ABCSalt
Advanced Biomass Catalytic Conversion

Advanced Biomass Catalytic Conversion to Middle Distillates in Molten Salts

Prof. Erik Heeres (Project Co-ordinator)

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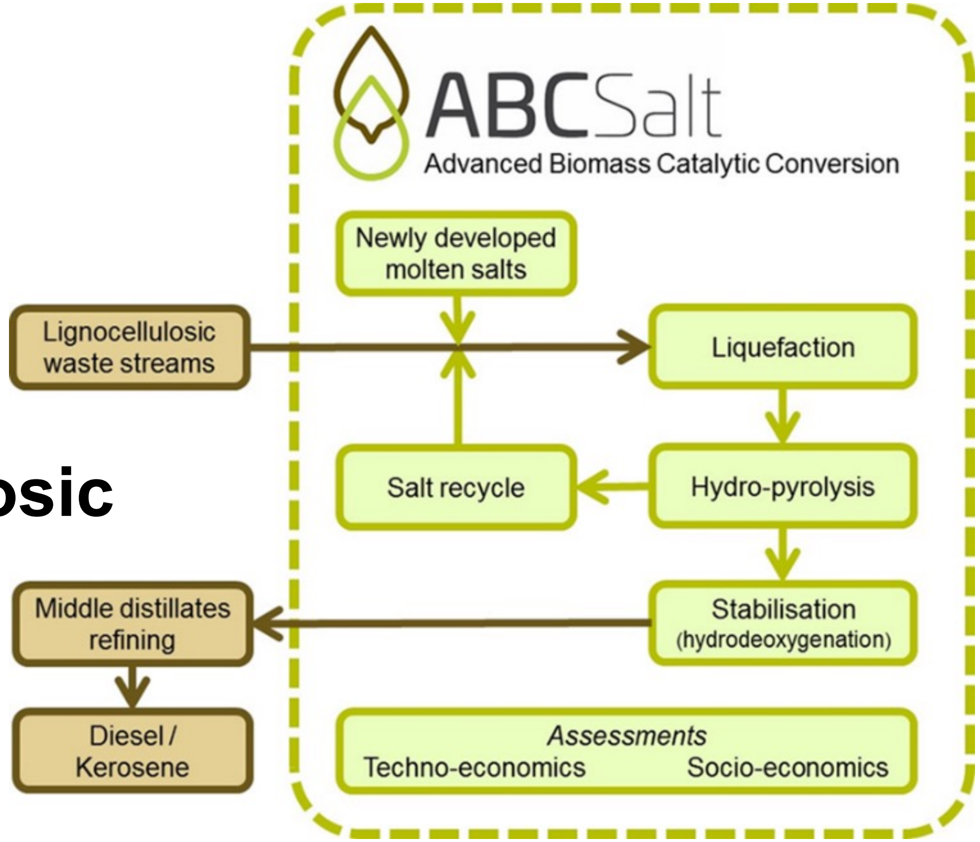
ABC-Salt identity

- **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



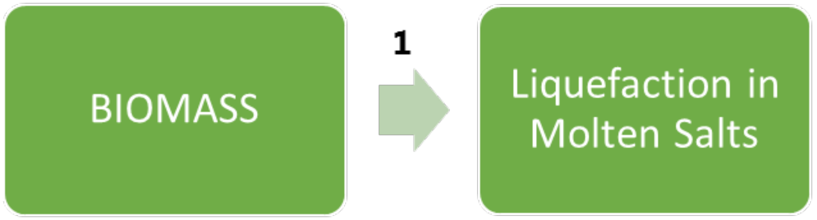
Project partners

University of Groningen	Netherlands	Erik Heeres
Aston University Birmingham	United Kingdom	Daniel J. Nowakowski
Ghent University	Belgium	Frederic Ronsse
Norwegian University of Life Sciences	Norway	Heidi Nygård
btg biomass technology group	Netherlands	Robbie Venderbosch
RISE	Sweden	Maria Sedin
DLR	Germany	Ralph Uwe-Dietrich
Sapienza Università di Roma	Italy	Marino Bonaiuto
benkei strategy • innovation • development	France	Fabienne Brutin/Laurence Naiglin

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.



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

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BIOMASS $\xrightarrow{1}$ Liquefaction in Molten Salts $\xrightarrow{2}$ (Catalytic) Hydro-Pyrolysis

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

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

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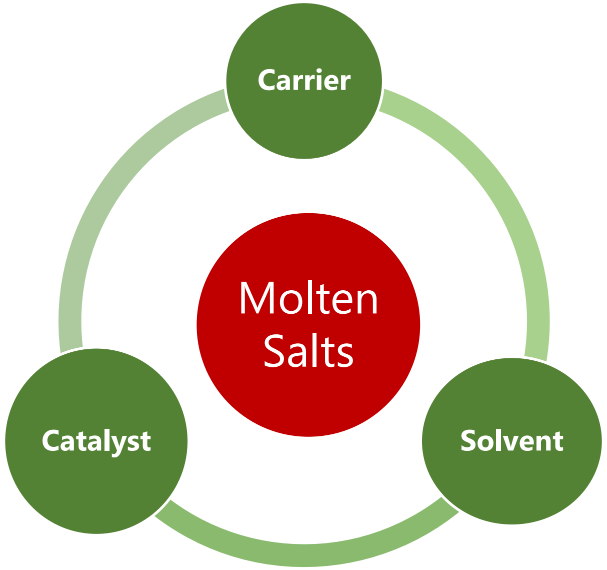
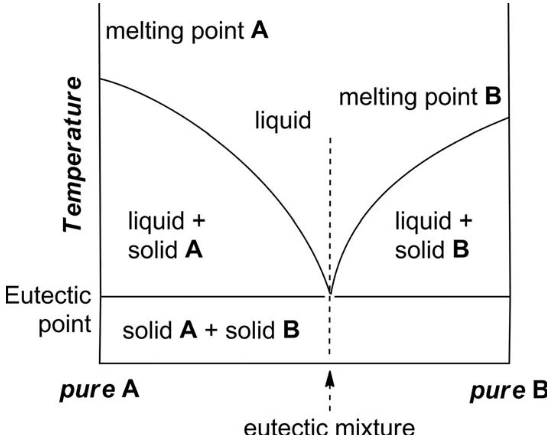
Step 2: Biomass vaporisation at elevated pressure (H_2) and temperature

