Hydrodeoxygenation (HDO) of bio-oils

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VTT

BL2F

Transforming Black Liquor to Biofuel

This project has received funding from the European Union Grant Number 884111

Outline

1. Basics of HDO
2. HDO of bio-oils from biomass liquefaction
    1. Slurry hydrotreatment
    2. Hydrothermal HDO
3. Summary

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Basics of hydrodeoxygenation (HDO)

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Upgrading by hydrodeoxygenation (HDO)

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Deoxygenation of bio oils

Oxygen is removed in the form of

- H_2O
  - Hydrodeoxygenation, hydrogenolysis
  - Various amounts of hydrogen is needed
  - Example reaction for saturated fatty acid:

$$RCOOH + 3H_2 \rightarrow R'H + 2H_2O$$

- CO, CO_2
  - Decarbonylation, decarboxylation
  - Some carbon is typically lost, less hydrogen needed
  - Example reactions for saturated fatty acid

$$RCOOH + H_2 \rightarrow RH + CO + H_2O$$

$$RCOOH \rightarrow RH + CO_2$$

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Catalysts for HDO

- Sulfided catalyst (NiMo or CoMo on γ-Al_2O_3)
  - Adopted from hydrotreatment (HDS, HDN) of petroleum fractions
  - Active in sulfided form => sulfur addition often needed if no sulfur in the feed
  - HDO mainly through hydrogenolysis, decarboxylation & decarbonylation can also play a role
- Noble metal catalysts
  - Rh, Ru, Pd, Pt
  - Carbon, Al2O3, ZrO2 as support
  - No sulfur needed
  - Hydrogenolysis activity lower, decarbonylation, decarboxylation in important role
  - Deactivation often significant, especially if no hydrogen is used (DO)
- Supported metal carbides (Mo_2C and W_2C), phosphides (Ni_2P, Co_2P, MoP), nitrides (Mo_2N) and oxides (MoO_3, NiO-MoO_3, CoO-MoO_3)

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HDO of bio-oils: conditions

Temperature, °C	250-400
Pressure, MPa	10-18
Liquid hourly space velocity, (vol. bio-oil)/(vol. catalyst)/h	0.1-0.8
H_2 feed rate, (L H_2)/(L bio-oil)	100-700
Catalyst active metals	CoO/MoO_3, NiO/MoO_3, NiO/WO_2, Ni, Pt
Catalyst support	Al_2O_3, γ-Al_2O_3, silica-alumina, Y-zeolite/Al_2O_3

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HDO of bio-oils by biomass liquefaction

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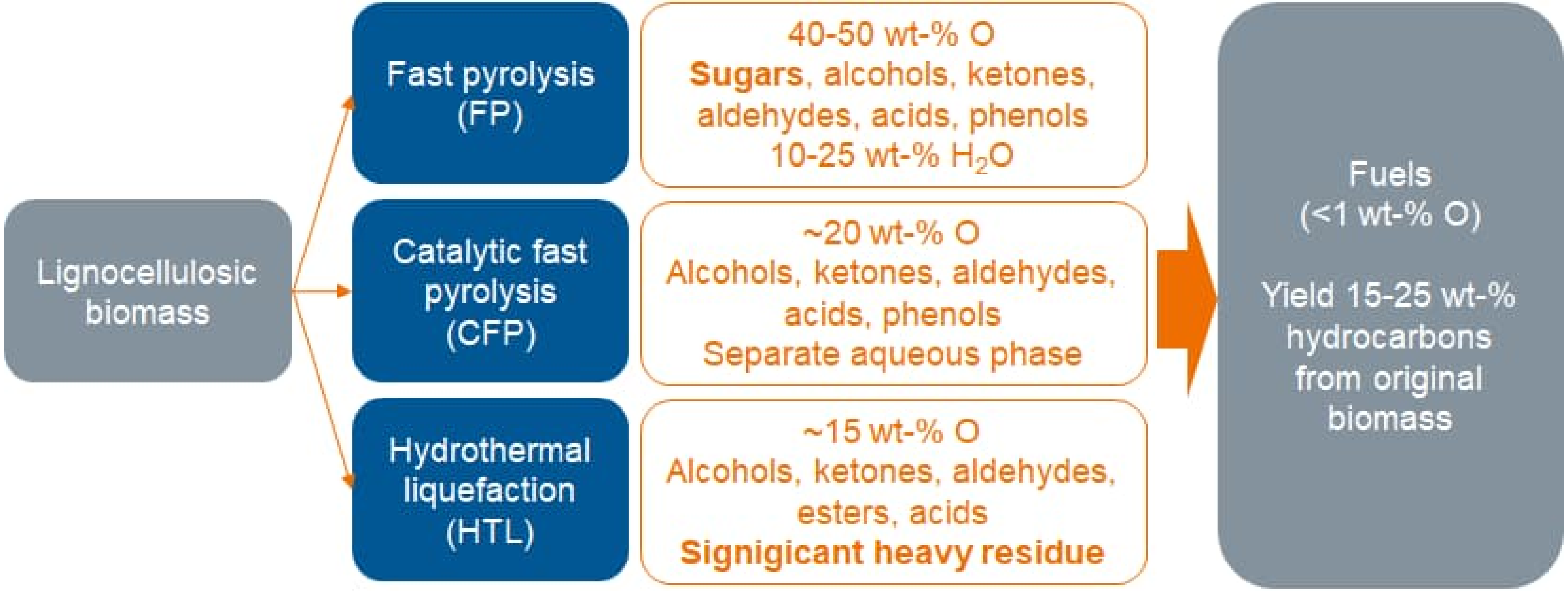
Biofuels from lignocellulosic biomass by liquefaction



