Production of aviation and marine fuels by biomass liquefaction and upgrading by HDO

Research professor Juha Lehtonen

Sari Rautiainen, Tyko Viertiö

VTT

BL2F

Transforming Black Liquor to Biofuel

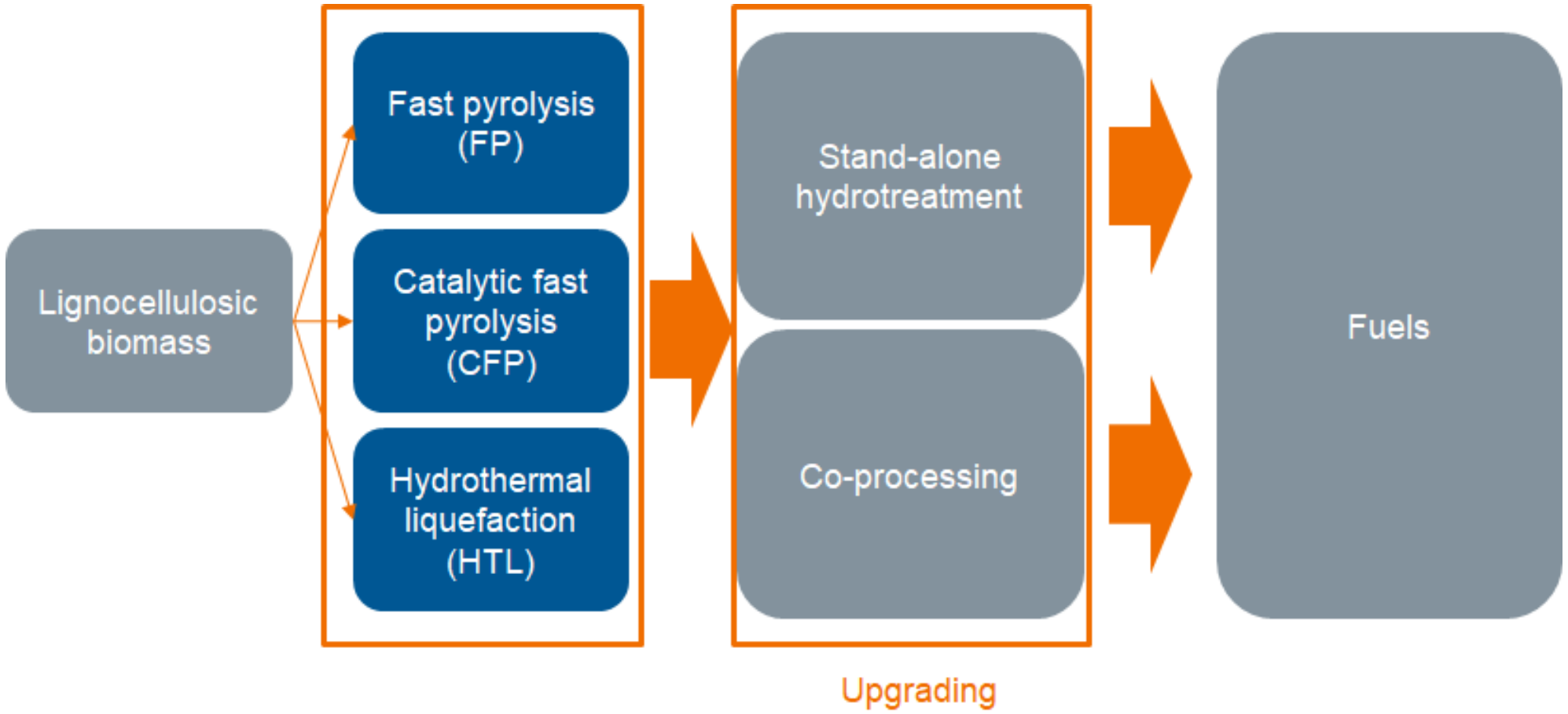
This project has received funding from the European Union Grant Number 884111

Outline

1. Introduction to biomass liquefaction and upgrading by hydrotreatment
2. Catalytic slurry hydrotreatment
3. Hydrothermal HDO
4. Summary

