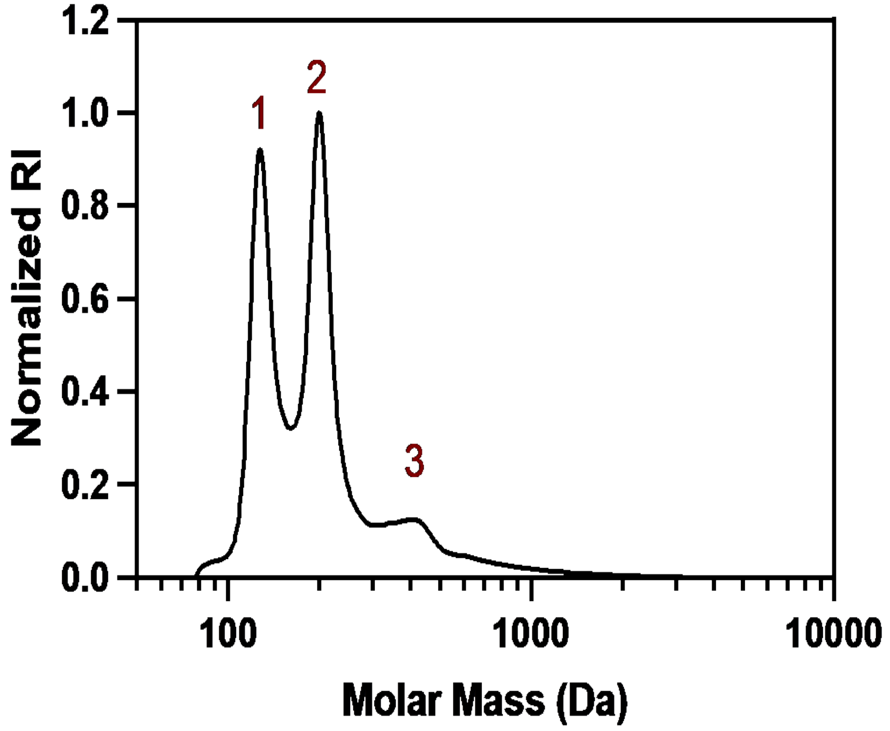
Limited amount of organics in the liquid

- Lignin derived (heavy)
- Propylene (light)

pyrolysis temperature of 375 °C, salt to lignin ratio of 1:5, rotational speed 80 rpm and a gas flow rate of 500 mL/min