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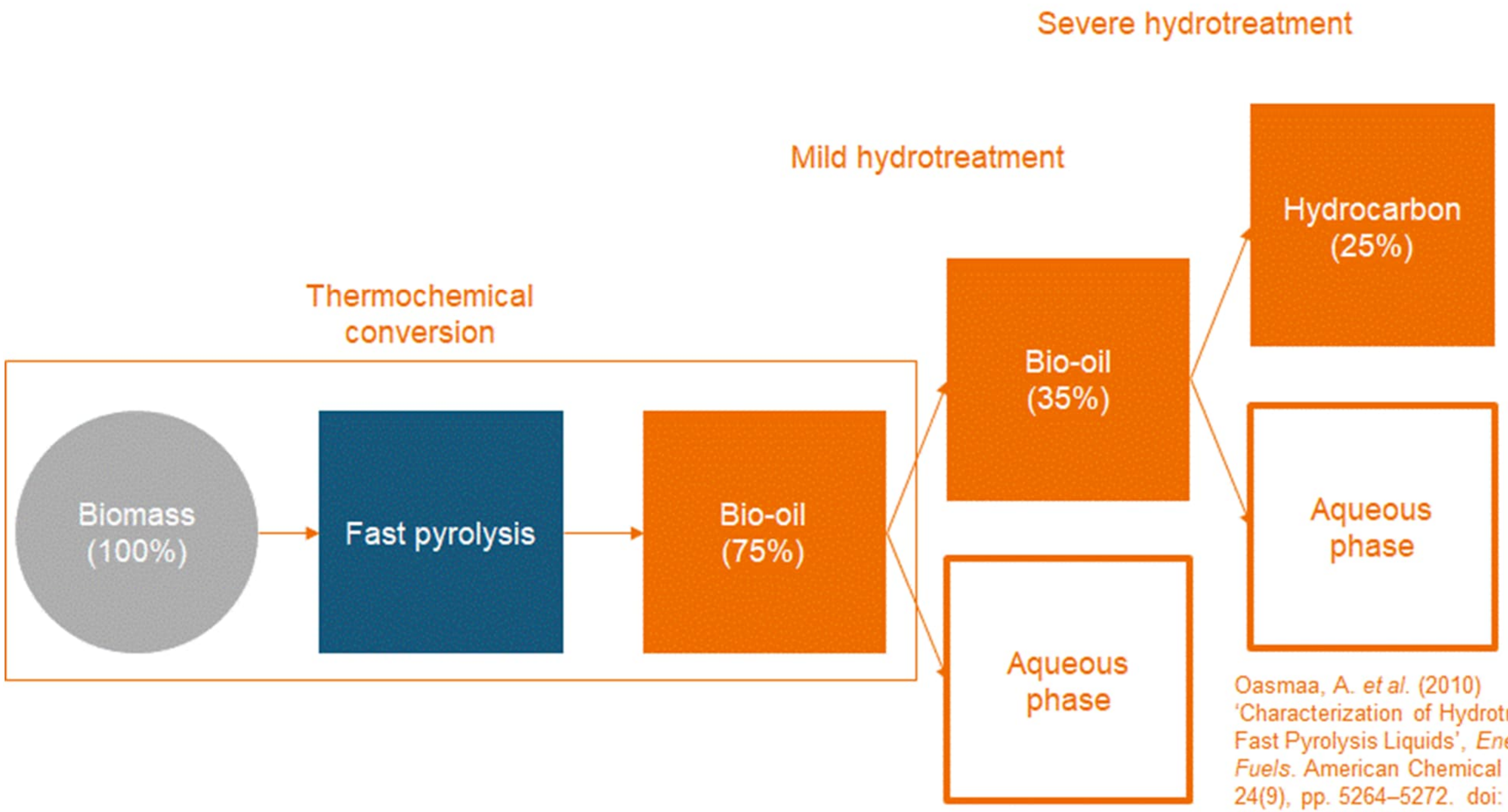
Bio-oils liquefaction by fast pyrolysis and upgrading by HDO



Oasmaa, A. *et al.* (2010) 'Characterization of Hydrotreated Fast Pyrolysis Liquids', *Energy & Fuels*. American Chemical Society, 24(9), pp. 5264–5272. doi: 10.1021/ef100573q.