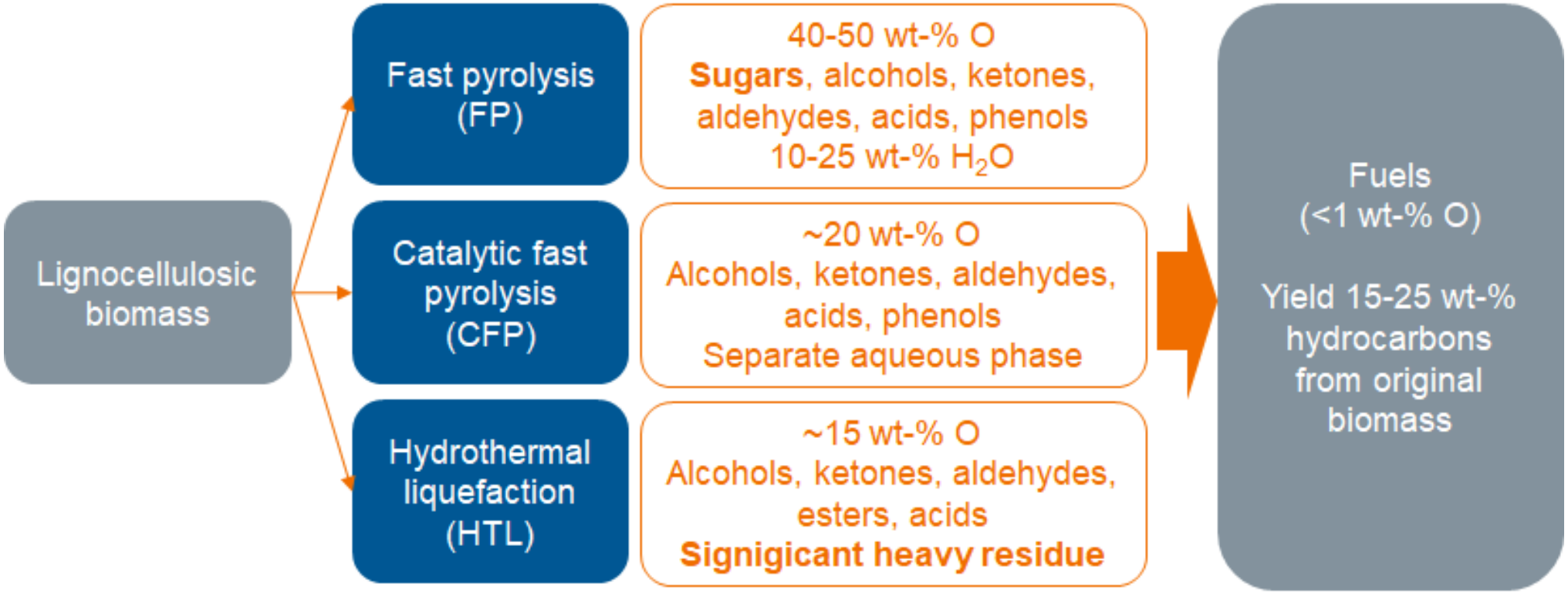
This project has received funding from the European Union Grant Number 884111

Biofuels from lignocellulosic biomass by liquefaction



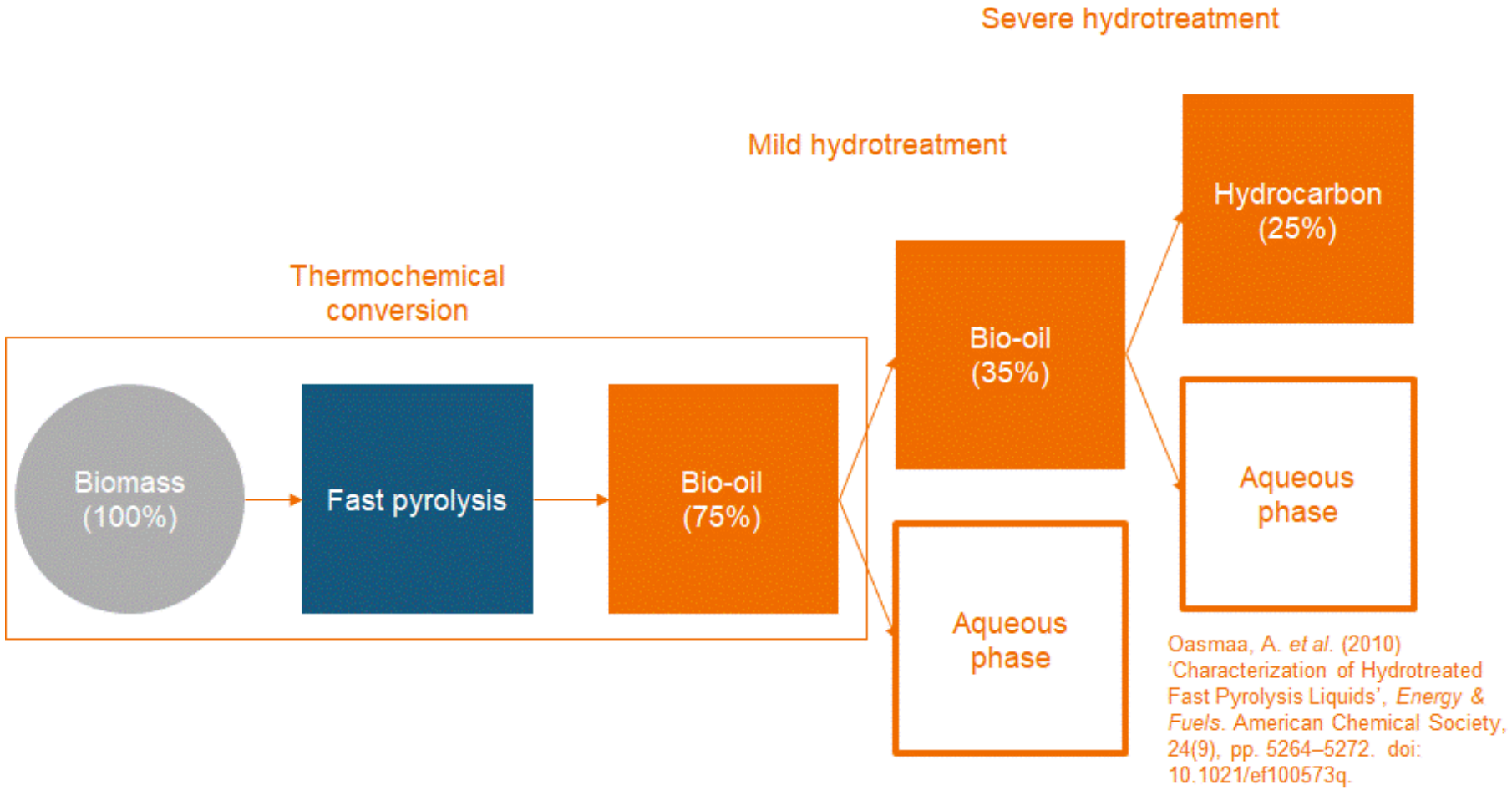
This project has received funding from the European Union Grant Number 884111

Biofuels from lignocellulosic biomass by liquefaction



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

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.

