Catalyst Development for HDO & Aqueous Phase Reforming

BL2F Mid-Term Workshop
Research professor Juha Lehtonen

Tyko Viertiö, Sari Rautiainen, Jasmiina Palo, Matti Reinikainen

VTT

BL2F
Transforming Black Liquor to Biofuel

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

Outline

1. Catalysts and processes for hydrodeoxygenation (HDO)
2. Catalyst development for aqueous phase reforming (APR)
3. Summary

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Hydrodeoxygenation (HDO)

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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 increases the solubility of hydrogen and decreases coke formation
- BioFlex
  - Setting the requirements for oxygen-content and storage stability for power plants and marine fuels
- Catalytic Slurry Hydrotreatment
  - Catalyst development, regeneration and recovery for slurry-phase hydrotreatment of bio-oil

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BUSINESS FINLAND

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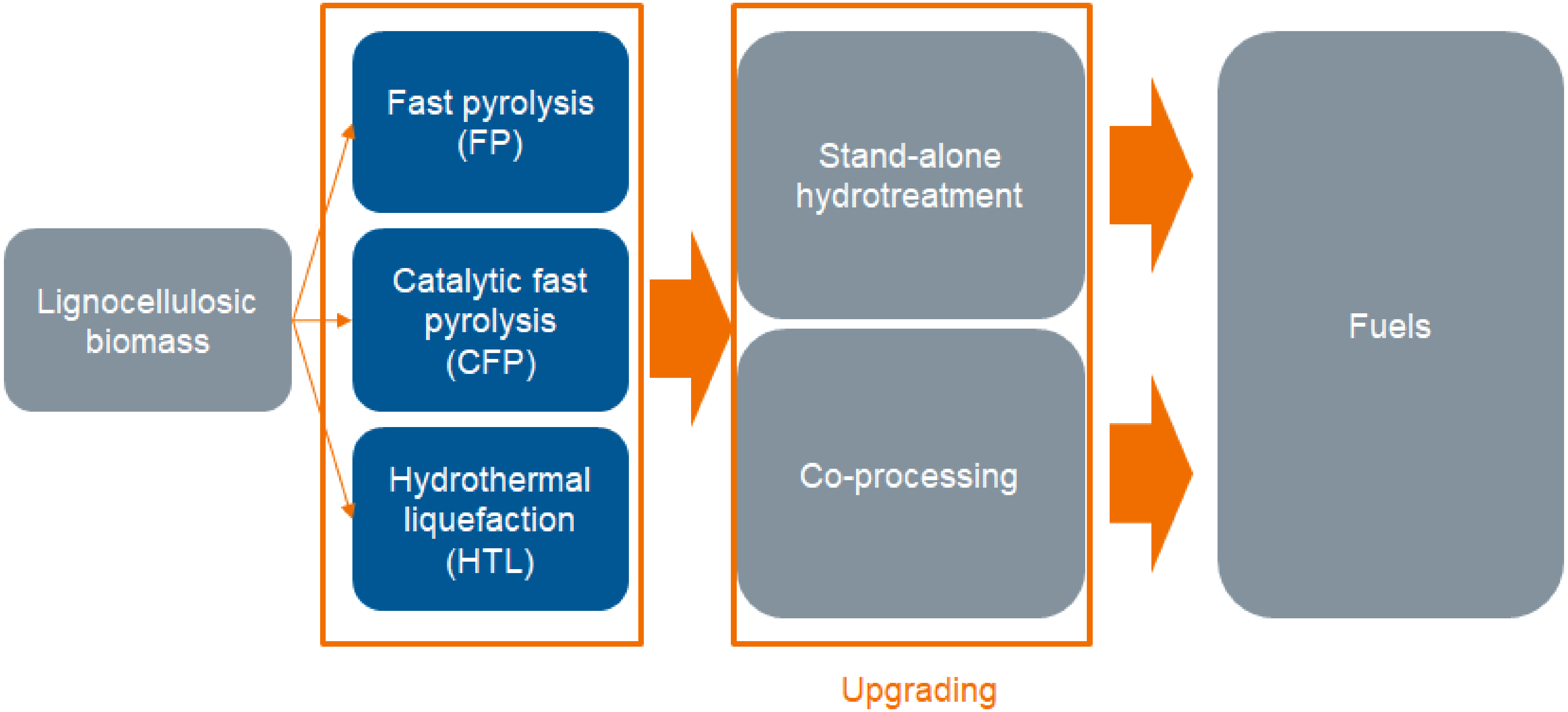
Biofuels from lignocellulosic biomass by liquefaction