Hydropyrolyis: composition heavy phase

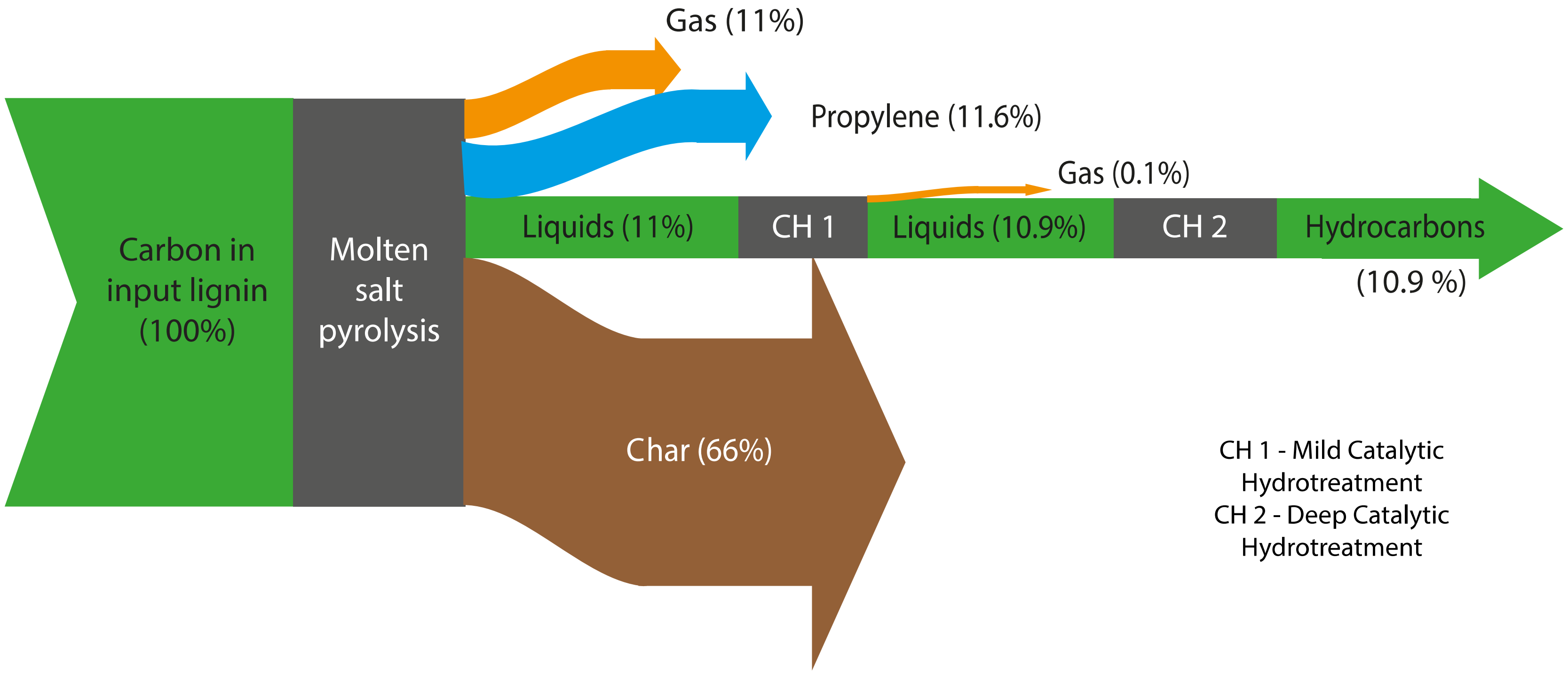




Mainly low molecular weight alkyl phenolics, loss of -OMe groups

Results

- Low yields in the hydropyrolysis step for lignin



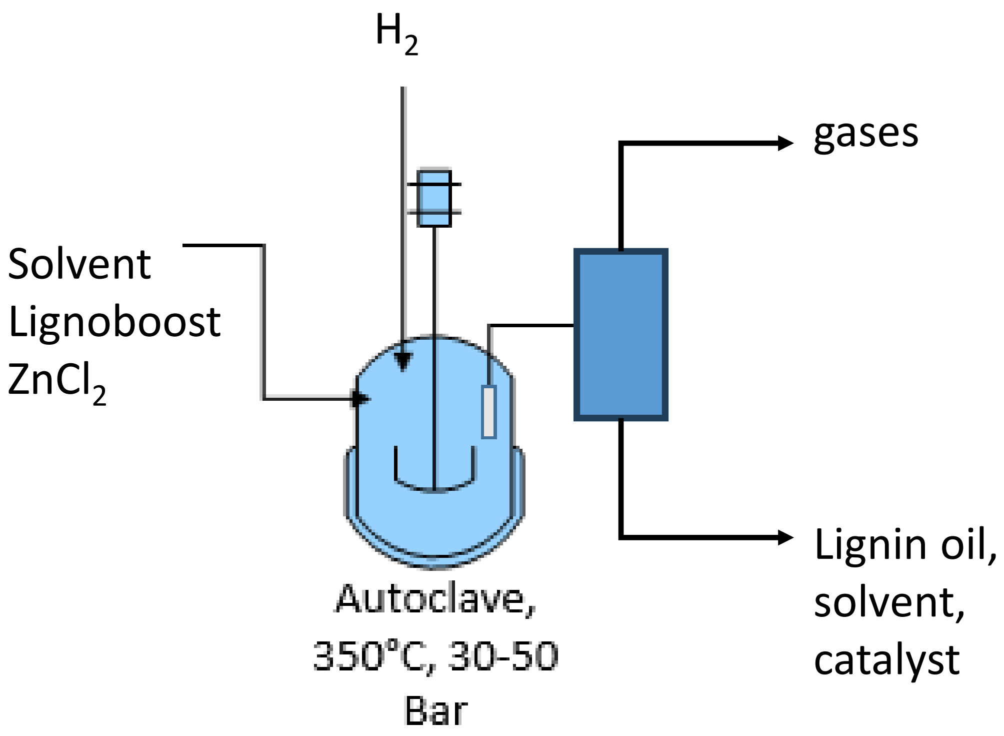
CH 1 - Mild Catalytic Hydrotreatment
CH 2 - Deep Catalytic Hydrotreatment

How to improve?