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

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

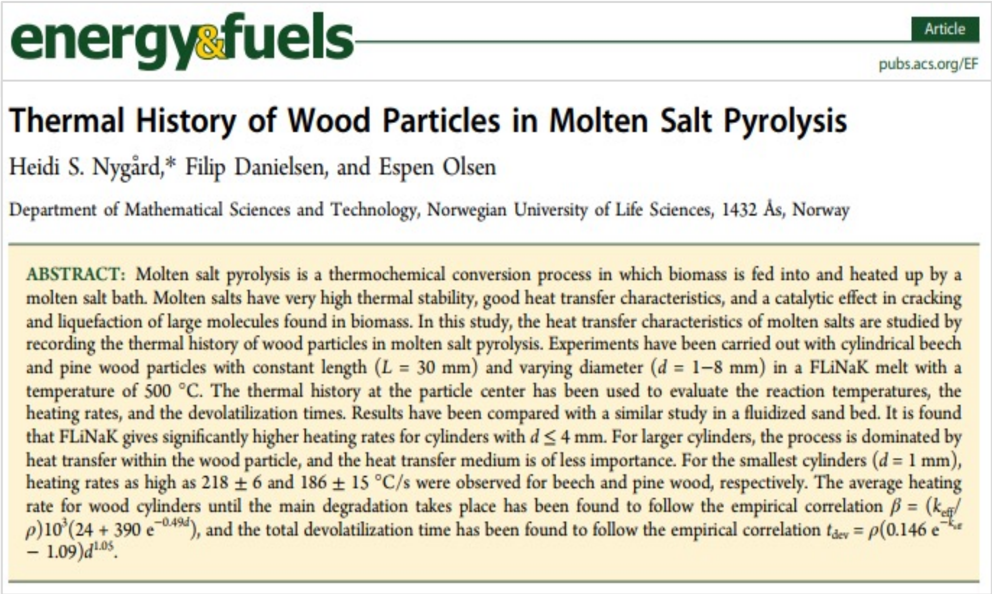




Lovering, D. G. *Molten Salt Technology;* Plenum Press: New York, **1982**
J. Sol. Energy Eng. **2004**, *126*, 850-857

Thermochemical Conversion of Biomass in Molten Salts

- Sada et al. (1992): Kraft and solvolysis lignins (500-800 oC, 1 atm) to liquids (phenolics) and gas, $ZnCl_2$-KCl
- Kudsy and Kumazawa (1999): Kraft lignin (500-600 oC)
- Nygård and Olsen (2012): Thermal history of wood particles
- Dtta and Dittami (2016): Patent application Molten salt pyrolysis for bio-oil and chemicals lignocellulosic biomass (300-400 oC)



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Thermal History of Wood Particles in Molten Salt Pyrolysis

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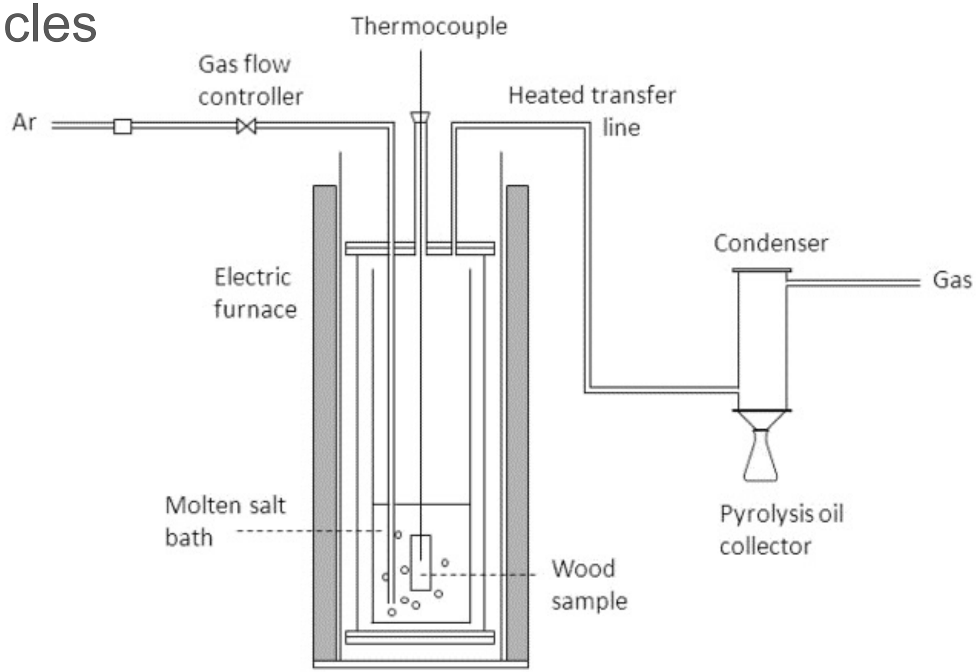
ABSTRACT: Molten salt pyrolysis is a thermochemical conversion process in which biomass is fed into and heated up by a molten salt bath. Molten salts have very high thermal stability, good heat transfer characteristics, and a catalytic effect in cracking and liquefaction of large molecules found in biomass. In this study, the heat transfer characteristics of molten salts are studied by recording the thermal history of wood particles in molten salt pyrolysis. Experiments have been carried out with cylindrical beech and pine wood particles with constant length (L = 30 mm) and varying diameter (d = 1−8 mm) in a FLiNaK melt with a temperature of 500 °C. The thermal history at the particle center has been used to evaluate the reaction temperatures, the heating rates, and the devolatilization times. Results have been compared with a similar study in a fluidized sand bed. It is found that FLiNaK gives significantly higher heating rates for cylinders with $d \leq 4$ mm. For larger cylinders, the process is dominated by heat transfer within the wood particle, and the heat transfer medium is of less importance. For the smallest cylinders (d = 1 mm), heating rates as high as 218 ± 6 and 186 ± 15 °C/s were observed for beech and pine wood, respectively. The average heating rate for wood cylinders until the main degradation takes place has been found to follow the empirical correlation $\beta = (k_{eff}/\rho)10^3(24 + 390\,e^{-0.49d})$, and the total devolatilization time has been found to follow the empirical correlation $t_{dev} = \rho(0.146\,e^{-k_{e}} - 1.09)d^{1.05}$.