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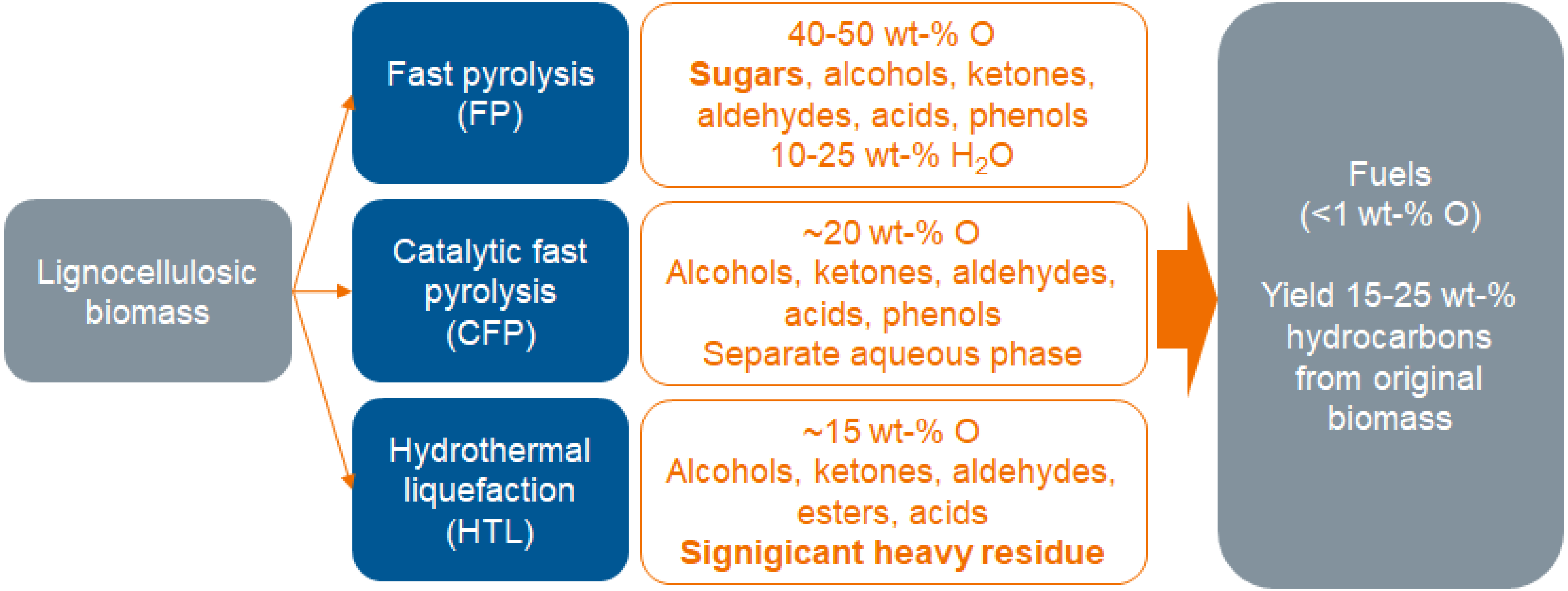