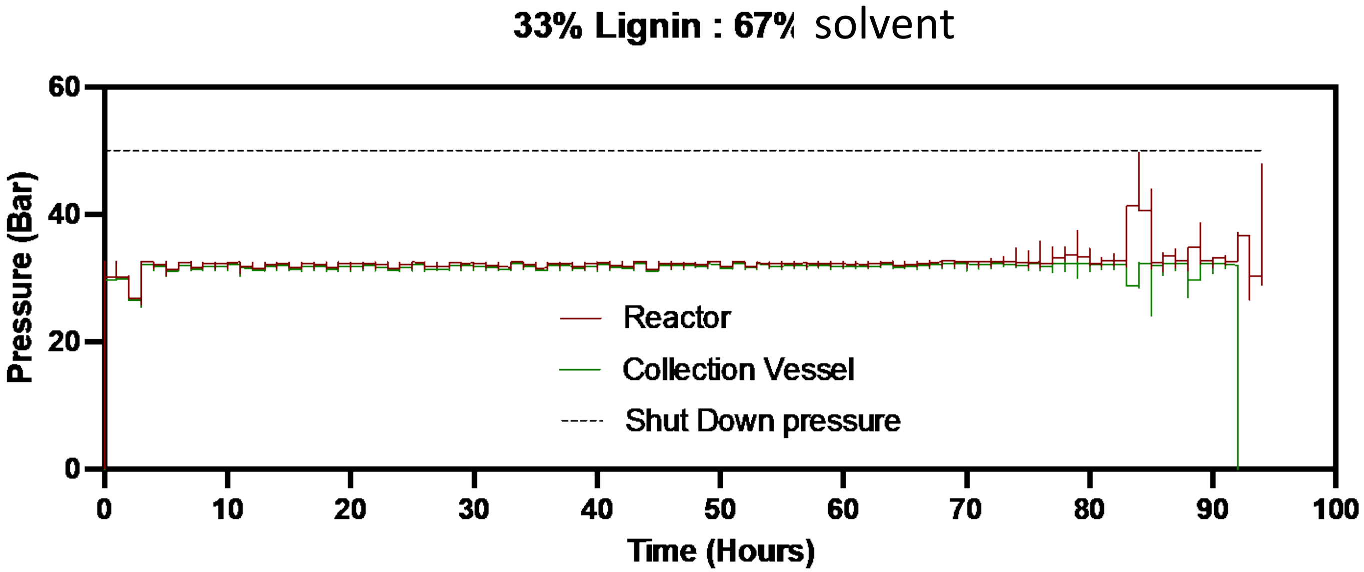
- Hydropyrolysis step
  - Use of an organic solvent[1] to dissolve the lignin / reduce concentration reactive component (in addition to a stirred tank approach)
  - Substantially reduce the amounts of the salts
- Hydrotreatment step: no major changes
- Demonstrated at continuous scale for 100 h with lignin input of ≈30 g/h

