Upgrading of Fast Pyrolysis Bio-oil for Aviation and Marine Applications

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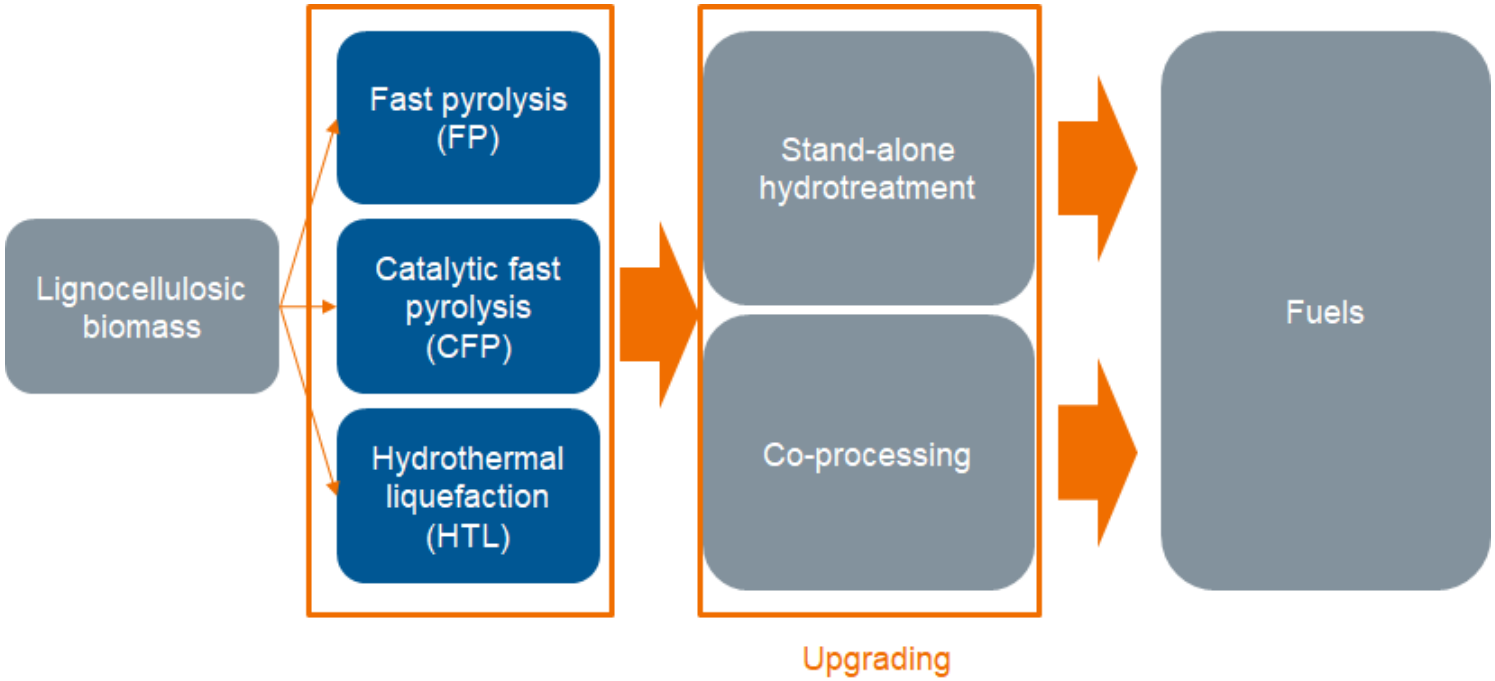
Outline