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Instability of bio-oils

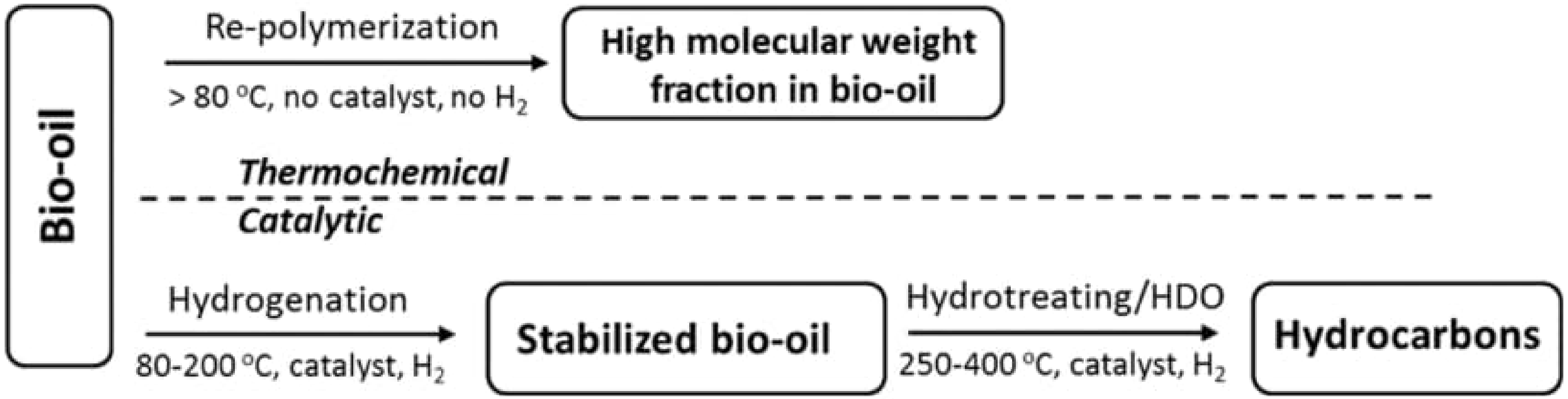

Figure from Wang *et al.* 2016

- Bio-oils tends to thermally repolymerize and form plugs in process units
- First signs of thermal condensation at <100 °C, severe at high temperature
- High carbohydrate and carbonyl content

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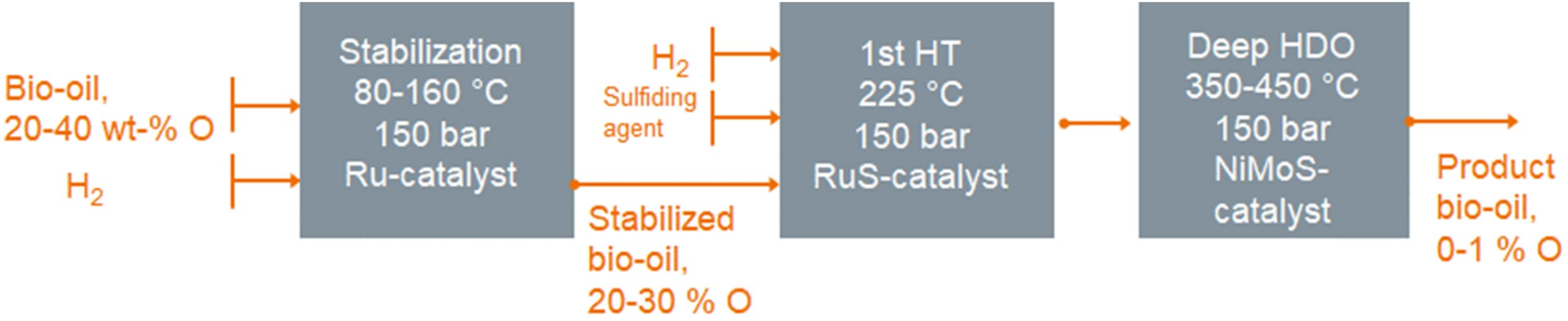
Wang, H. *et al.* (2016) 'Bio-oil Stabilization by Hydrogenation over Reduced Metal Catalysts at Low Temperatures', *ACS Sustainable Chemistry & Engineering*. American Chemical Society, 4(10), pp. 5533–5545. doi: 10.1021/acssuschemeng.6b01270.

Stepwise processing

- The plug formation can be hindered by hydroprocessing the bio-oil in multiple steps in fixed bed hydrotreater reactors
- Problems: expensive catalysts, deactivation during 1st stabilising hydrogenation step due to sulphur and coke formation



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Zacher, A. H. *et al.* (2019) 'Technology advancements in hydroprocessing of bio-oils', *Biomass and Bioenergy*. Pergamon, 125, pp. 151–168. doi: 10.1016/J.BIOMBIOE.2019.04.015.