Int. J. Low-Carbon Technol., **2012**, *7*, 318-324

Ind. Eng. Chem. Res., **1992**, *31*, 612-616

Can. J. Chem. Eng., **1999**, *77*, 1176-1184

PCT/US2016/041063

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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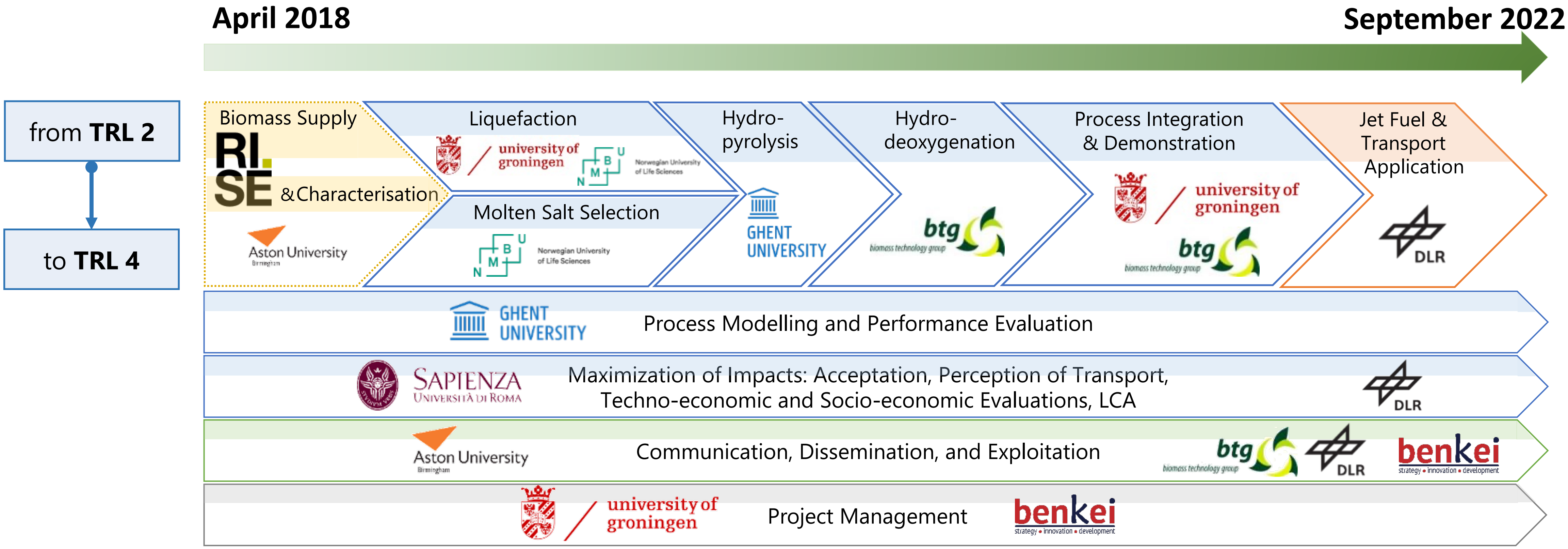
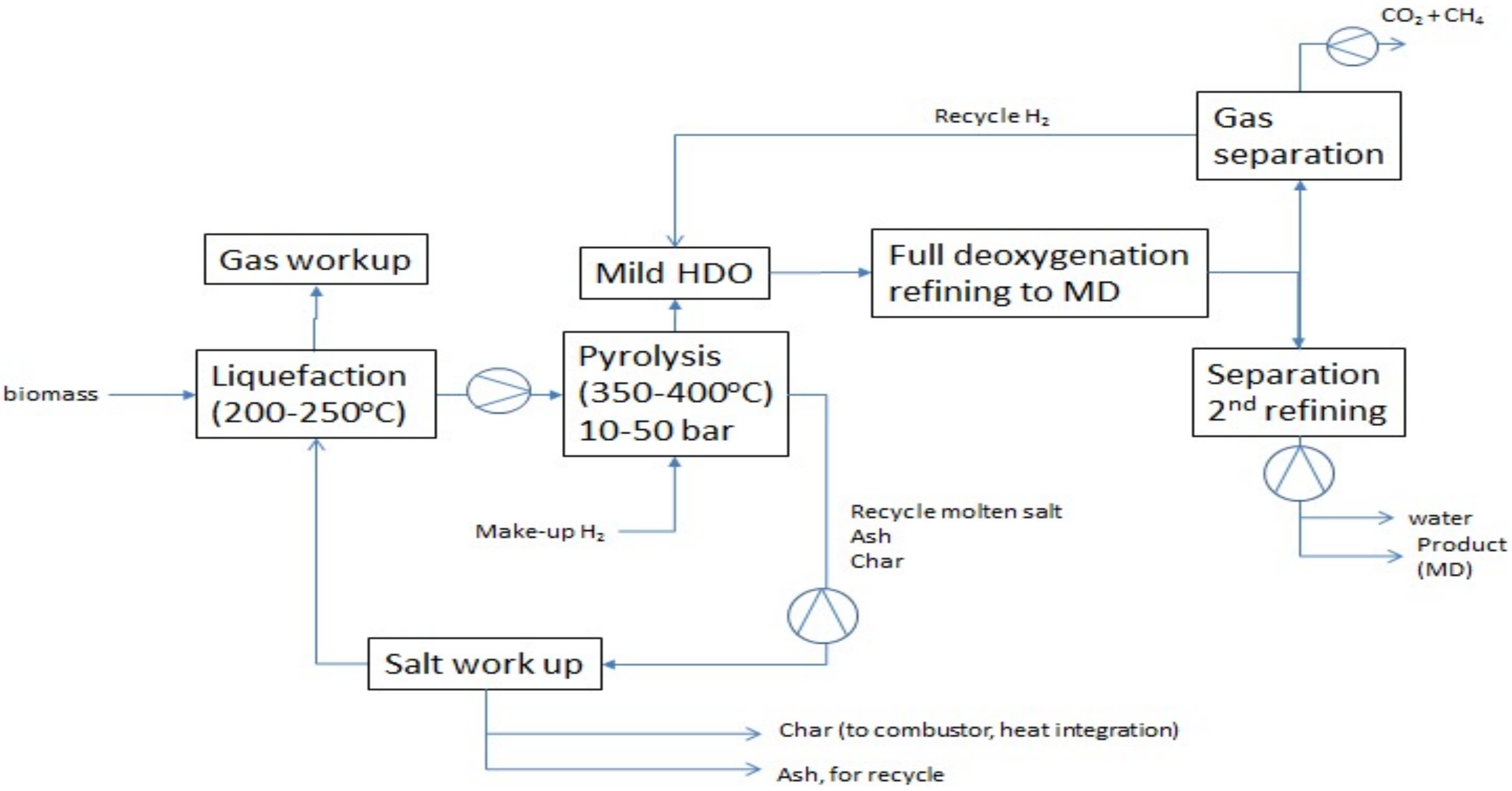
1. Ensure pumping of molten salts with the liquefied biomass.
2. Use of solubilized biomass source with excellent heat transfer medium.