Introduction to biomass liquefaction and upgrading by hydrotreatment

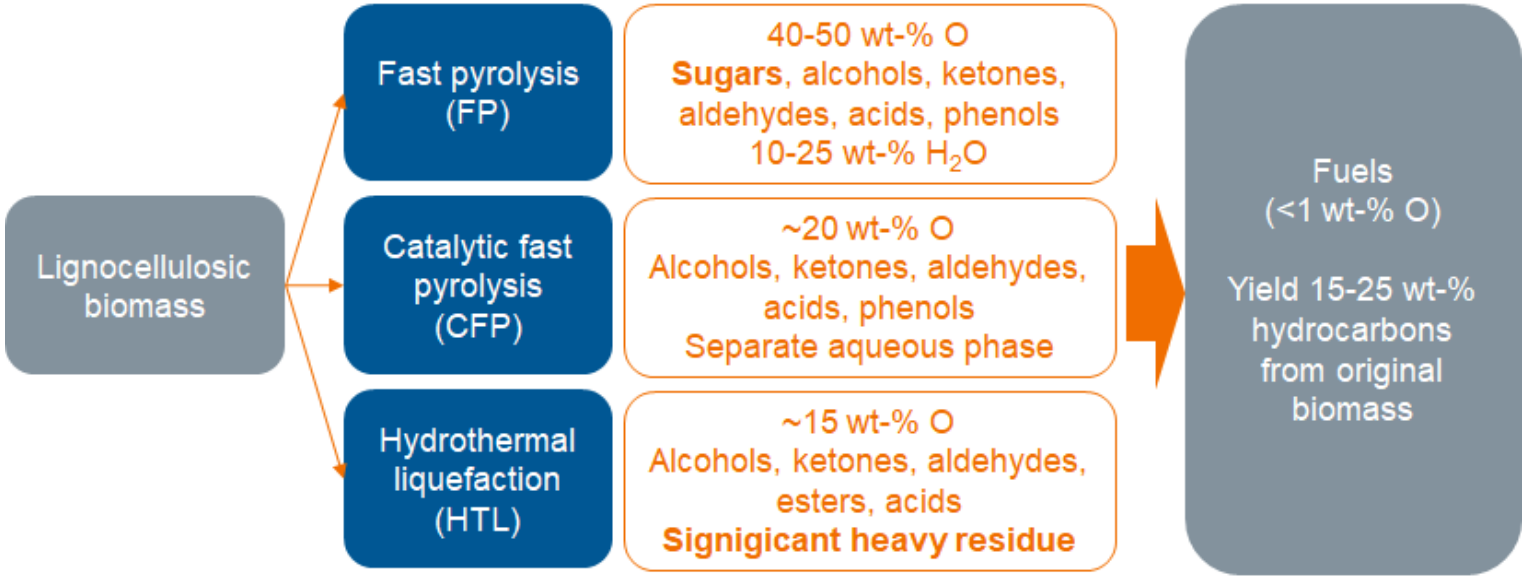
Upgrading by catalytic slurry hydrotreatment

Summary

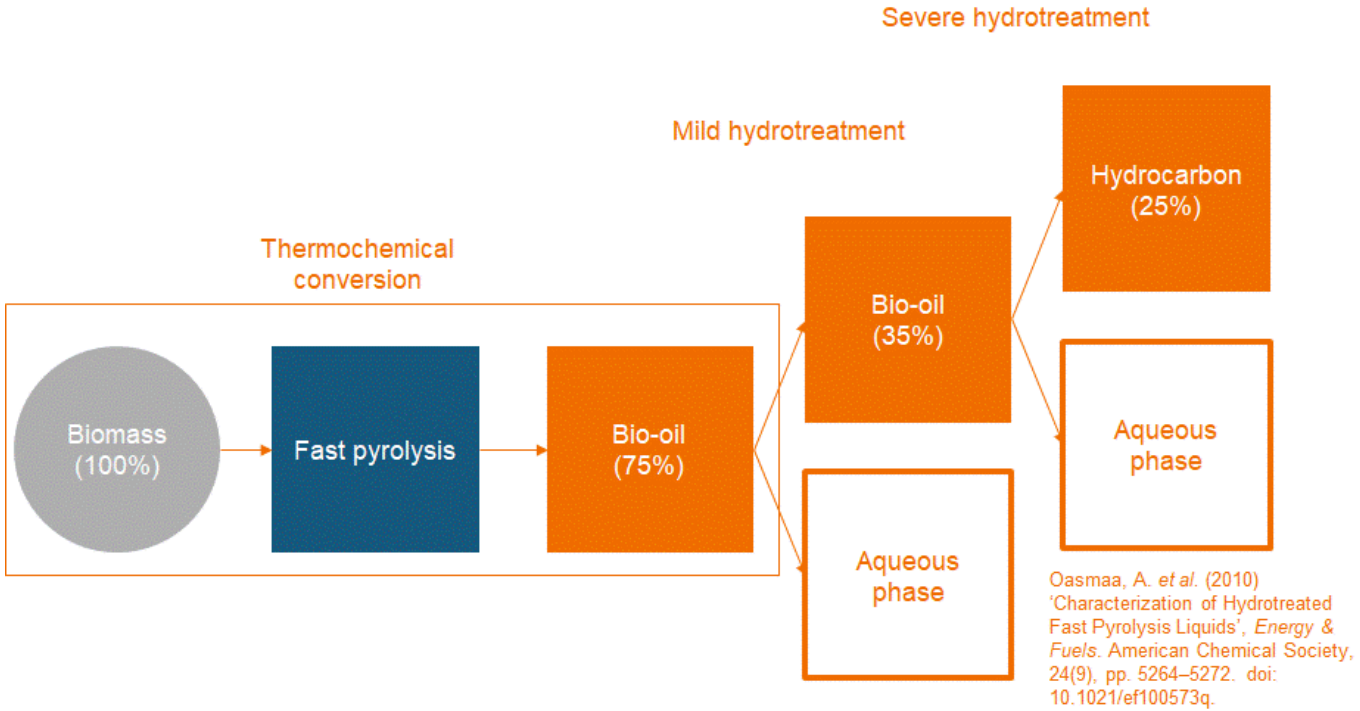
Biofuels from lignocellulosic biomass by liquefaction