Catalytic slurry hydrotreatment

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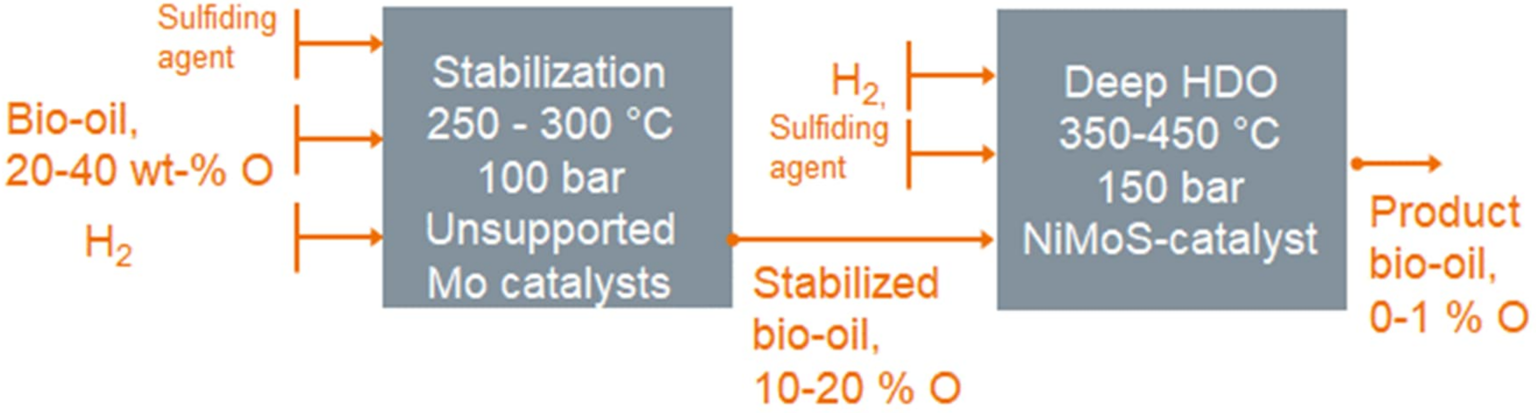
Alternative: slurry hydrotreatment applied for the stabilisation

- Bio-oil stabilization by slurry hydrotreatment applying sulfided Mo-based catalysts
  - Continuous addition of fresh and removal of spent catalyst enabled
- Rest oxygen removal by fixed bed hydrotreatment by supported sulfided catalysts
  - Severity defined by product specification



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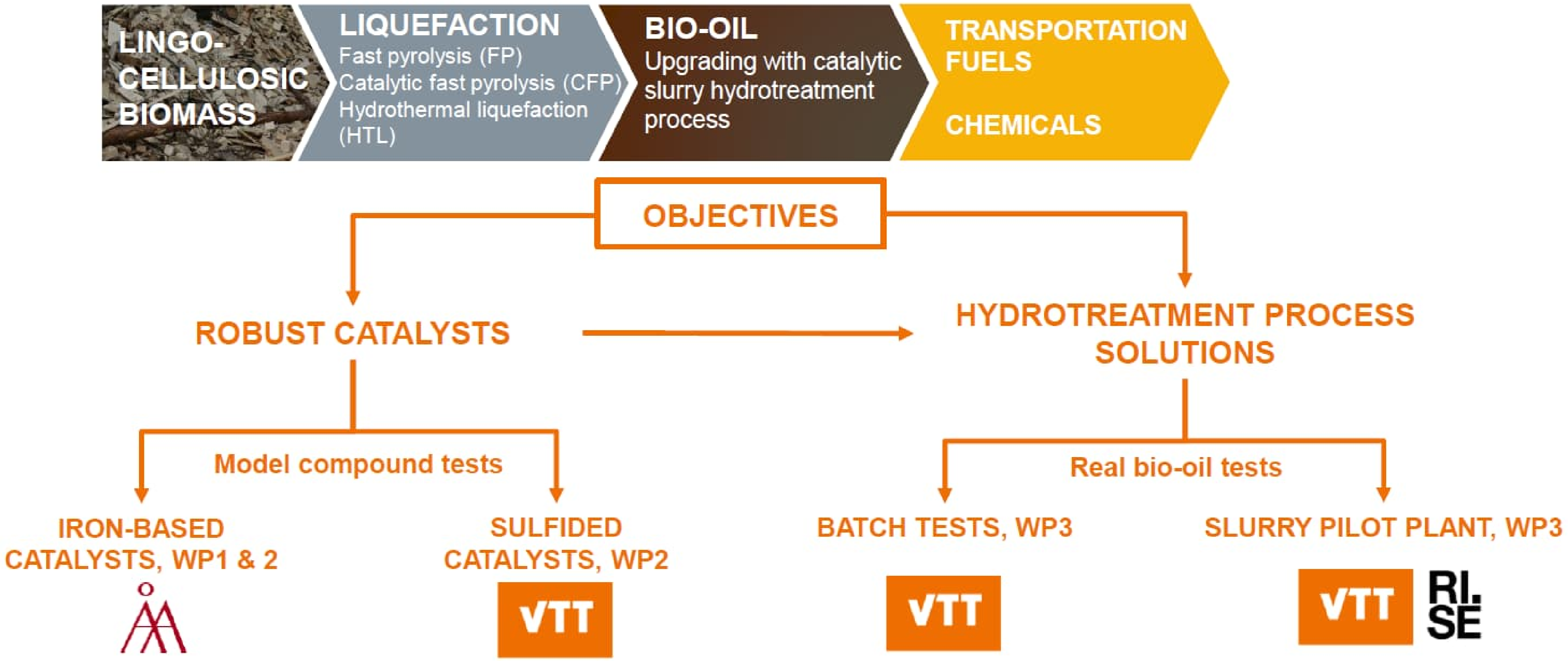
CaSH - Catalytic slurry hydrotreatment