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

Instability of bio-oils

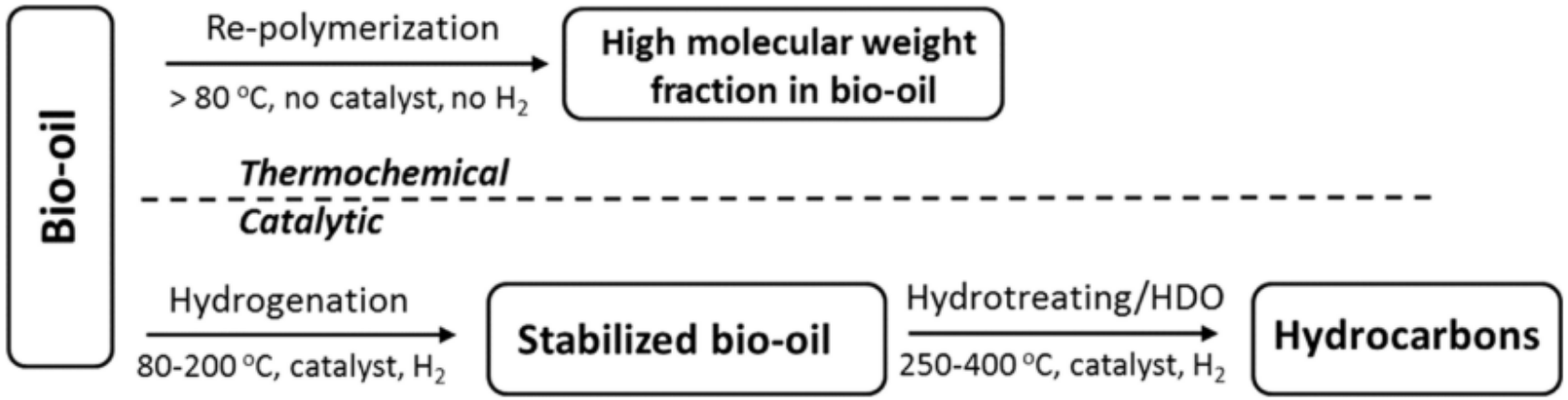


Figure from Wang *et al.* 2016

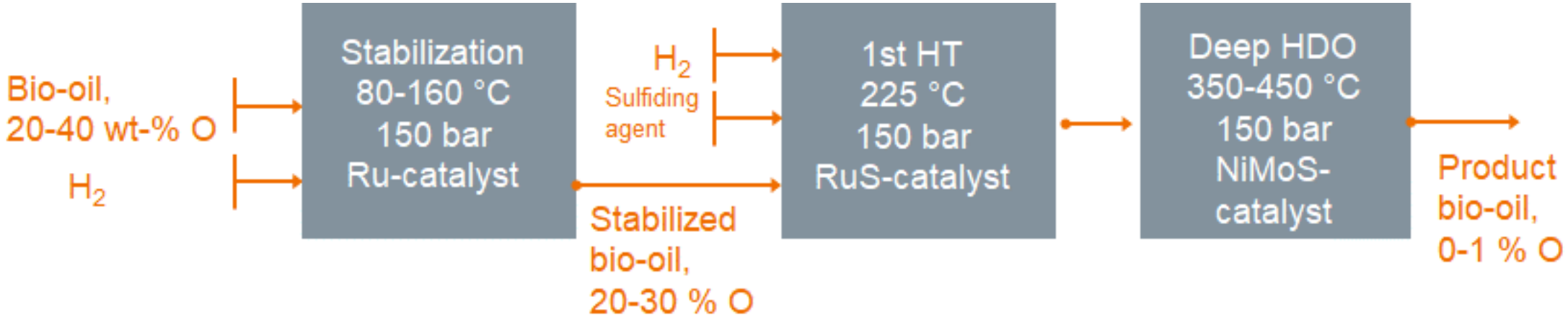
- Bio-oils tends to thermally repolymerize and form plugs in process units
- First signs of thermal condensation at <100 °C, severe at high temperature
- High carbohydrate and carbonyl content

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

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



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

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
- Catalytic Slurry Hydrotreatment
  - Catalyst development, regeneration and recovery for slurry-phase hydrotreatment of bio-oil

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

BUSINESS FINLAND

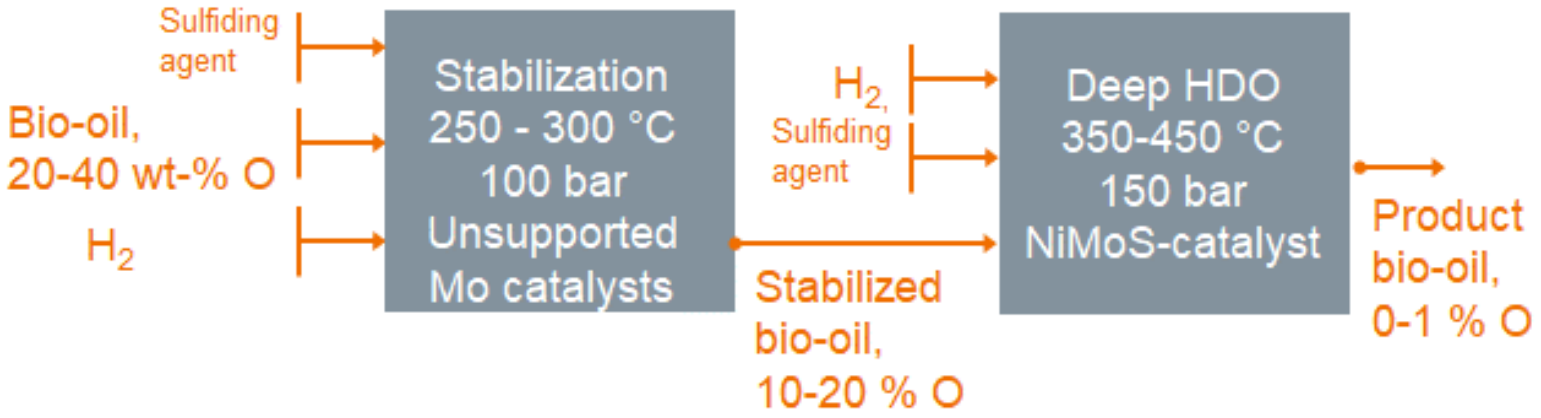
This project has received funding from the European Union Grant Number 884111