Biofuels from lignocellulosic biomass by liquefaction

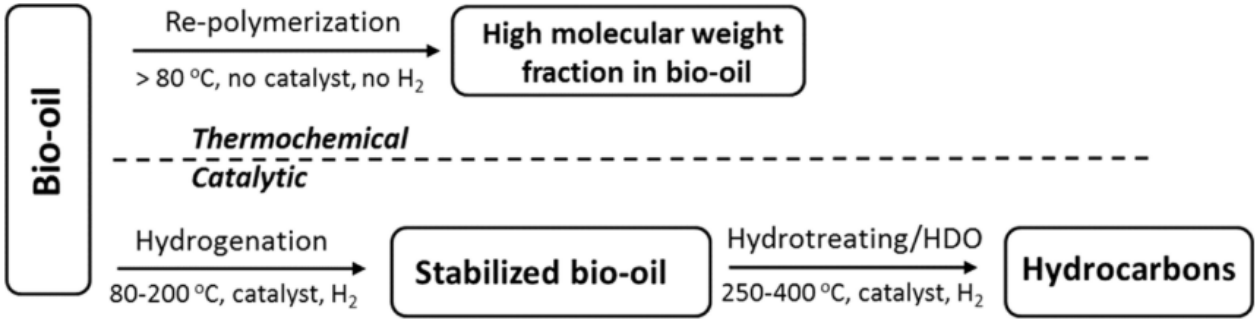


Bio-oils liquefaction by fast pyrolysis and upgrading by HDO



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.

Instability of bio-oils

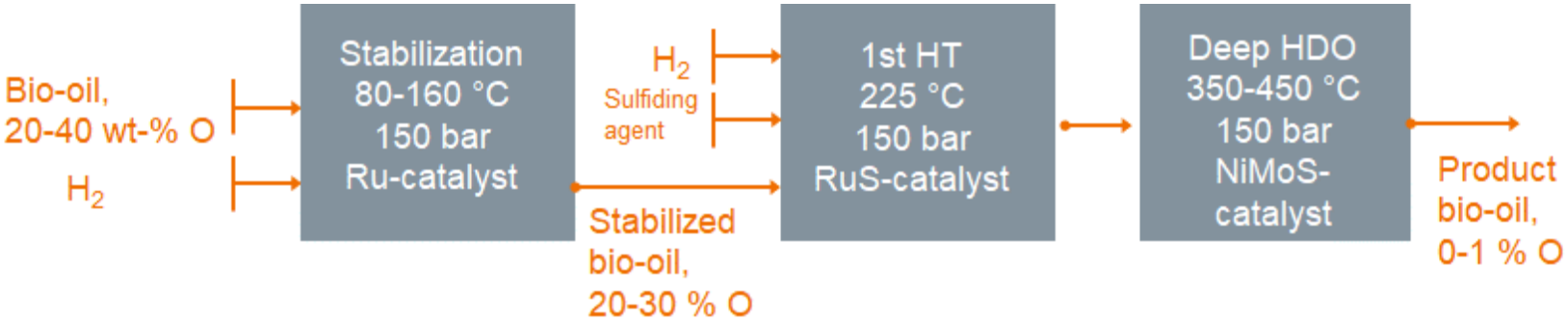


- Bio-oils tends to thermally repolymerize and form plugs in process units
- First signs of thermal condensation at <100 °C, severe at high temperature
- High carbohydrate and carbonyl content

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



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.