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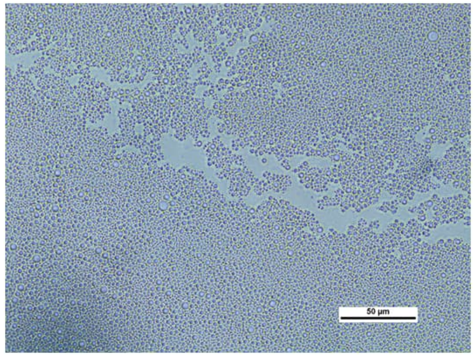
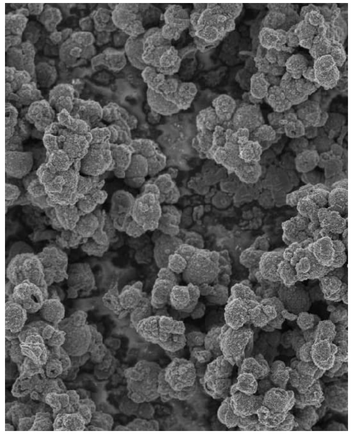
Preparation of unsupported Mo and promoted Mo catalysts

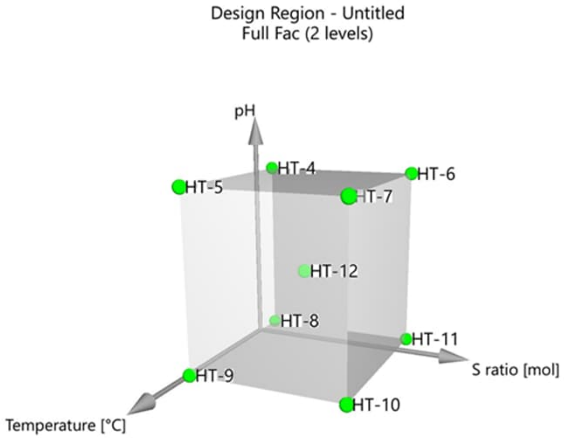
Emulsion- templated synthesis



HDO activity correlation with:
- Emulsion properties
- Precursor properties
- Emulsion sulfidation

One-pot hydrothermal precipitation





Catalyst properties and HDO activity correlation with:
- Synthesis pH
- Synthesis temperature
- Sulfur amount in synthesis

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Tests with real bio-oils

BATCH TEST RUNS

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- ✓ Batch reactor operation validated with model compounds
- ➢ Transition to real bio-oil starting in early 2022

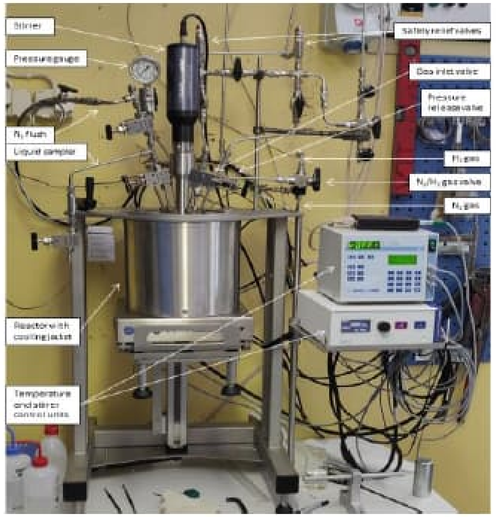
ACTIVITIES

- ➢ Identifying and procuring suitable bio-oils
- ➢ Discharged catalyst characterization
- ➢ Production of larger catalyst batch for slurry pilot test run

SLURRY PILOT PLANT

VTT RI. SE

- ➢ Test run performed with the best catalyst from WP1 and WP2 catalyst development.
- ➢ Objective few test runs, in the range of total 50 hours of operation.