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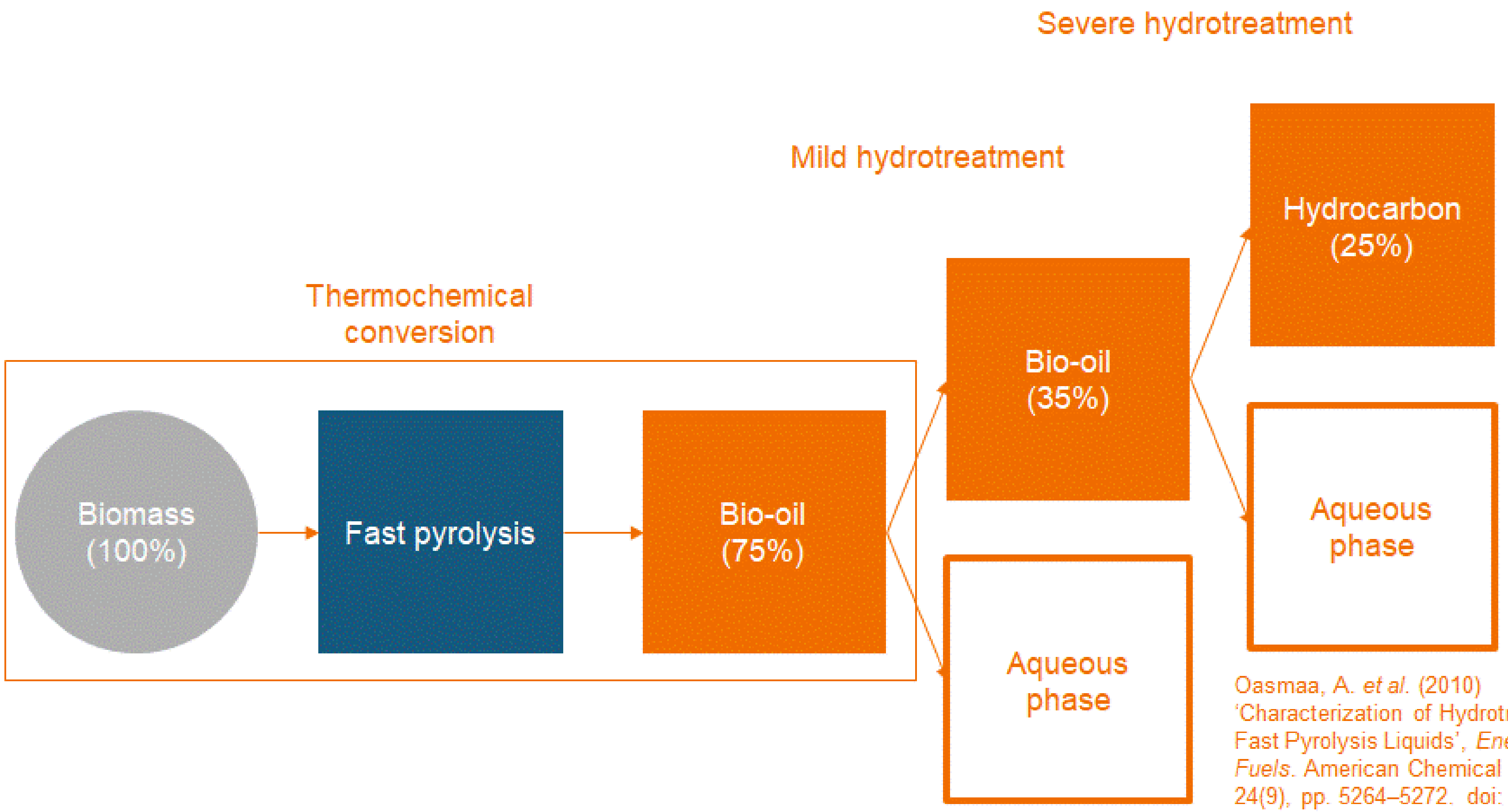
Bio-oils upgrading by HDO