Value Chain and Partner Contributions



Process concept



Ambitions

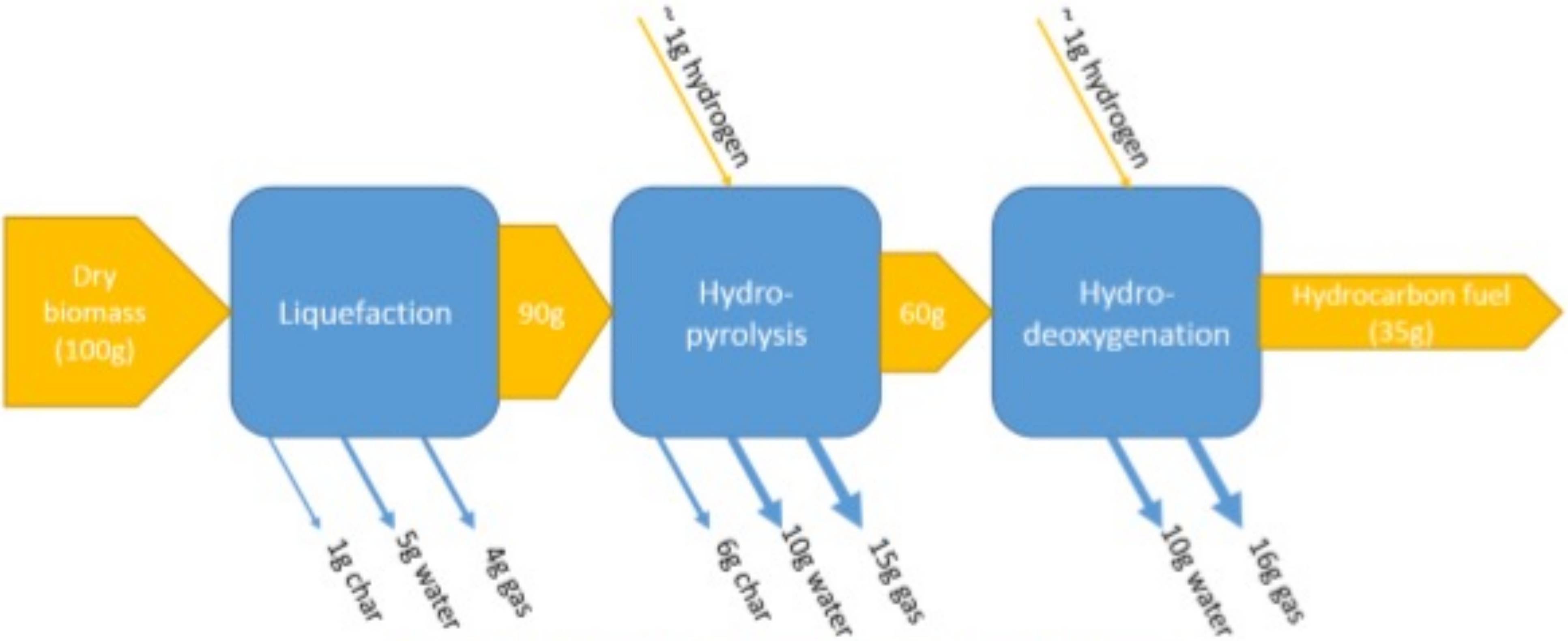


Figure 3 - Proposed yield ambition, as a mass balance

Main results achieved so far

Objective 1: Enable the development of an economically viable, environmentally friendly and socially acceptable process for the conversion of lignocellulosic waste streams to middle distillates.