[1]organic solvent – recycle stream from process

Hydropyrolysis set-up

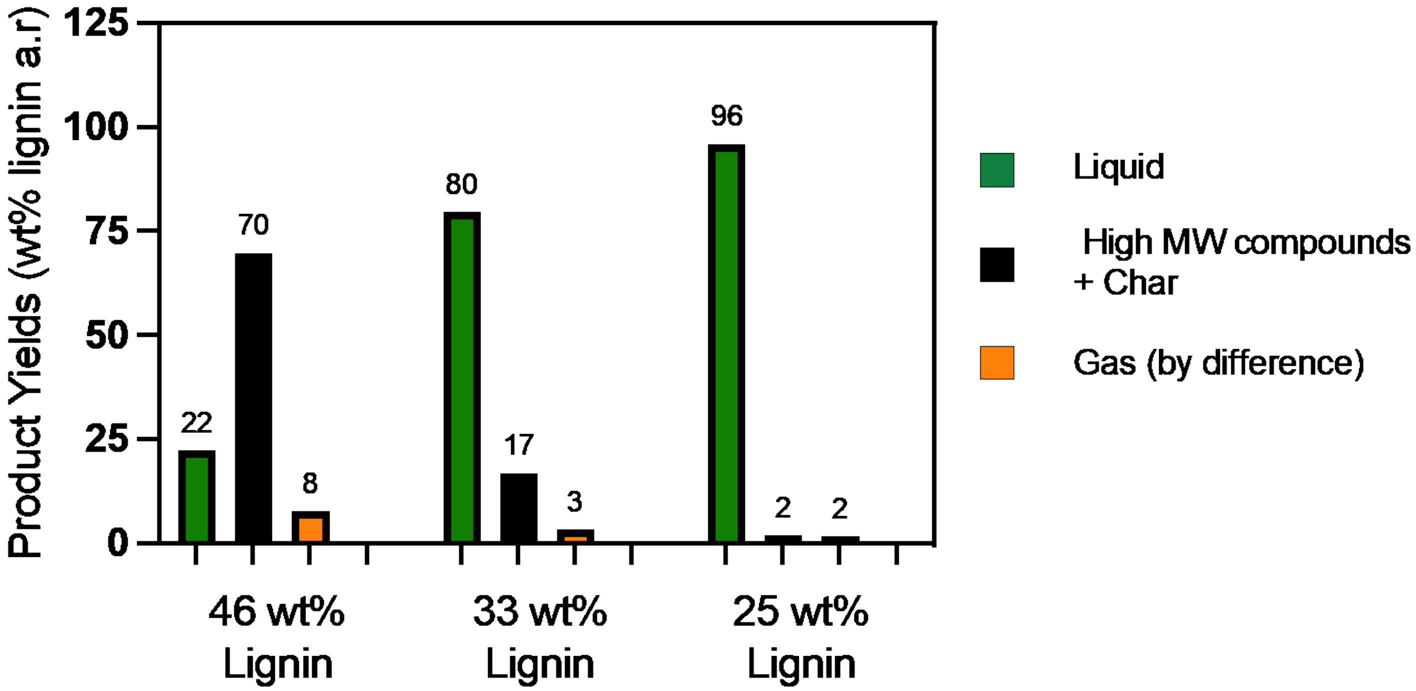


Results: Hydropyrolysis



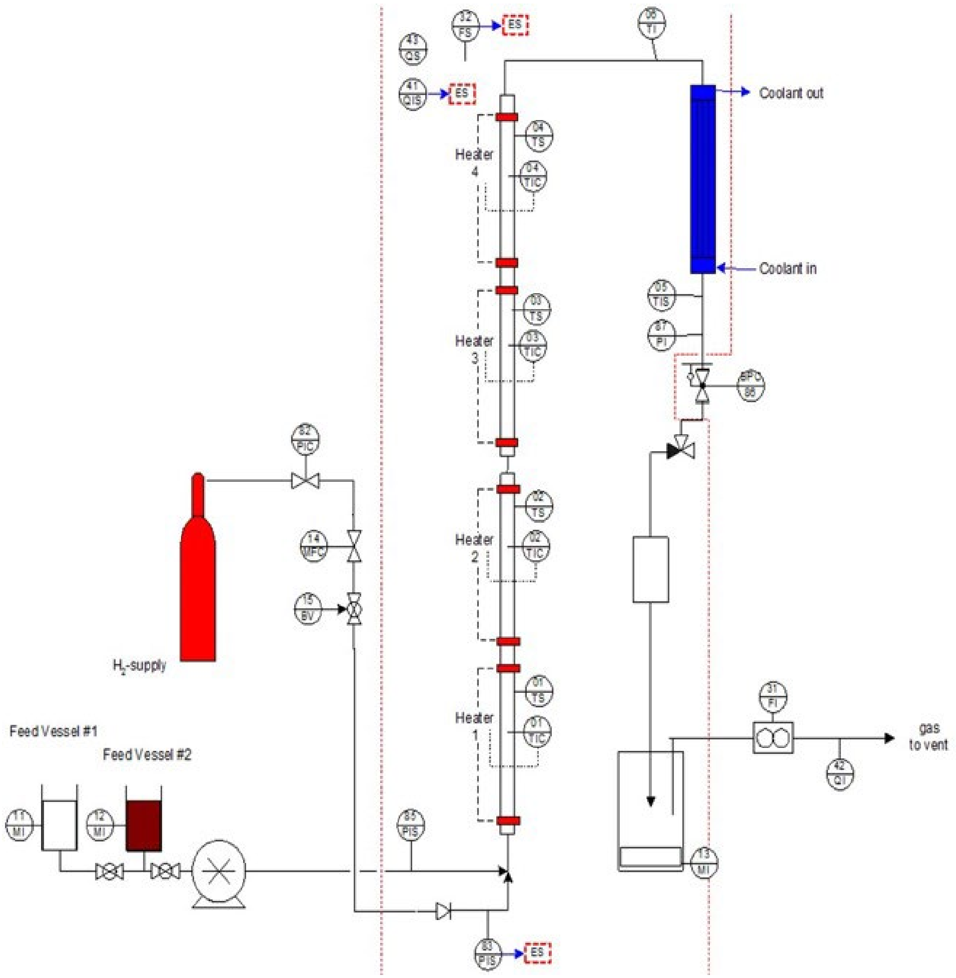
- 33% Lignin mixture showed good operability -> successful 80$^+$ h run
- The experiment stopped due to blockage in the delivery line (after the reactor)

Results: Hydropyrolysis Mass Balances



- Product yields of continuous hydropyrolysis experiments at different feed composition
- Mass balances of all experiments high (> 95%)
- Liquid yield promoted by dilution
- Higher Mw fragments and char reduced significantly with dilution