VTT activities in bio-oils upgrading by HDO

- BL2F – Black liquor to fuel
  - Integrated HTL and upgrading of black liquor to fuels
  - Performing the HDO in near-critical or supercritical water
- BioFlex
  - Low cost methods to produce marine fuels by fast pyrolysis and upgrading by fixed bed HDO
- CaSH (Catalytic Slurry Hydrotreatment)
  - Catalyst development, regeneration and recovery for slurry-phase hydrotreatment of bio-oil

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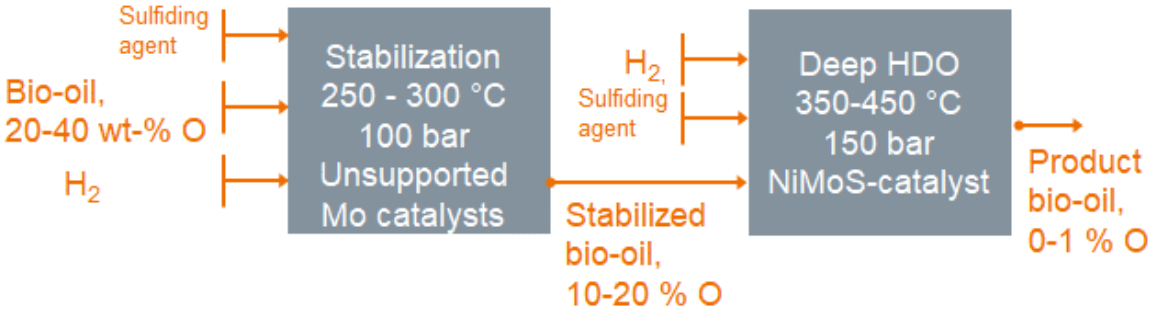
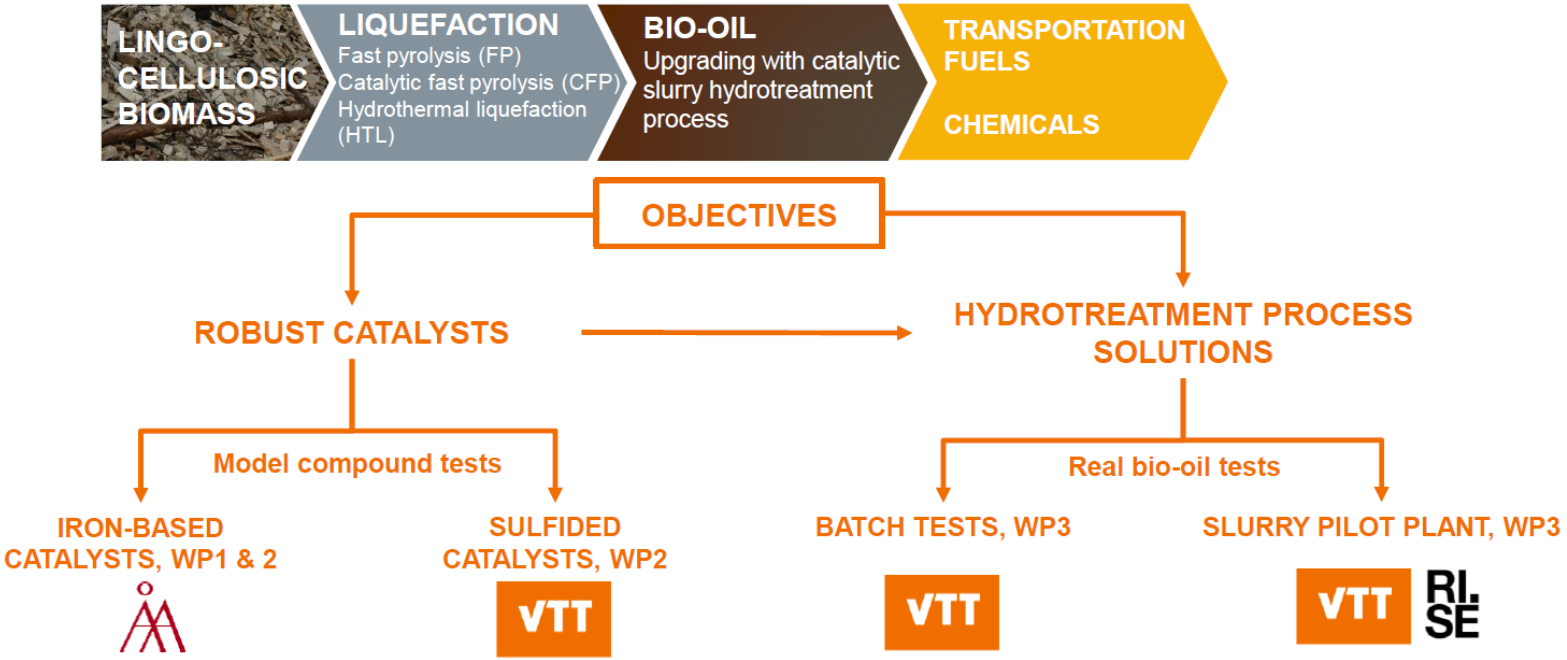
Catalytic slurry hydrotreatment