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

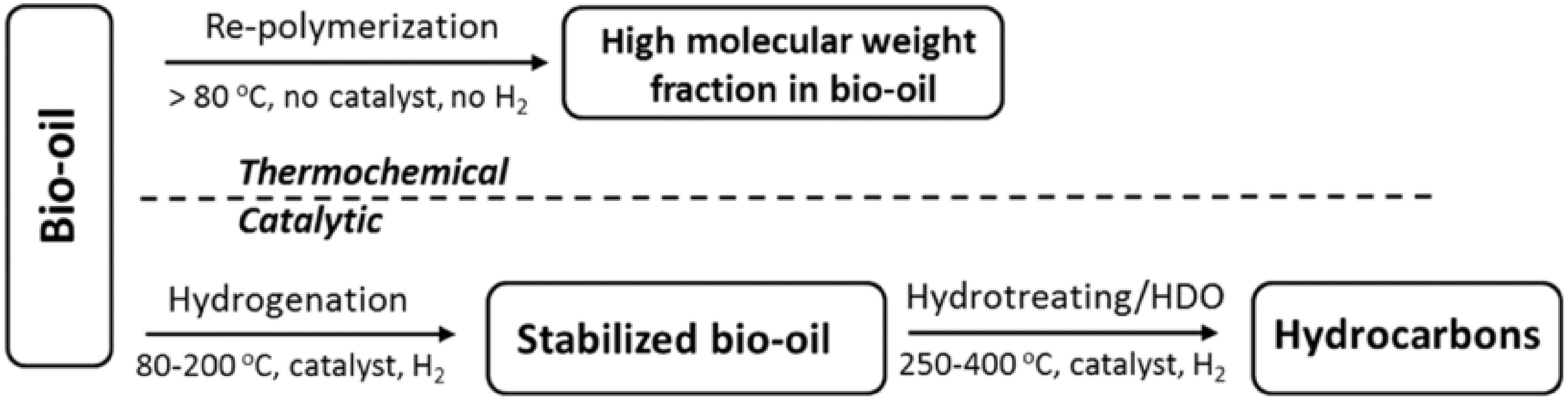

Figure from Wang *et al.* 2016

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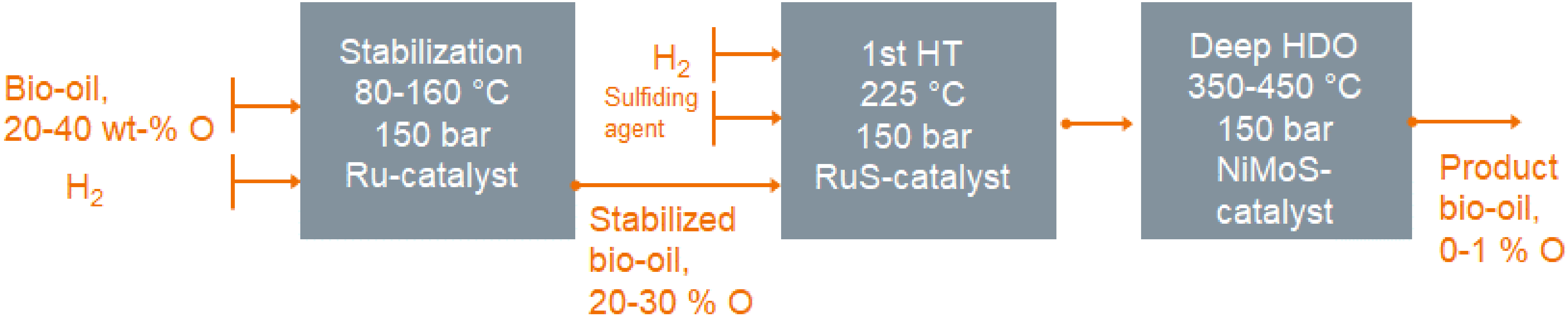
Wang, H. *et al.* (2016) 'Bio-oil Stabilization by Hydrogenation over Reduced Metal Catalysts at Low Temperatures', *ACS Sustainable Chemistry & Engineering*. American Chemical Society, 4(10), pp. 5533–5545. doi: 10.1021/acssuschemeng.6b01270.

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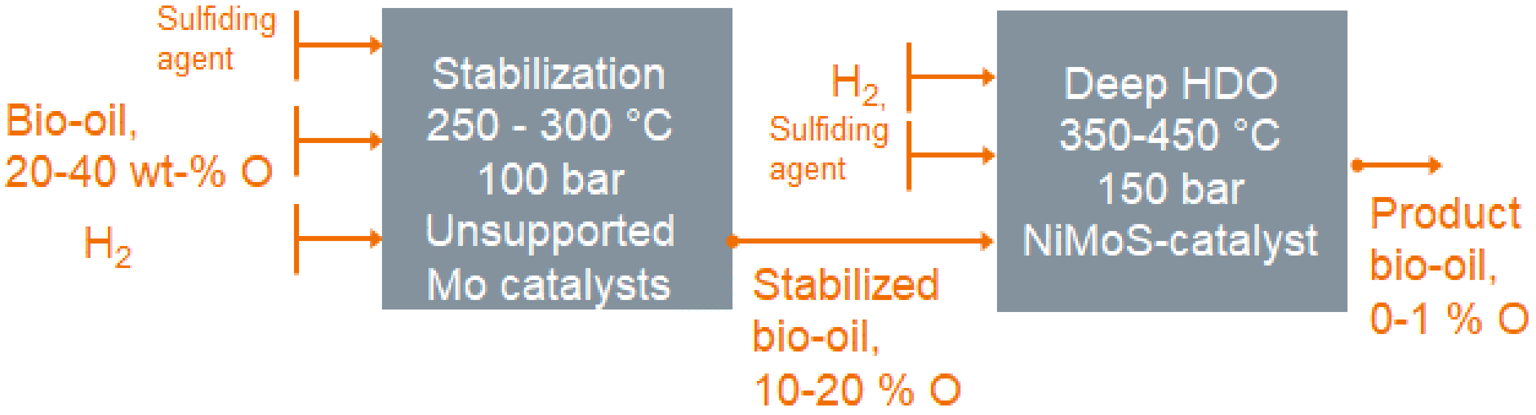
Zacher, A. H. *et al.* (2019) 'Technology advancements in hydroprocessing of bio-oils', *Biomass and Bioenergy*. Pergamon, 125, pp. 151–168. doi: 10.1016/J.BIOMBIOE.2019.04.015.