Catalytic slurry hydrotreatment

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

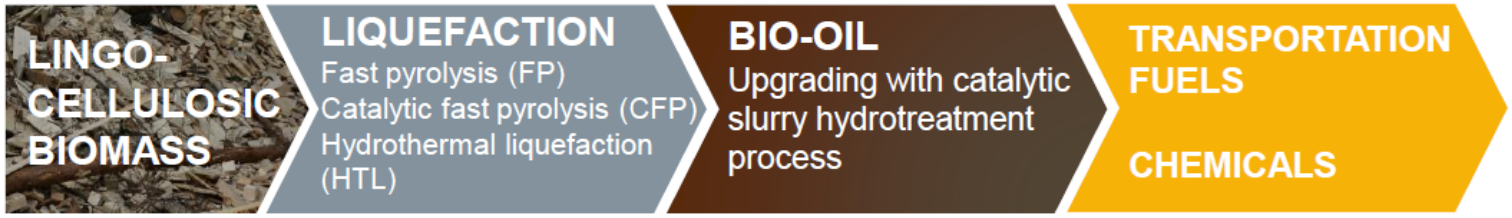
Alternative: slurry hydrotreatment applied for the stabilisation

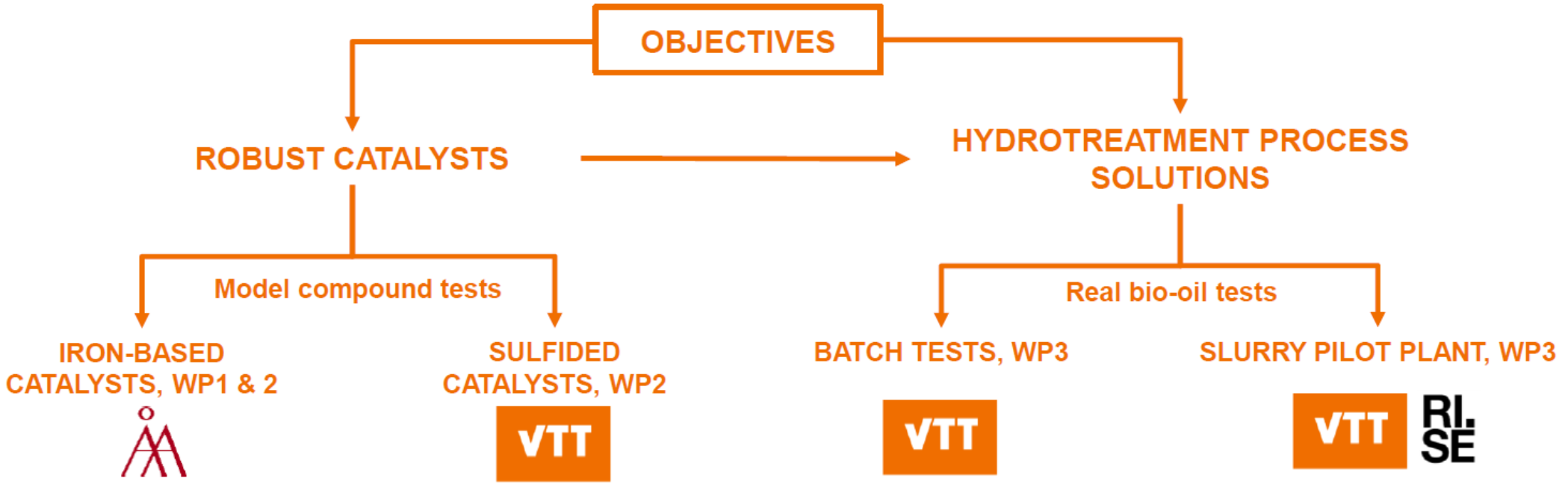
- State-of-the-art: multi-staged approach
  - Bio-oil stabilization by slurry hydrotreatment applying sulfided Mo-based catalysts
    - Continuous addition of fresh and removal of spent catalyst enabled
  - Rest oxygen removal by fixed bed hydrotreatment by supported sulfided catalysts
    - Severity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