- Multiple rounds of techno-economic assessment have been carried ot based on the process design and experimental data. Pulp mill integration studies have been conducted by RISE and DLR to improve the techno-economic viability.
- The results of a qualitative and quantitative socio-economic assessment are available to identify barriers and opportunities for biofuels

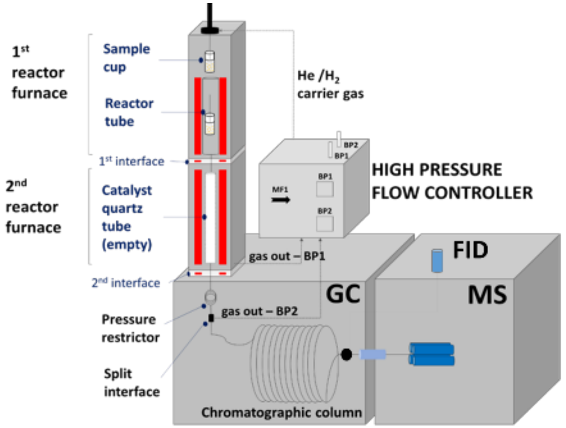
Objective 2: Select the most appropriate lignocellulosic waste streams and assess the ability of molten salts to liquefy such streams below 200 °C and atmospheric pressure with 90 wt% yield based on biomass input.

- Feedstock selection and characterization has been finalized
- Investigations to address effects of ash and other impurities on performance and recycle options are in progress
- Preferred salt has been selected and thermal and hydrolytic stability assessed (experimental/modeling)
- The viscosity and corrosivity of preferred salt have been determined
- Yield targets have been met successfully for the liquefaction step

Main results achieved so far

Objective 3: Conversion of the liquefied biomass to MD’s using hydro-pyrolysis followed by hydro-deoxygenation with a yield of 38 wt% based on biomass input (55% based on carbon input)

- Micro-(hydro)-pyrolysis studies with ABC-Salt feedstocks have been successfully performed
- Hydropyrolysis experiments have been performed in small scale batch units using lignin and wood. Liquid yields > 50 wt.% have been obtained using a vapour phase approach and the liquid products were analysed in detail
- Recyclability of molten salts has been successfully proven (> 98% recovery).
- Hydrotreatment experiments have been performed successfully at larger scale with high carbon yields



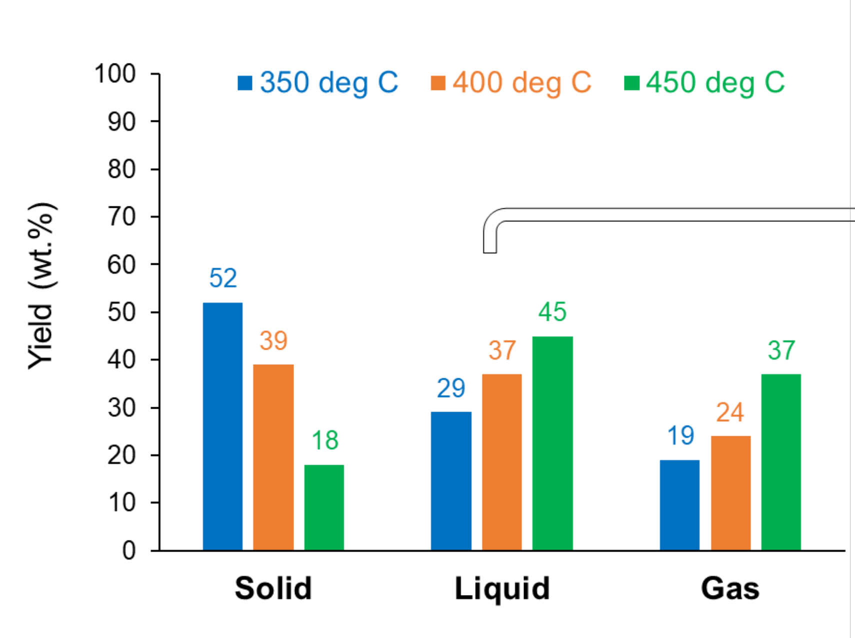
Main results achieved so far

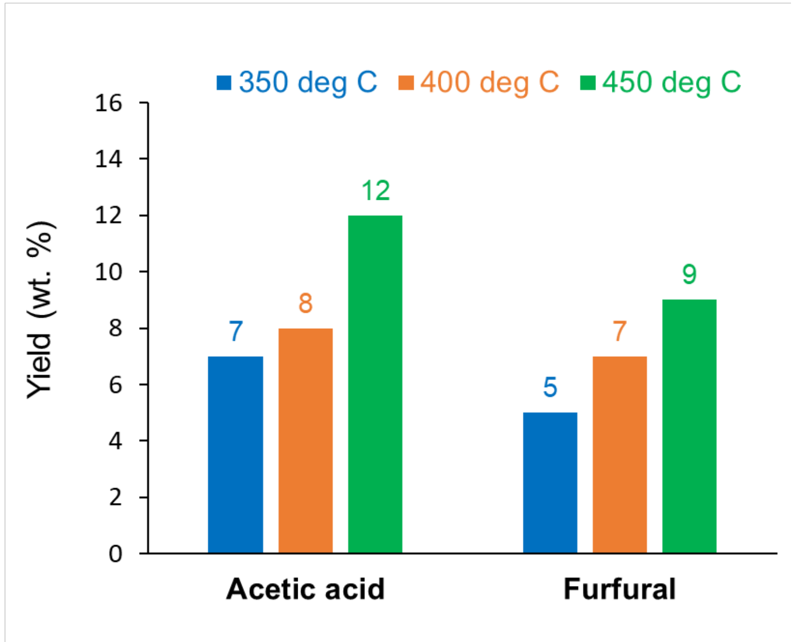
Objective 4: Demonstrate the conversion of the lignocellulosic waste streams into a MD biofuel in an integrated process with over 35% yield based on dry biomass input (55 wt% based on carbon input) for at least 100 hours at a minimum scale of 100 g/h input

- Centered around the design, construction and operation of an integrated prototype unit for the testing and demonstration of the ABC-Salt concept.
- Unit has been designed, constructed and commissioned and the test phase has started.