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

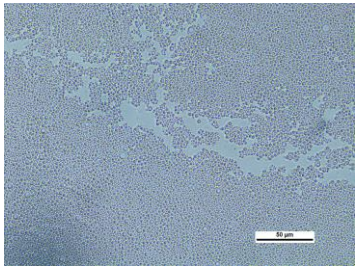


CaSH - Catalytic slurry hydrotreatment



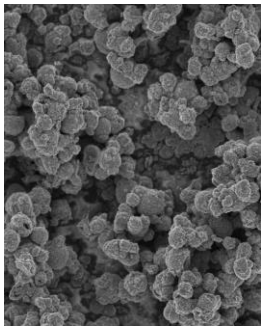
Preparation of unsupported Mo and promoted Mo catalysts

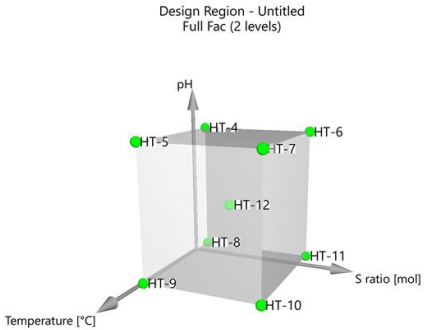
Emulsion- templated synthesis



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

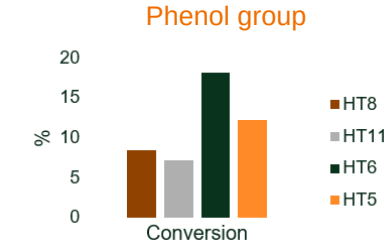
One-pot hydrothermal precipitation

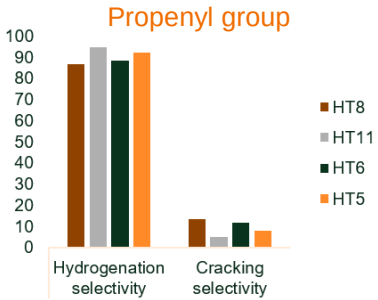


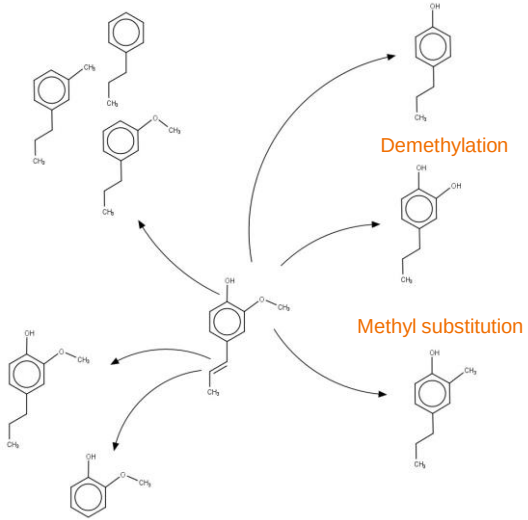


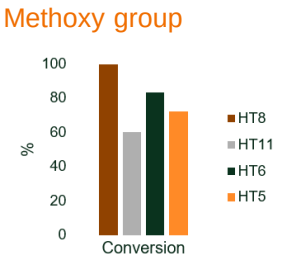
Catalyst properties and HDO activity correlation with:
- Synthesis pH
- Synthesis temperature
- Sulfur amount in synthesis

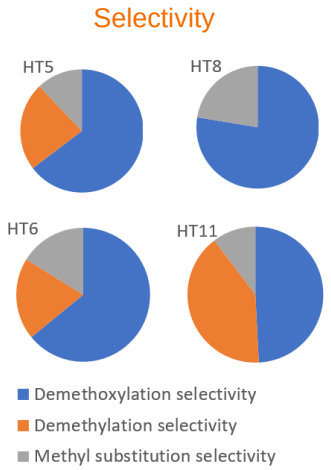
Model component studies - catalyst preparation affecting HDO activity











Tests with real bio-oils

BATCH TEST RUNS

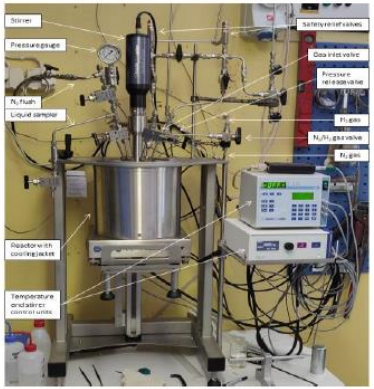
- ✓ Batch reactor operation validated with model compounds
- ➢ Transition to real bio-oil starting in early 2022

ACTIVITIES

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

SLURRY PILOT PLANT

- ➢ 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.



Semi-batch testing of fast pyrolysis bio-oil HDO

- Semi-batch reactor setup with continuous gas phase and batch liquid phase
  - Prevention of hydrogen depletion in experiments with feeds of high hydrogen uptake
  - Enables continuous monitoring of gas phase

Preliminary results with real bio-oil feed

Feed bio-oil			80%	15%	Water	26%		
Catalyst	Temperature (°C)	Pressure (bar)	Oil carbon content, wt-% (dry)	Oil oxygen content (difference), wt-% (dry)	Degree of deoxygenation, oil phase, mass-based (dry)	Oil yield, mass-based (dry)	Carbon recovery to oil, mass-based	Mass balance (all)