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

CaSH - Catalytic slurry hydrotreatment

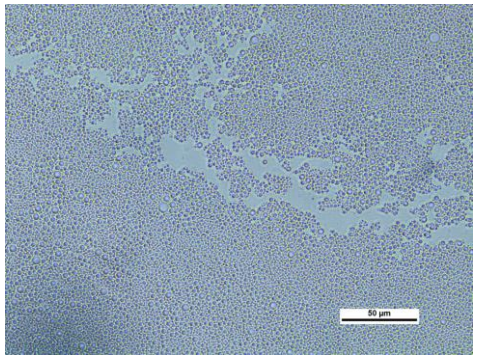




This project has received funding from the European Union Grant Number 884111

Preparation of unsupported Mo and promoted Mo catalysts

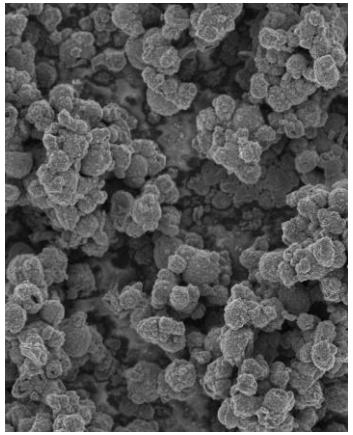
Emulsion- templated synthesis

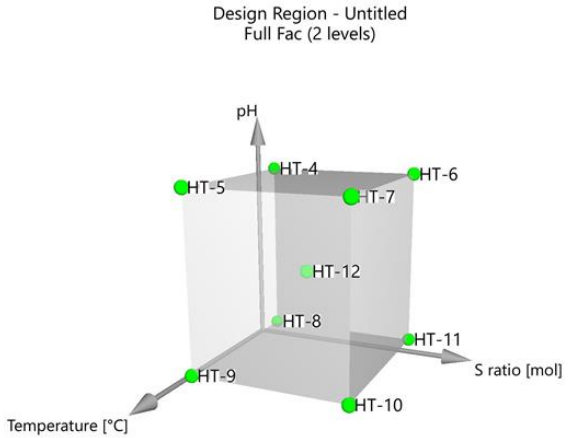


HDO activity correlation with:

- Emulsion properties
- Precursor properties
- Emulsion sulfidation

One-pot hydrothermal precipitation





Catalyst properties and HDO activity correlation with:

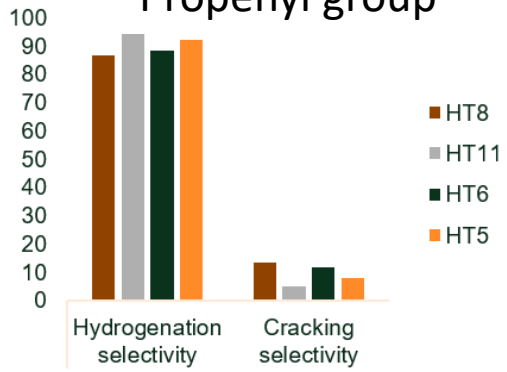
- Synthesis pH
- Synthesis temperature
- Sulfur amount in synthesis

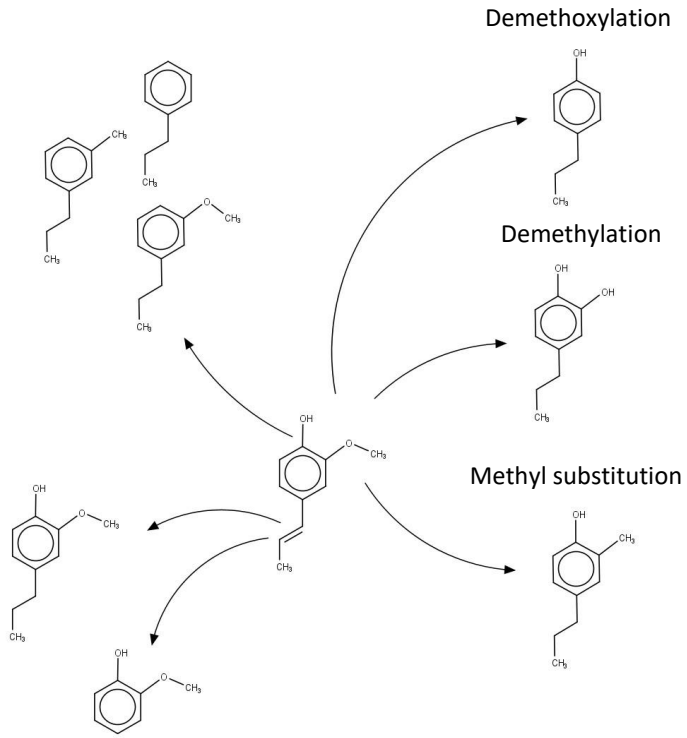
This project has received funding from the European Union Grant Number 884111

Catalyst preparation affecting HDO activity

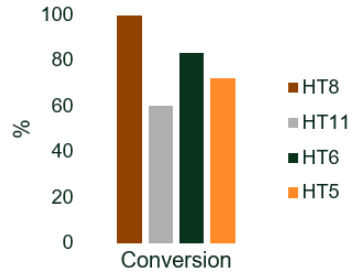
Phenol group

Propenyl group

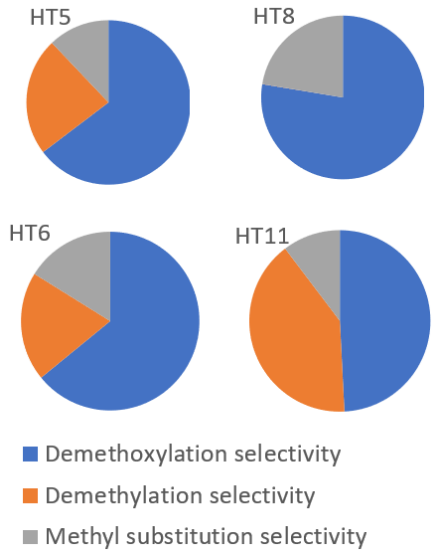




Methoxy group



Selectivity



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

Tests with real bio-oils

BATCH TEST RUNS

VTT

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

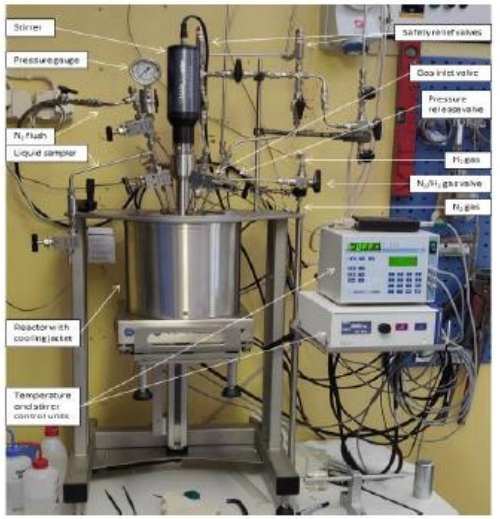
ACTIVITIES

- ➢ 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.