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



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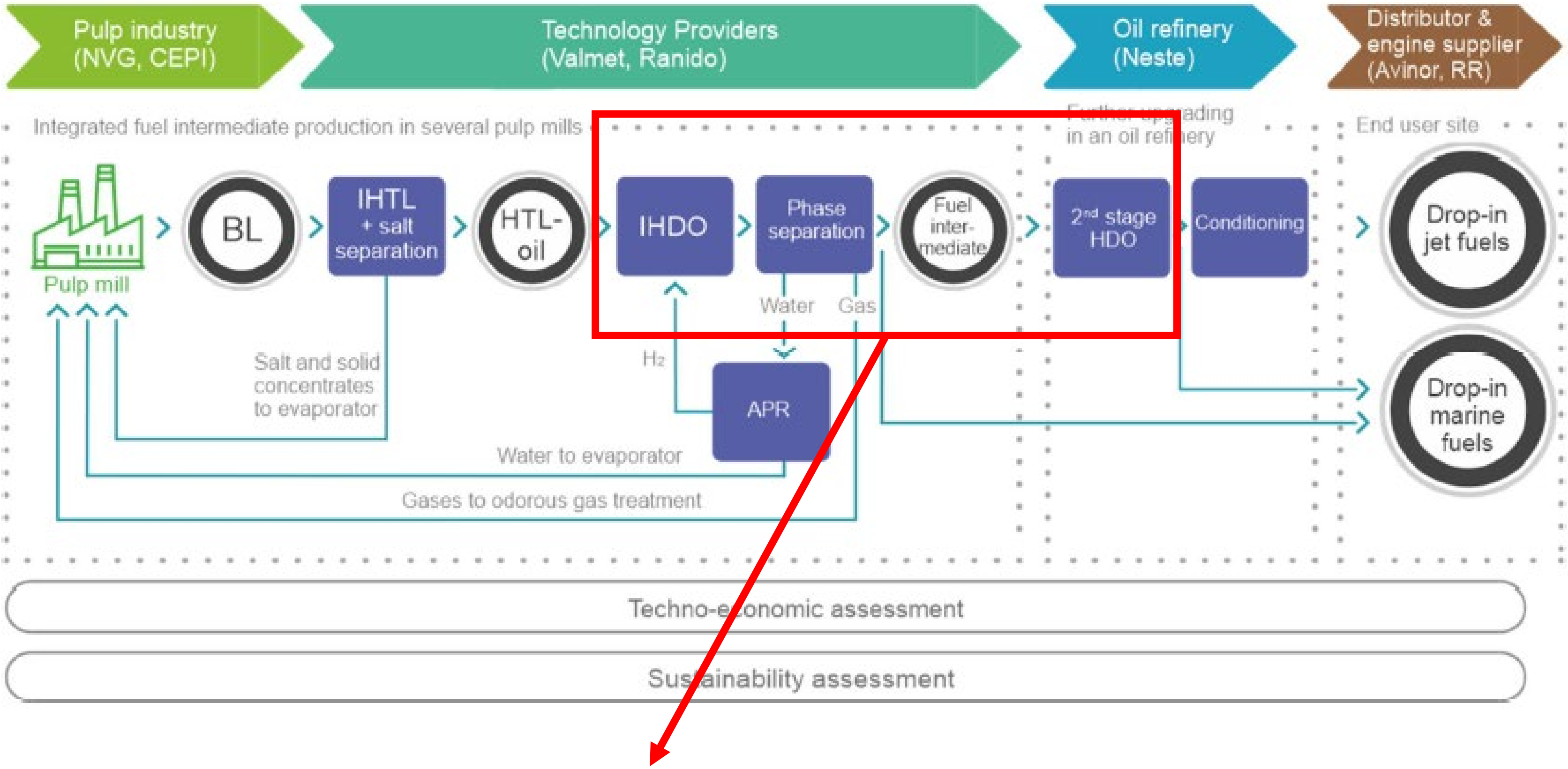
Another alternative: BL2F upgrading concept