Hydropyrolysis of wood in molten salts: an overview

Wood → Liquefaction (molten salts) → (Hydro) Pyrolysis (molten salts) → (Hydro) Deoxygenation → Middle distillates



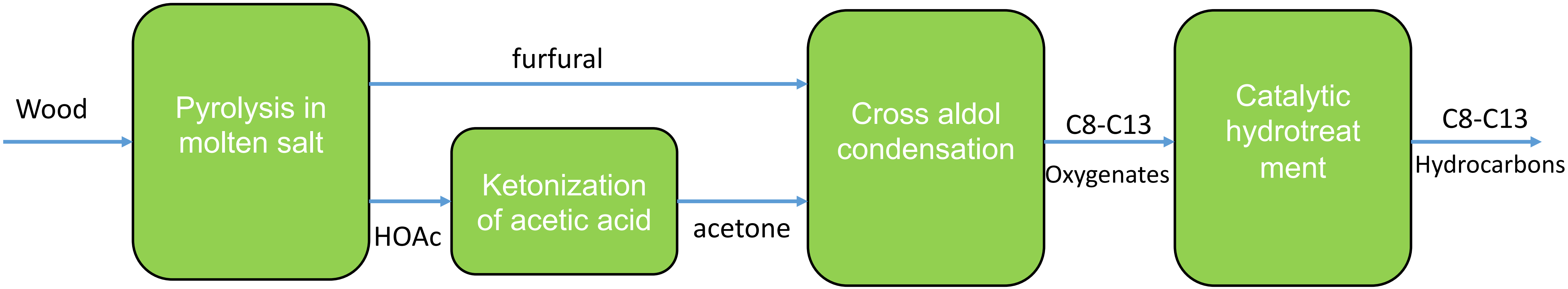


C_3 C_5

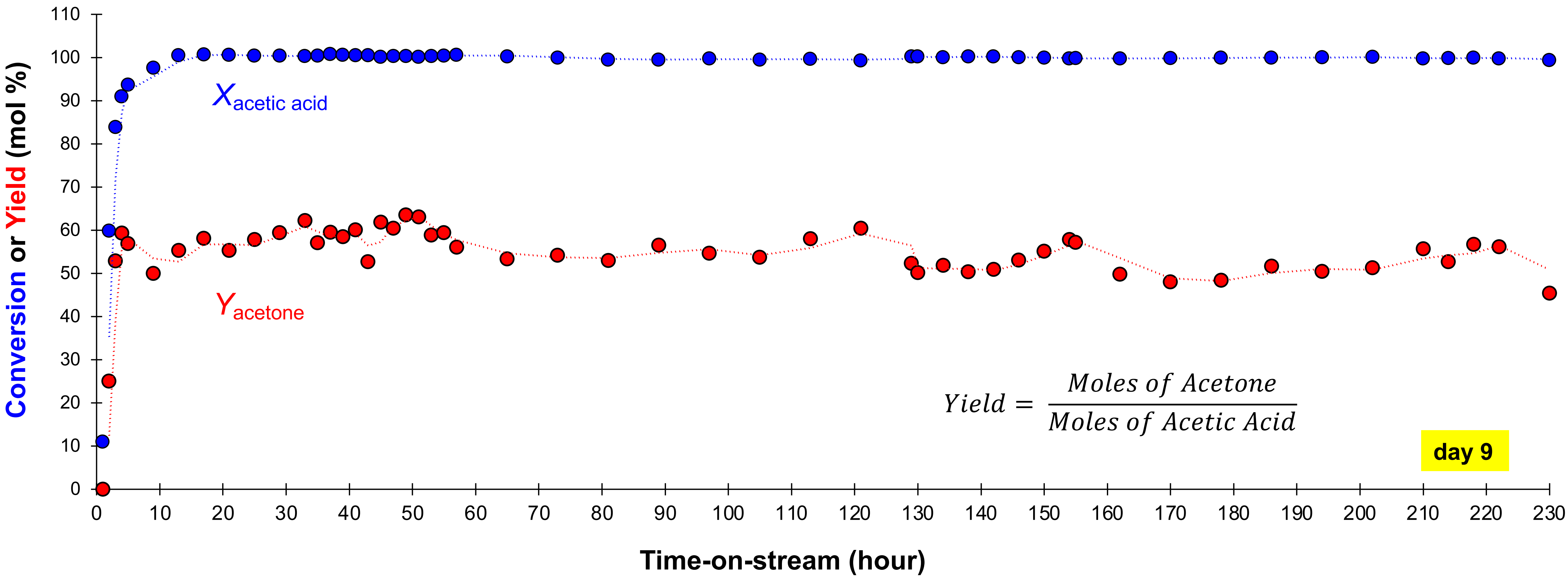
1:6 wt. ratio pinewood:$ZnCl_2$-KCl-NaCl (60:20:20), 30 mL min^{-1} N_2; 50 min

Molten salts change chemoselectivity: mainly furfural and acetic acid

How to obtain middle distillates from furfural and acetic acid?