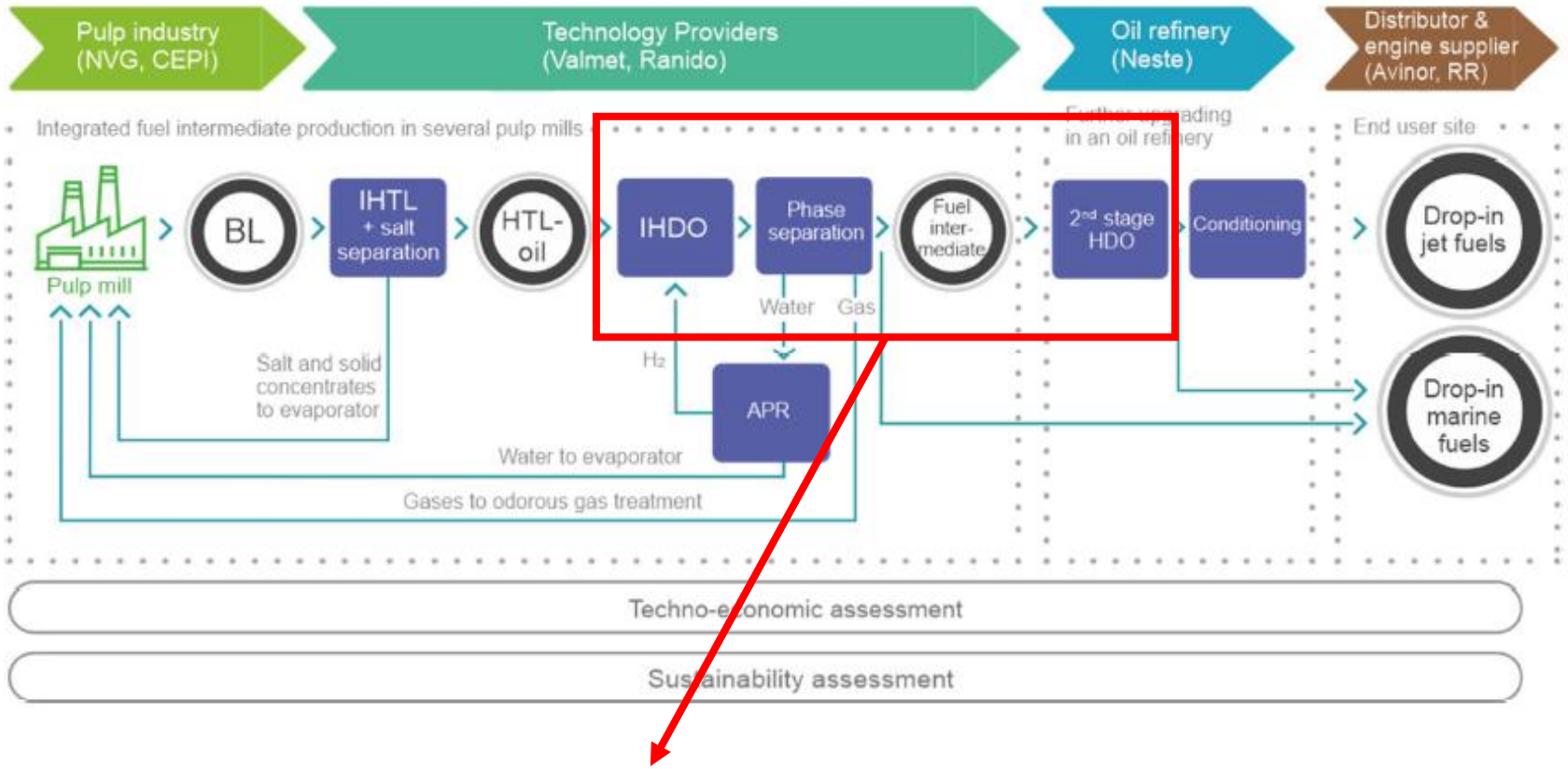


This project has received funding from the European Union Grant Number 884111

Hydrothermal HDO

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

Another alternative: BL2F upgrading concept



IHDO = HDO in hydrothermal conditions

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

Hydrothermal HDO

HDO in hydrothermal conditions in BL2F

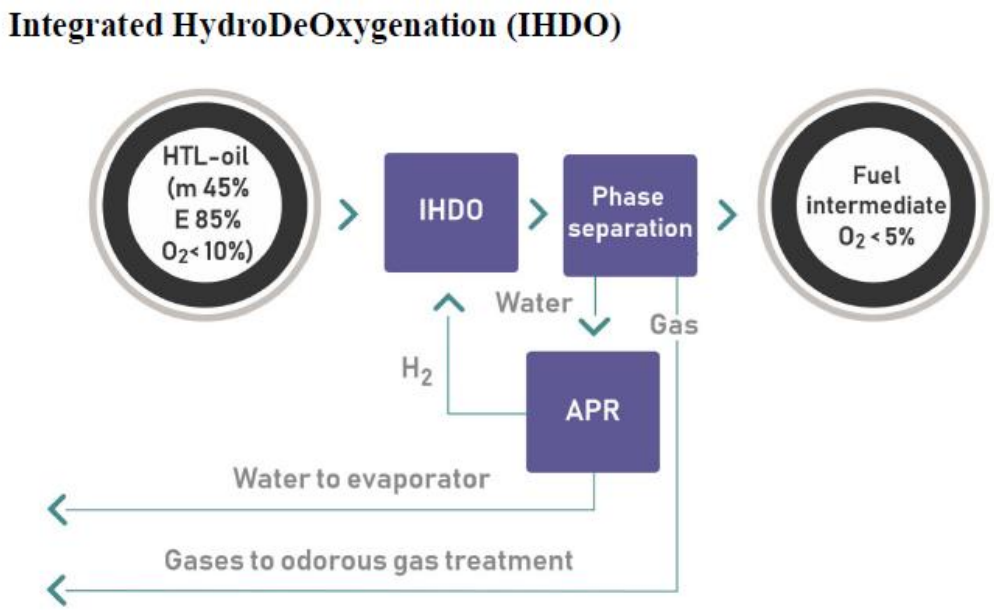