VTT Unsupported CoMoS	300	30	80%	12%	17%	82%	82%	88%
Commercial supported CoMoS	300	30	77%	13%	9%	75%	72%	85%
VTT Unsupported CoMoS	350	30	81%	10%	31%	89%	90%	90%
VTT Unsupported CoMoS	350	30	80%	12%	21%	94%	94%	92%
VTT Unsupported CoMoS	350	60	82%	10%	32%	96%	98%	95%

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VTT Unsupported CoMoS	300	30	80%	12%	17%	8		
Commercial supported CoMoS	300	30	77%	13%	9%	7		
VTT Unsupported CoMoS	350	30	81%	10%	31%	8		
VTT Unsupported CoMoS	350	30	80%	12%	21%	9		
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Sampling changed after first three runs to improve mass balance calculations

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T has clear effect on DOD and oil oxygen content

P slightly less important in studied range

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Even though mass-balance deviation makes comparison challenging, better performance assigned to unsupported catalysts

Summary

- Upgrading of bio-oils to transportation fuels challenging due to instability of bio-oils and impurities in bio-oils (sulfur etc.)
- New solutions seeked to commercialize bio-oils upgrading by HDO
  - Slurry hydroprocessing is a potential alternative enabling continuous addition and removal of the catalyst
  - Promising results achieved with unsupported MoS catalysts developed at VTT
- Next step: slurry hydroprocessing piloting using the developed catalysts

Thank you!

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beyond

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