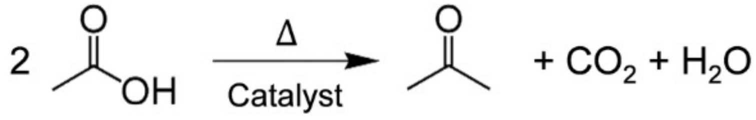


Ketonization using a $CeZrO_x$ catalyst at 300 °C

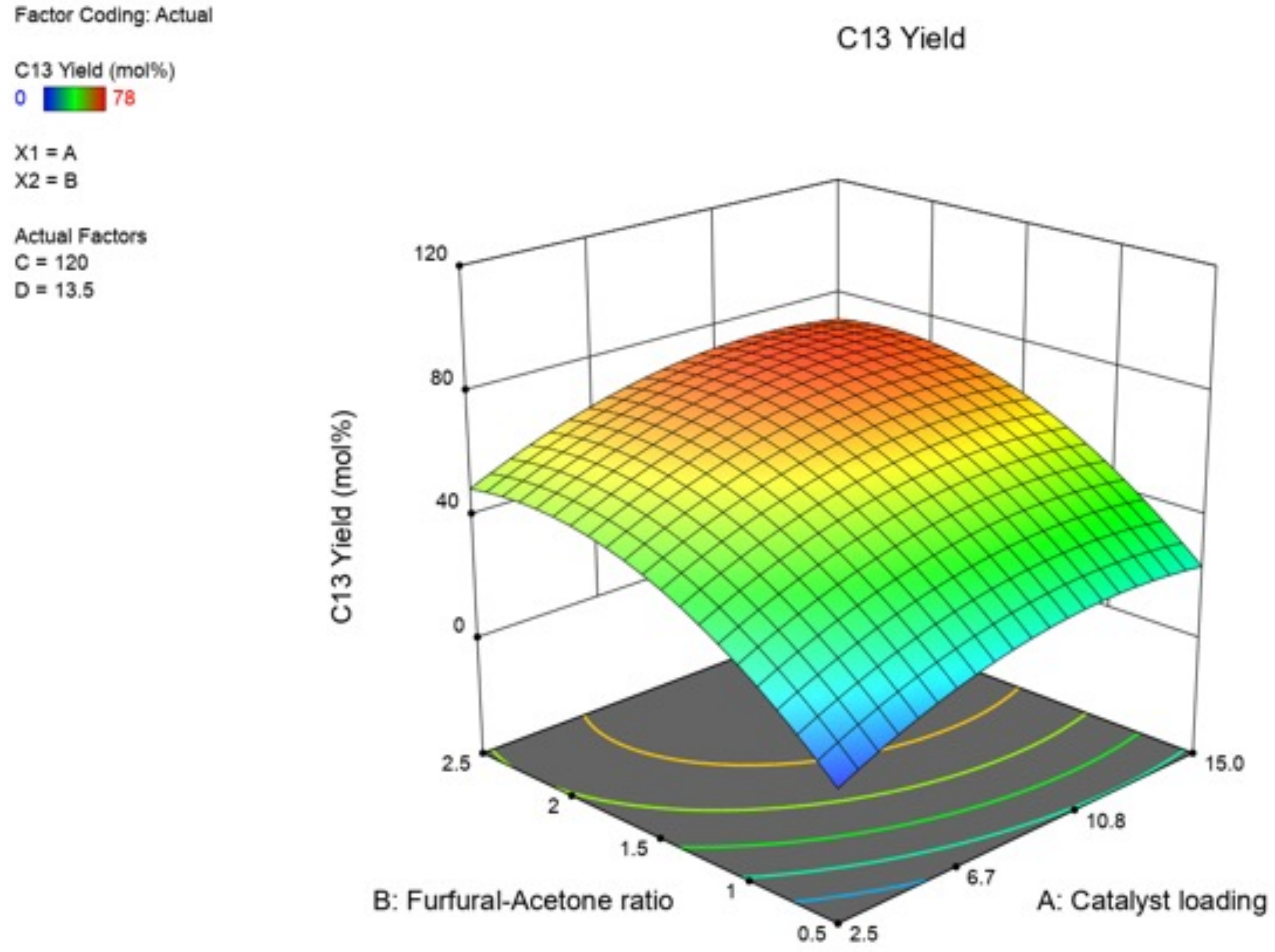


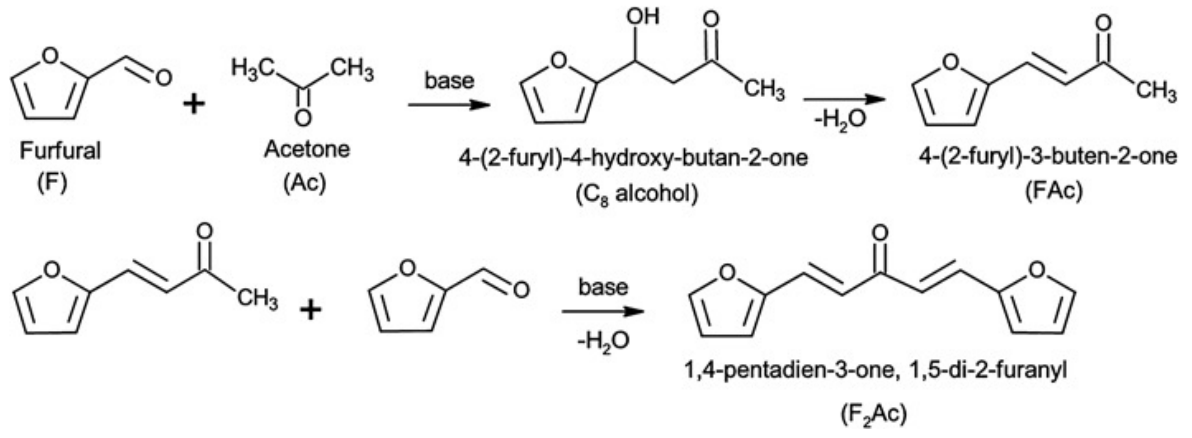
$$Yield = \frac{Moles\ of\ Acetone}{Moles\ of\ Acetic\ Acid}$$