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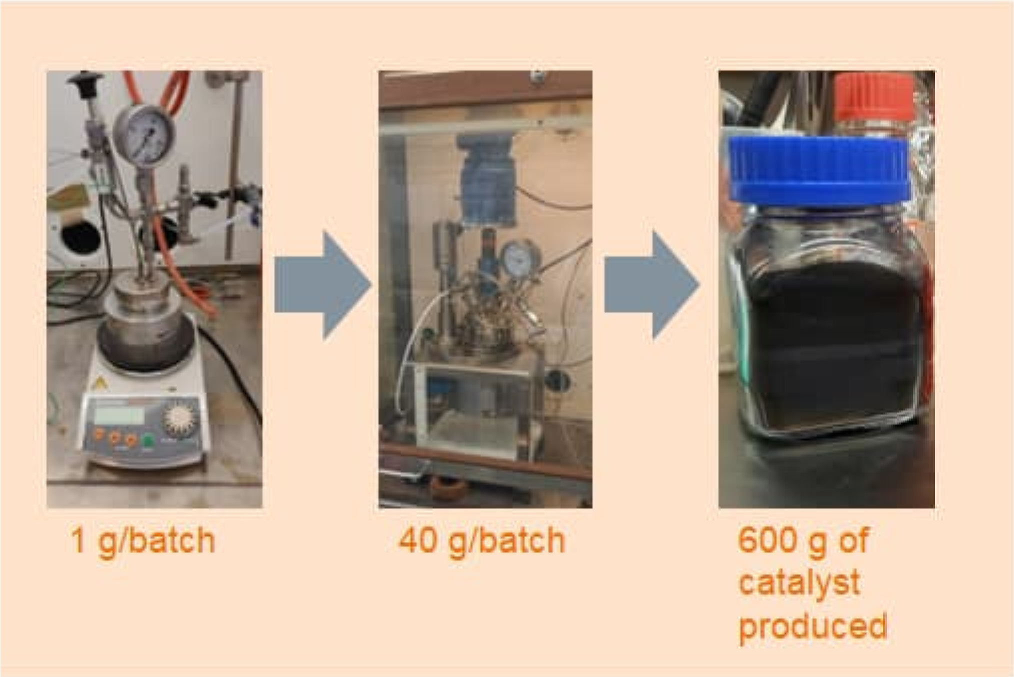
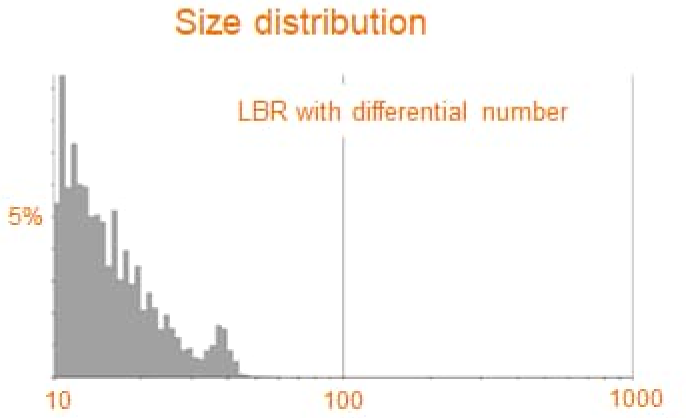
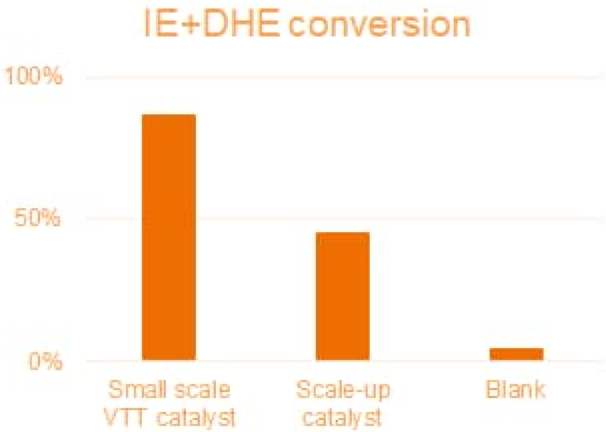
Catalyst synthesis scale-up for bio-oil pilot tests







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Successful proof of concept in total 70 hours of continuous operation

Catalyst	Temperature	Pressure bar	Hydrogen consumption g/kg bio-oil	Degree of deoxygenation	Oil product yield (dry)
VTT	350 °C	140	30.1	37%	47%
Reference	350 °C	140	31.6		
VTT	380 °C	75	36.8	46%	46%
VTT	380 °C	140	35.7	48%	43%
Reference	380 °C	140	41.8	50%	45%
VTT	410 °C	140	45.5	48%	37%
Reference	410 °C	140	43.3	51%	41%