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

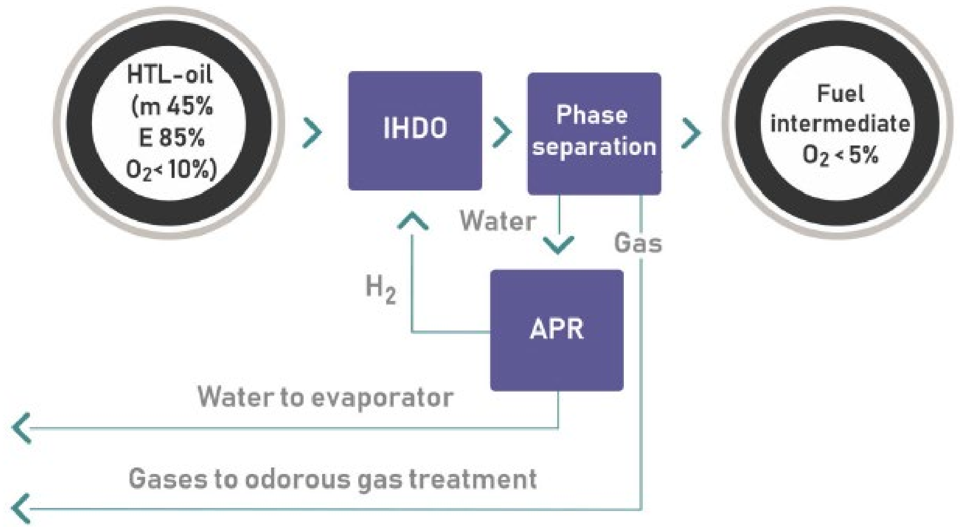
Benefits:

- 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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Aqueous phase reforming (APR)

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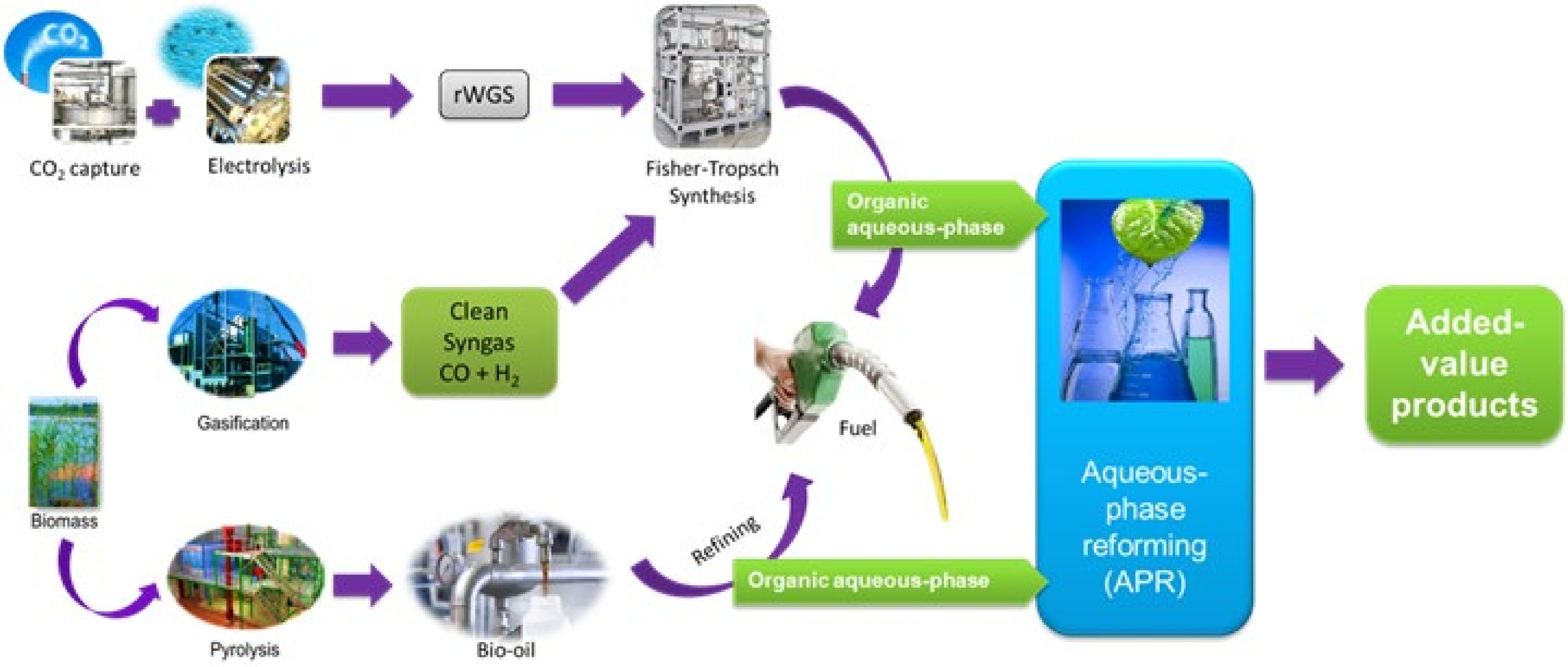
APR – A process to produce hydrogen from aqueous waste streams