10 wt.% acetic acid in water, 2.4 mL min^{-1}, 1.0 g catalyst, 300 °C



Cross aldol condensation

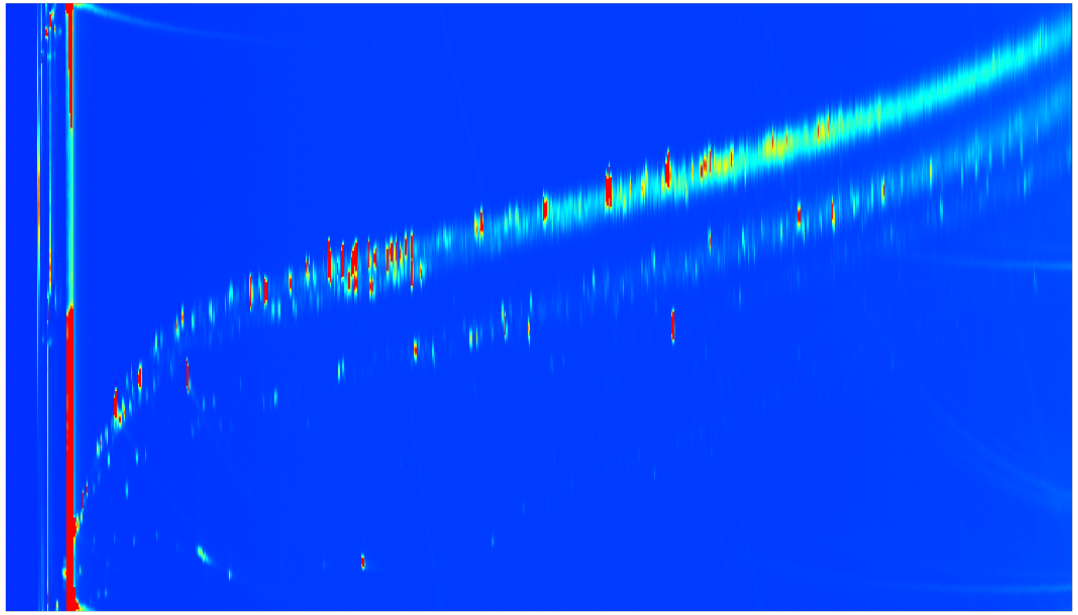




Catalyst: Commercial Mg/Al hydrotalcite

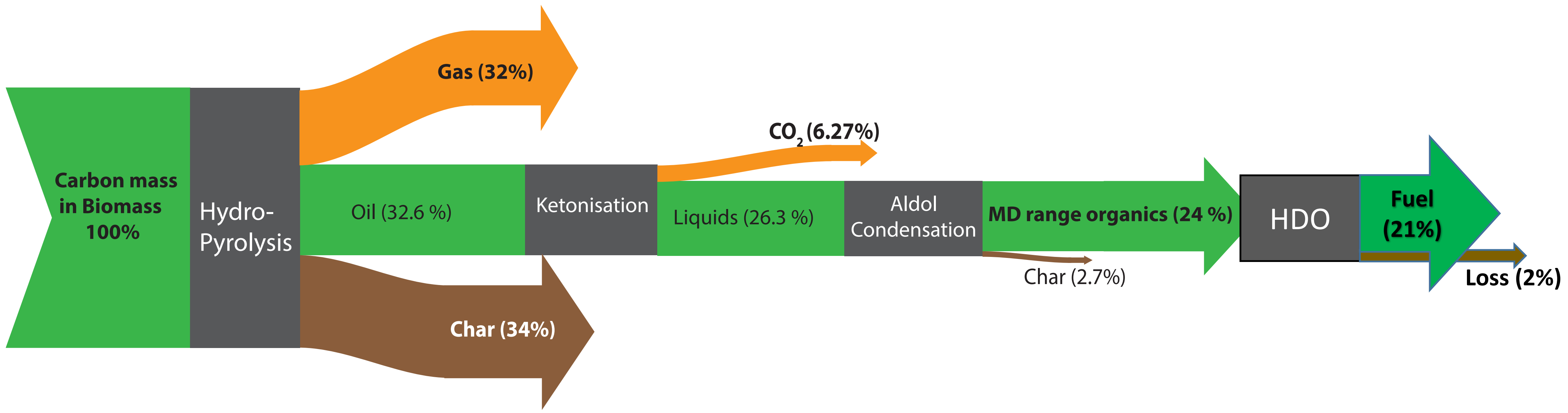
Catalytic hydrotreatment of cross aldol products

- Possible using catalytic hydrotreatment technology applied for pyrolysis oil
- Two step approach essential (low and high temperature)
- High levels of deoxygenation possible (< 2 wt%)



	After AC	After HDO1	After HDO2
C	71.71	71.63	85.84
H	6.02	11.53	12.48
O	22.2	16.84	1.68

From wood to MD's: overall carbon yield



- For wood: further improvements in hydropyrolysis step required
- For lignin: substantially higher carbon yields and actually in line with objectives (patent pending)

Acknowledgements

Project kick-off meeting ◆ Groningen - April 2018

university of groningen

Aston University Birmingham

btg biomass technology group

DLR Deutsches Zentrum für Luft- und Raumfahrt German Aerospace Center

NMBU Norwegian University of Life Sciences

RI. SE

GHENT UNIVERSITY

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ABC-Salt

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