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Hydrothermal HDO

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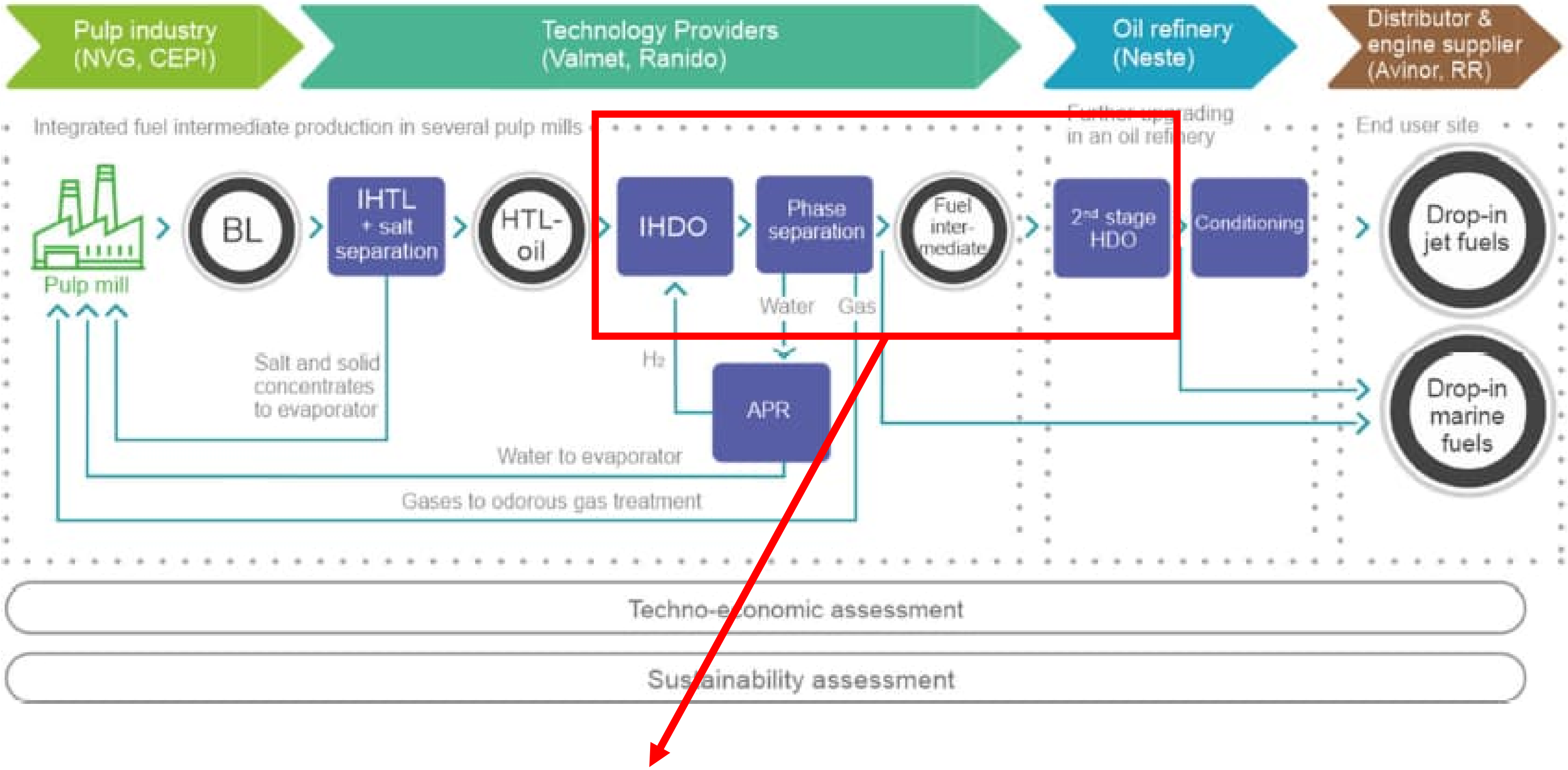
BL2F upgrading concept



IHDO = HDO in hydrothermal conditions

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Hydrothermal HDO

HDO in hydrothermal conditions in BL2F

- Utilization of biocrude from HTL in aqueous environment
- Performing hydrothermal catalytic HDO in near critical or supercritical conditions

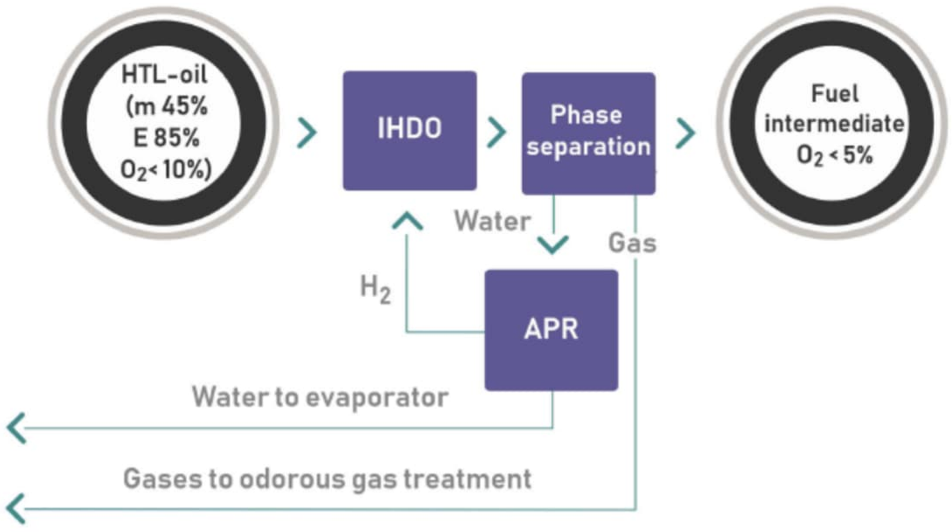
Benefits:

- No need to separate water before IHDO
- Water can act as solvent of hydrocarbons in such conditions
- Hydrogen can be generated in situ by catalytic transfer hydrogenation and APR in such conditions
- Reaction conditions can protect catalyst from deactivation by coke

Challenges:

- Residues of salts from IHTL to IHDO affect the catalyst deactivation
- Catalyst materials should tolerate aqueous near/supercritical conditions

Integrated HydroDeOxygenation (IHDO)



Green Chem., 23, 2021, 1114; *Catalysis Communications*, 90, 2017, 47-50; *Chemical Engineering Journal*, 407, 2021, 126332.