Catalytic hydrotreatment set-up



Reactors

Valve train

Feed

Products

Pump

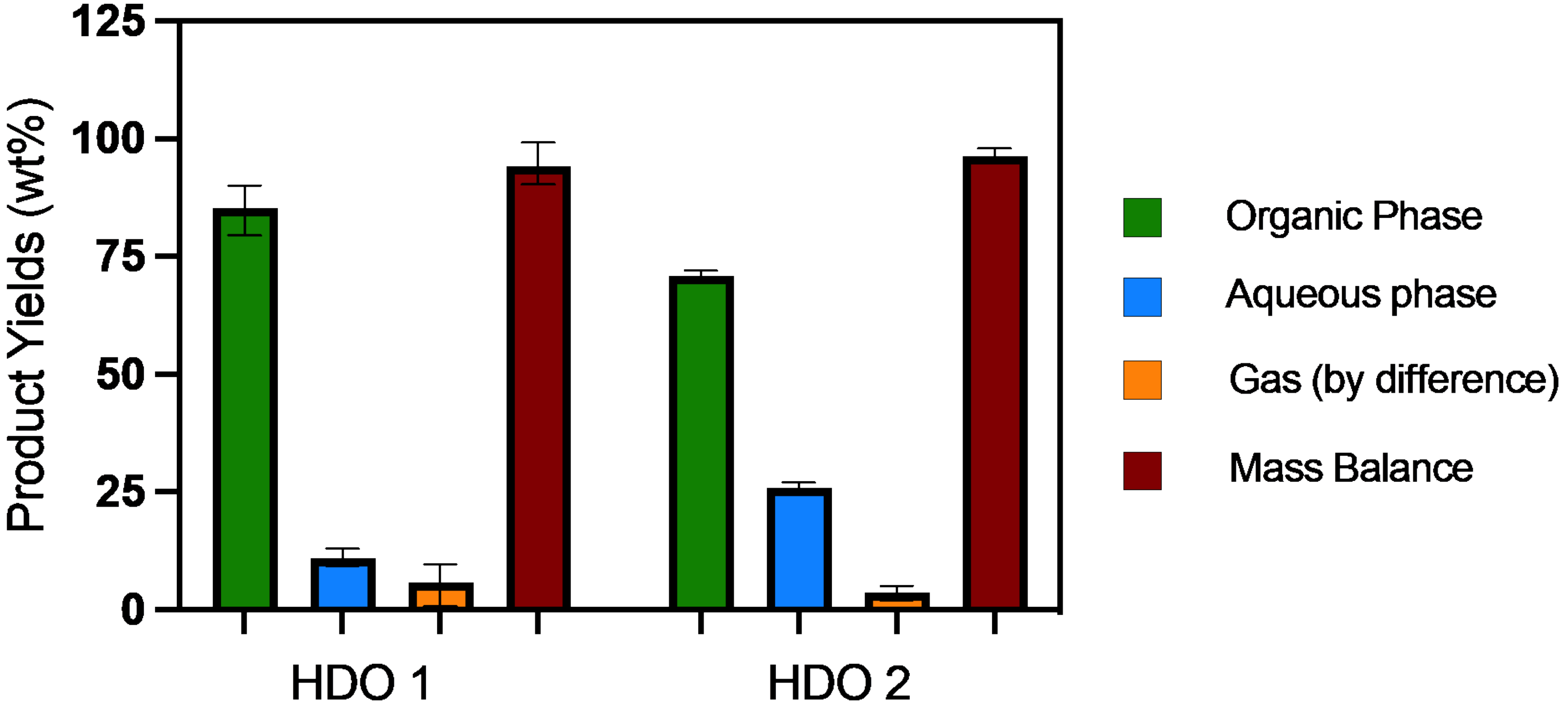
Catalytic Hydrotreatment

- Process conditions:

- Hydrotreatment 1:
  - Temperature: 250 – 250 – 275 – 275 °C
  - Pressure: 120 bar H_2
  - Feed rate: ≈ 60 g/h
  - Catalyst: presulfided $NiMo/Al_2O_3$
  - H_2 : 300 mL/min