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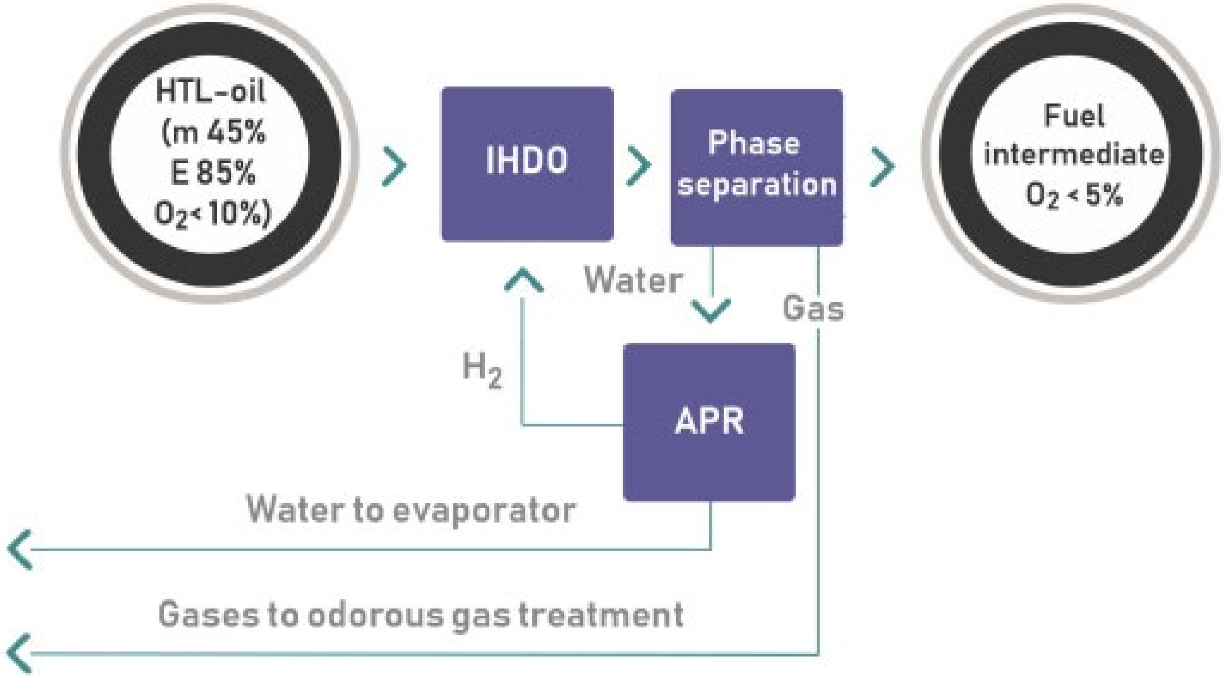
Coronado, I., 2021, Catalytic Aqueous-Phase Reforming of Biorefinery Water Fractions, Aalto University publication series DOCTORAL DISSERTATIONS, 3/2021.