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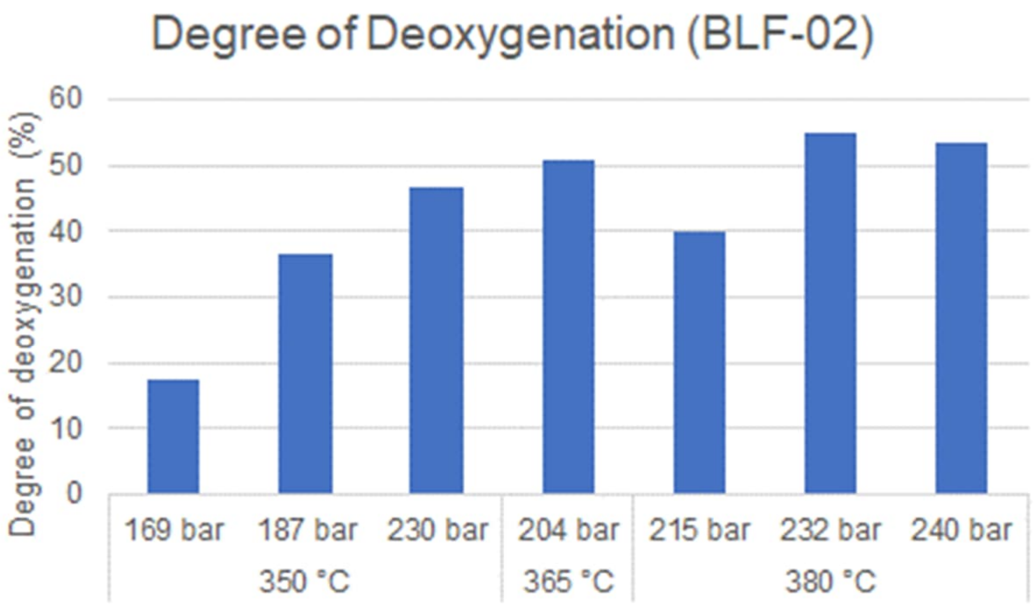
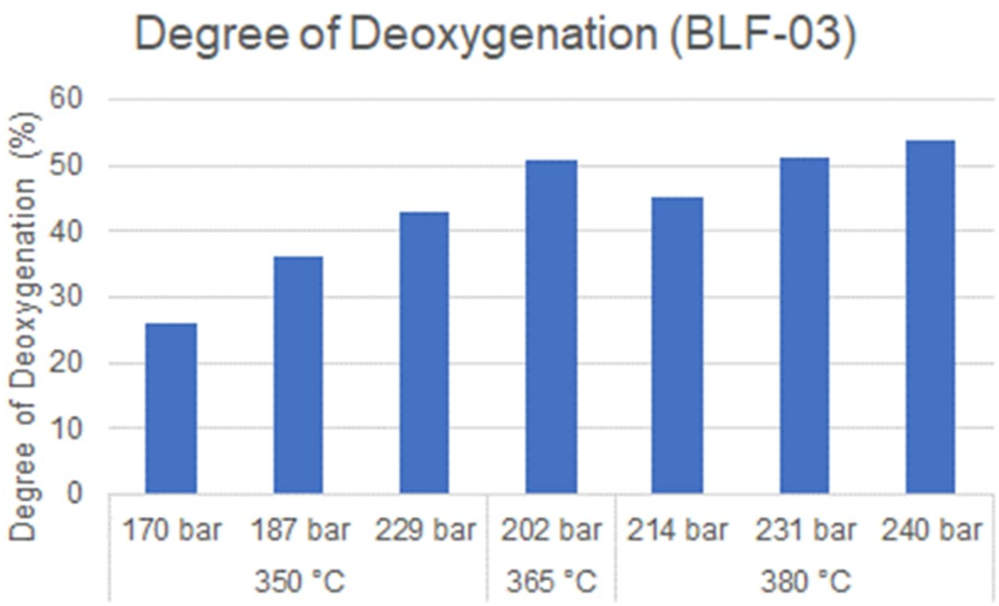
Hydrothermal HDO – model component testing

- BLF-03 performs slightly better especially in the “milder” conditions





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Summary

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Summary

- Upgrading of bio-oils to transportation fuels challenging due to instability of bio-oils and impurities in bio-oils (sulfur etc.)
- New solutions needed to commercialize bio-oils upgrading by HDO
  - Slurry hydroprocessing (CaSH project)
  - Hydrothermal HDO (BL2F project)
- Catalysts have been developed and tested for these two upgrading technologies
  - So far mainly tests with model components in BL2F
  - Piloting in slurry hydroprocessing at RISE
- So far slurry hydroprocessing looks the most promising concept
  - Hydothermal conditions challenging for solid catalysts => metal leaching etc.

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