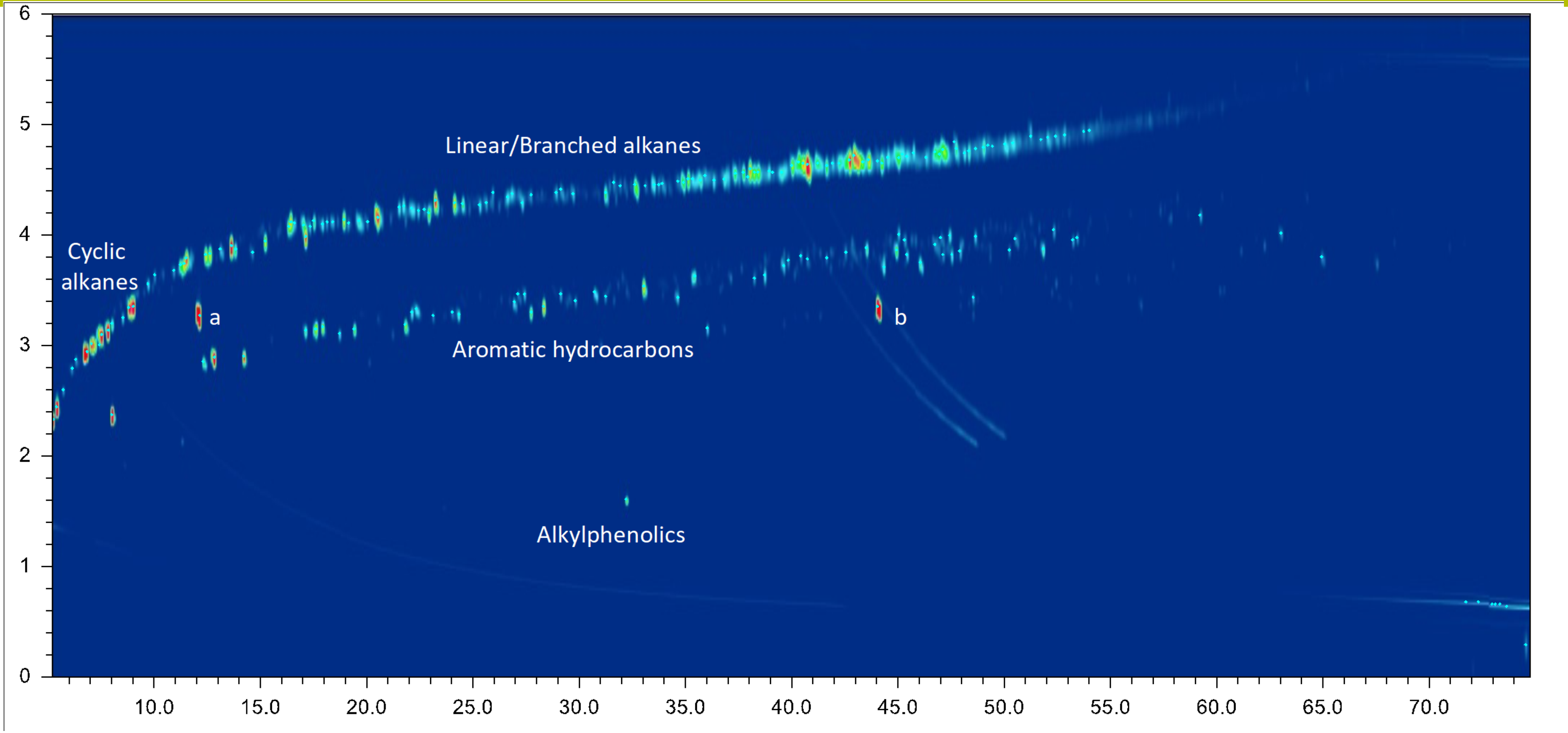
- Hydrotreatment 2
  - Temperature: 320 – 350 – 375 – 380 °C
  - Pressure: 150 bar H_2
  - Feed rate: 40 g/h
  - Catalyst: presulfided $NiMo/Al_2O_3$
  - H_2 : 1000 mL/min

Results: Catalytic Hydrotreatment



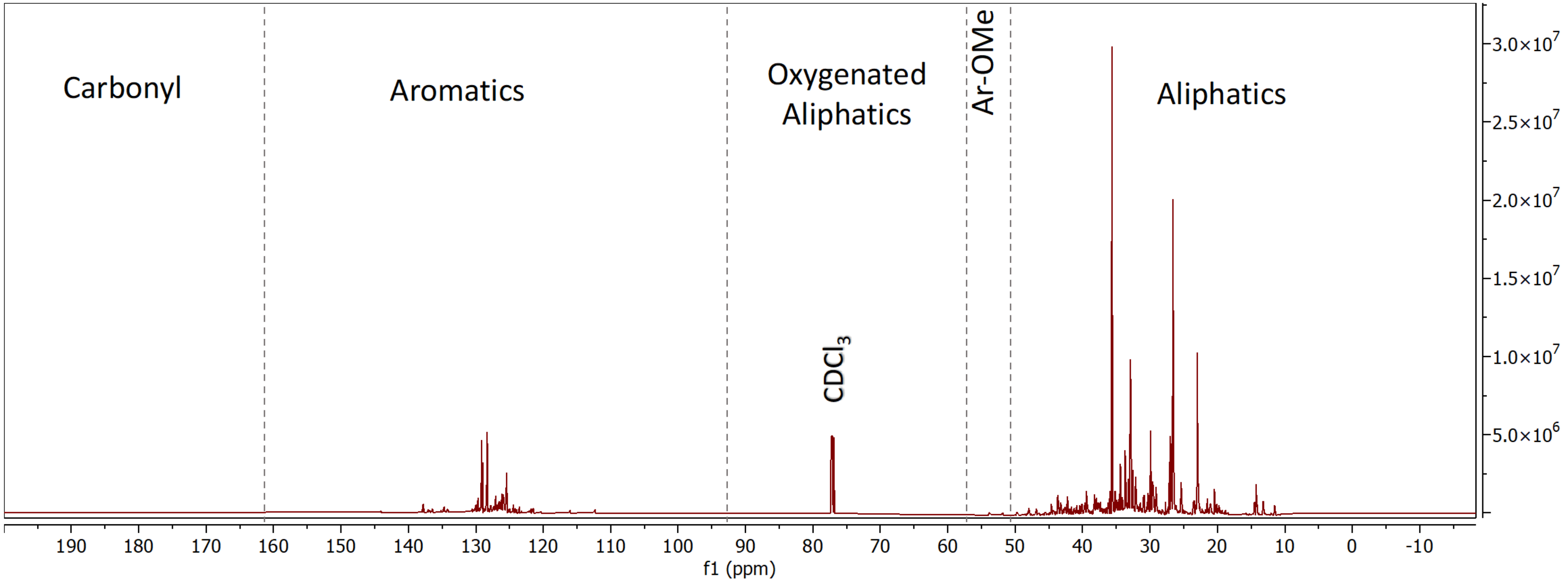
- Run > 100 h
- High liquid yield
- No char, some gas phase
- Water formed during reaction
- 97% C yield in each HDO step