APR in BL2F – way to produce hydrogen for IHDO



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Aqueous phase reforming

Typical reactions of APR:

- Full reforming of C:O=1:1 oxygenated hydrocarbons

$$C_nH_{2y}O_n(l) \leftrightarrow nCO\ (g) + yH_2\ (g) \quad (1)$$

- Full reforming of alcohols:

$$C_nH_{2n+1}OH(l) + (n-1)H_2O\ (l) \leftrightarrow nCO\ (g) + 2nH_2\ (g) \quad (2)$$

- WGS reaction:

$$CO\ (aq) + H_2O\ (aq) \leftrightarrow CO_2(g) + H_2\ (g) \quad (3)$$

Basis of APR:

- Typical conditions: 200 – 250 ºC, 30 – 50 bar, supported metal catalyst applied
- Catalysts need to be tolerant against hydrothermal conditions
- Catalysts should promote reactions 1-3 to maximize H_2
  - Active catalysts at low temperatures needed due to equilibrium limitations of (3)
- Current TRL 2-3:
  - Long term stability of catalyst to be solved
  - Catalyst not able to break C-C bonds in the organic feedstock molecules

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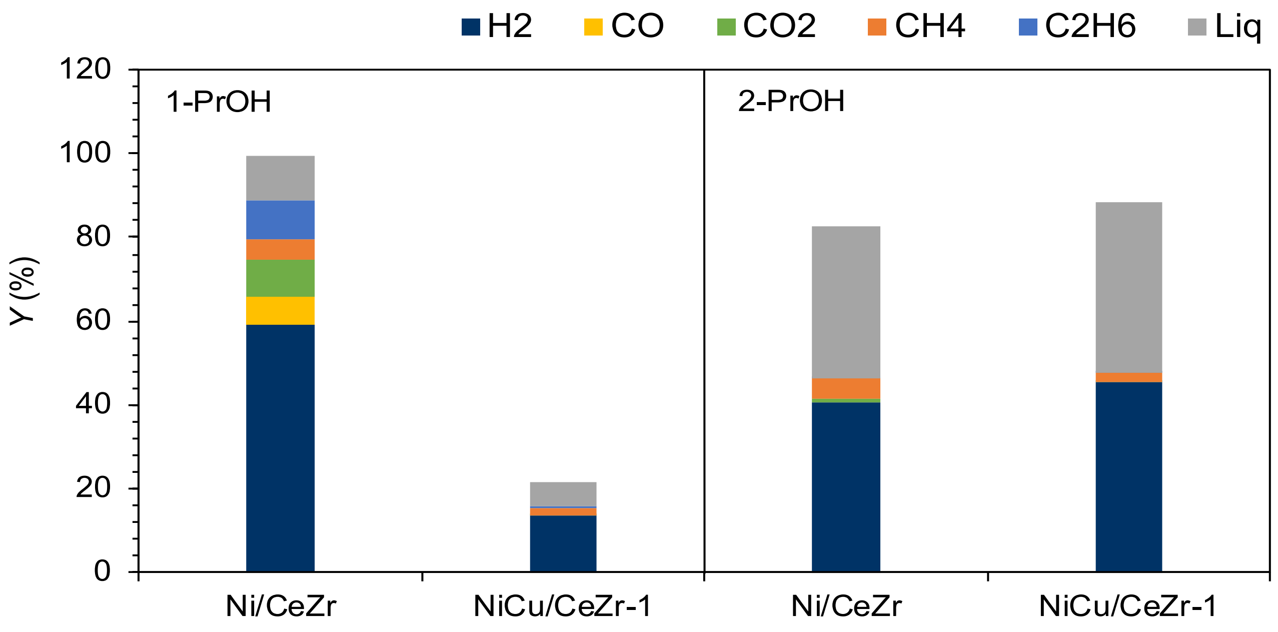
Background for the work in BL2F

- Further development of Ni-based catalysts developed by VTT in previous Aquacat project



Conversion of 1-propanol and 2-propanol over Ni-based catalysts developed in Aquacat project.

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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
    - Hydrothermal HDO
- APR is a new process to convert diluted aqueous solutions of organics to hydrogen and other valuable products
- TRL of APR still relatively low mainly due to catalyst stability questions not solved yet
    - Ni-based catalysts developed by VTT will be further developed in BL2F

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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

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