- Utilization of biocrude from HTL in aqueous environment
- Performing hydrothermal catalytic HDO in near critical or supercritical conditions

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

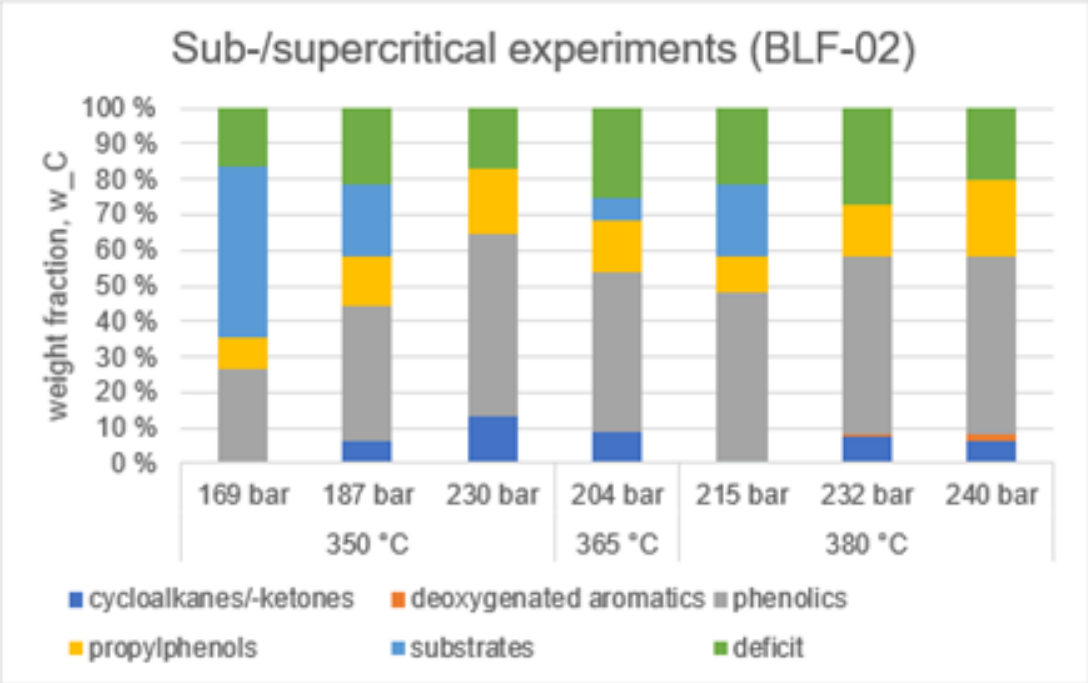


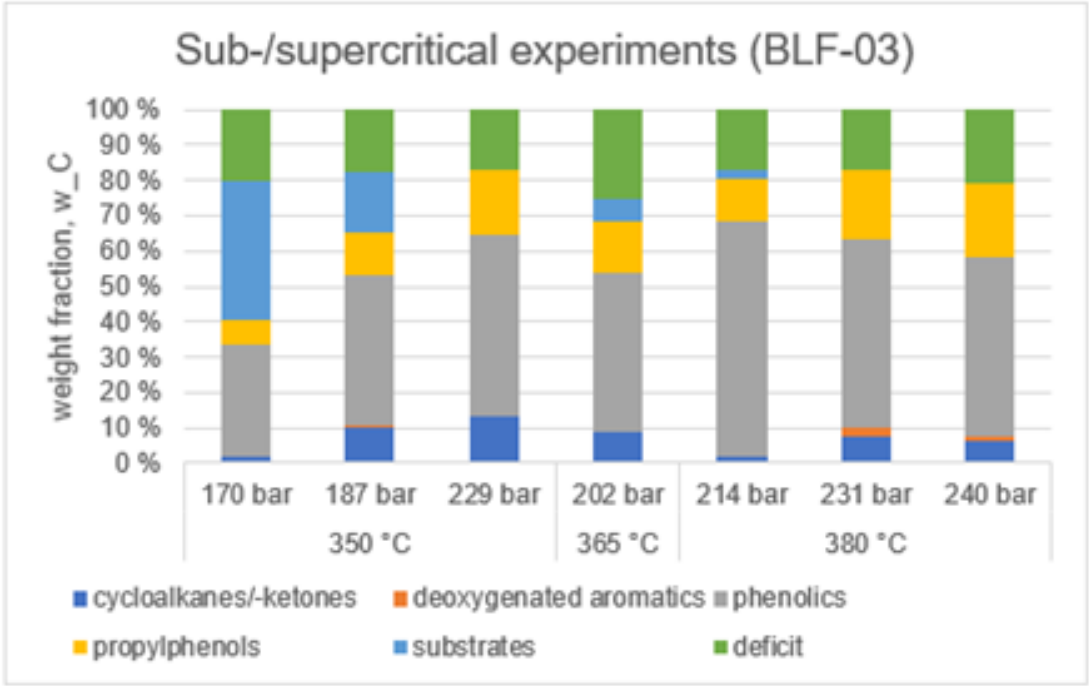
Green Chem., **23**, 2021, 1114; *Catalysis Communications*, **90,** 2017, 47-50; *Chemical Engineering Journal,* **407,** 2021, 126332.