Final hydrotreated product after solvent removal

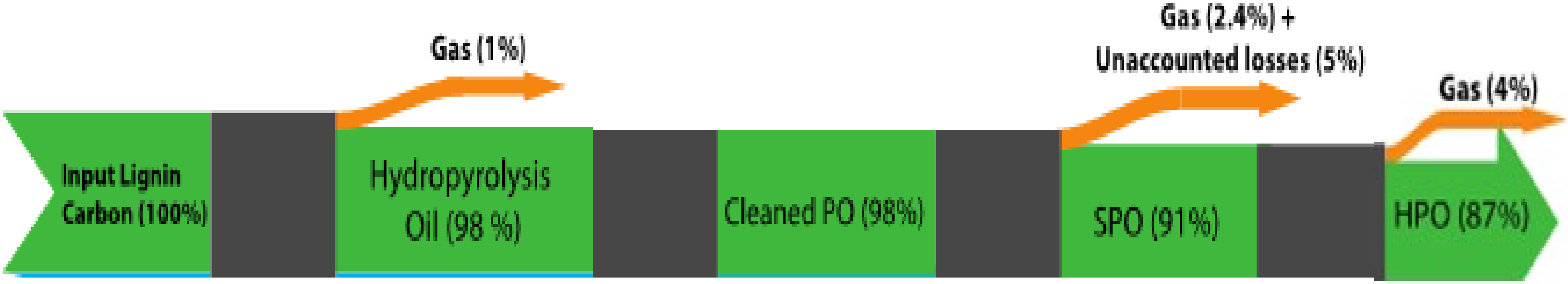


Oxygen content < 0.5 wt%

Final hydrotreated product after solvent removal

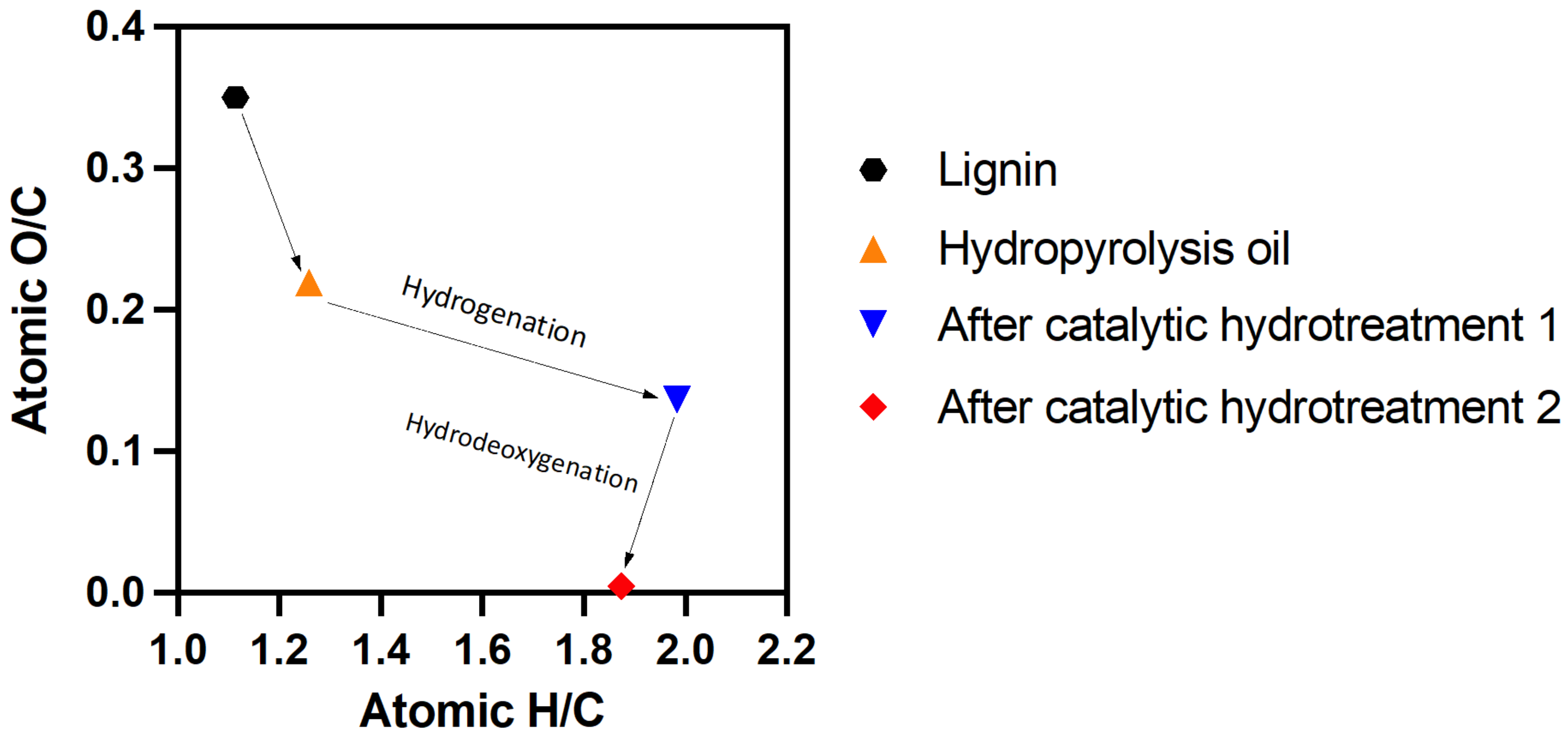


Carbon Sankey plot for the integrated concept



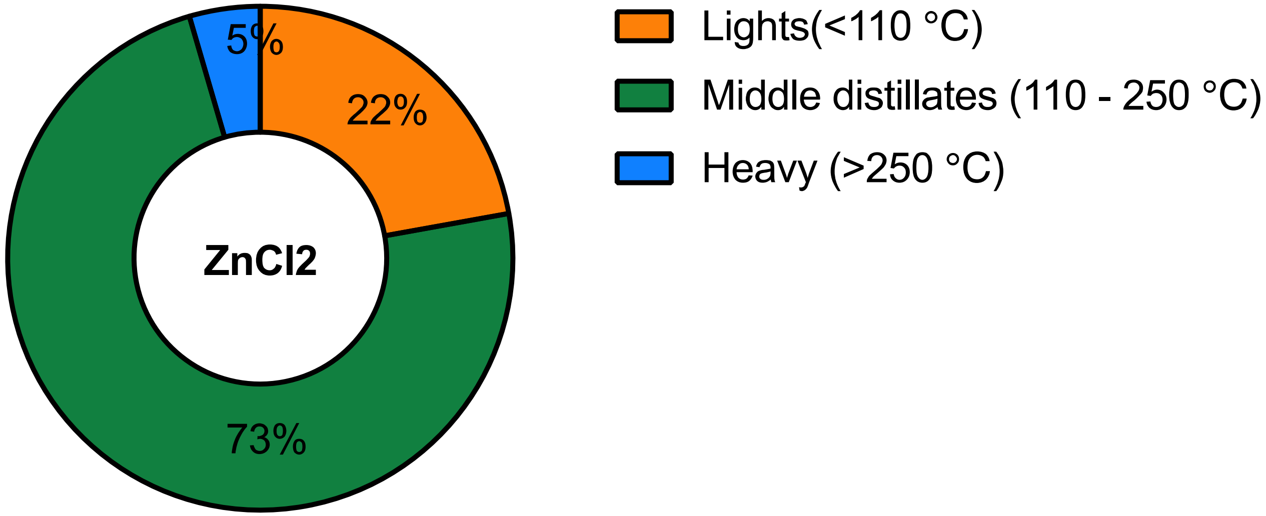
*Recycle stream not included in the diagram

Van Krevelen plot for the integrated concept



Distillation of final product

Fractional yields (wt%)



Conclusions

- A highly efficient catalytic pyrolysis/hydrotreatment approach has been develoepd to convert lignoboost lignin to hydrocarbons – *no optimisation done*

- Overall carbon yield close to 90% (60 wt%; comfort level)

- Key is high yields in the hydropyrolysis step by
  - cheap catalyst
  - solvent (in siru prepared)
  - use of a stirred tank reactor (ensuring high conversion)

- Concept demonstrated for 100^{+} h at a scale of 25-30 g/h lignin input

Thesis

Balaji Sridharan

Catalytic Conversion of Lignocellulosic Biomass to Biofuels and Bio-based Chemicals using Molten Salts

23 April 2024

Acknowledgements

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university of groningen

Aston University Birmingham

btg biomass technology group

DLR Deutsches Zentrum für Luft- und Raumfahrt German Aerospace Center

RI. SE

GHENT UNIVERSITY

benkei strategy • innovation • development

NMBU Norwegian University of Life Sciences

SAPIENZA UNIVERSITÀ DI ROMA

ABC-Salt

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HORIZON 2020

ec.europa.eu/inea/en/horizon-2020/projects/h2020-energy/biomass-biofuels-alternative-fuels/abc-salt

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