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

Hydrothermal HDO – model component testing

- HDO experiments of isoeugenol and 4-methylcatechol
  - 2 h reaction time, 2 g model compounds, 1g catalyst, 150 ml H_2O

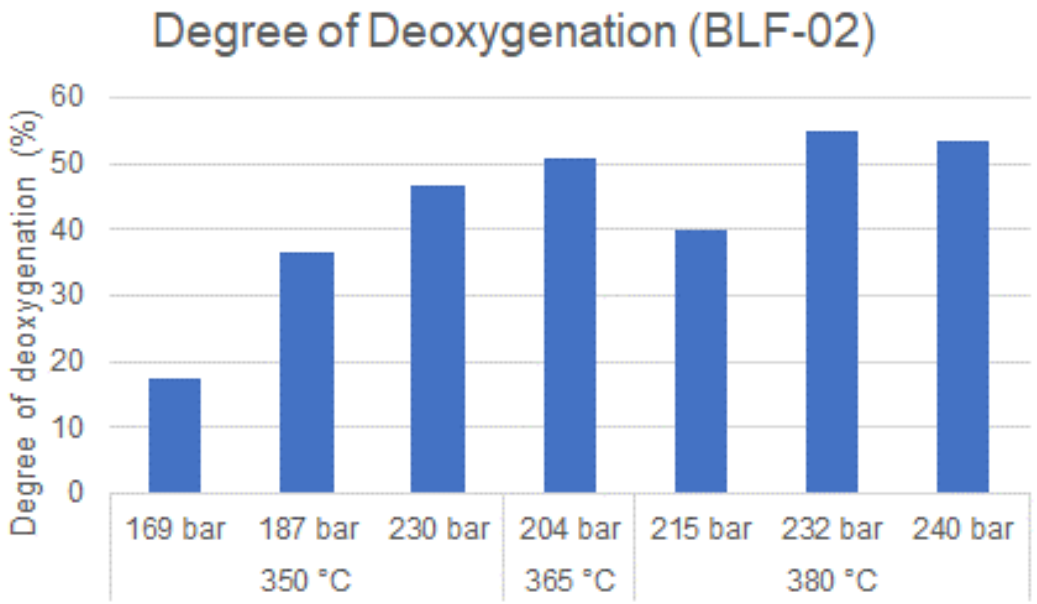


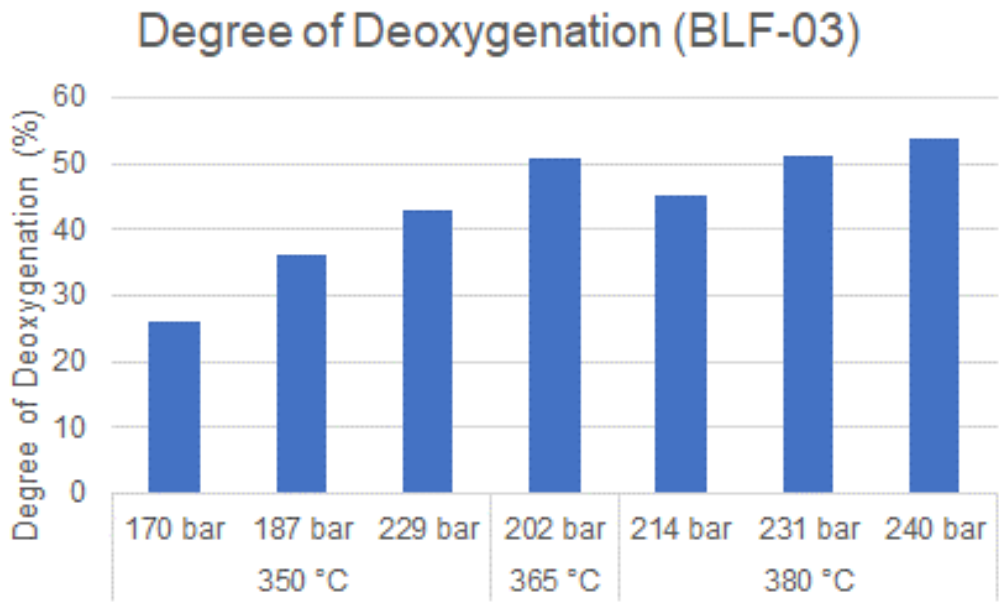


This project has received funding from the European Union Grant Number 884111

Hydrothermal HDO – model component testing

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





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

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
- Next steps: tests with real bio-oil feeds

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

Thank you!

Get in touch with the project:

- Coordinator: Prof. Dr. Tero Joronen, Tampere University
- Website: www.bl2f.eu

 hello@bl2f.eu  @BL2F_EU  BL2F_EU

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