Catalysts for renewables and sustainable fuels

BL2F Midterm workshop, 22.03.2022

Pavel Kukula, Ranido

BL2F

Transforming Black Liquor to Biofuel

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

Outline

Catalysts for renewables and sustainable fuels

- Introduction of Ranido company
- Catalysts and Processes for Biofuel production
  - Catalytic conversion of Biomass
  - Upgrading of bio-oils
- BioMates Project
  - AFP / HYD / HDO
- BL2F Concept
  - IHTL / IHDO / APR / 2nd stage HDO
- Summary and Outlook

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Ranido

Core business

- Custom catalysts manufacturing and toll manufacturing
- Catalyst scale up from laboratory to commercial production
- Custom R&D in the area of catalysis

Company info

- Founded 2005
- R&D performing micro-SME
- Based in the Czech Republic
- 3 locations: Prague, Kralupy nad Vltavou, Děčín
- See more at: www.ranido.cz

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R&D Projects

- BioMates: Production of hybrid fuels by fast pyrolysis followed by catalytic hydroprocessing

- BL2F: Transformation of black liquor by IHTL and IHDO processes to a high-quality biofuel for aviation and shipping

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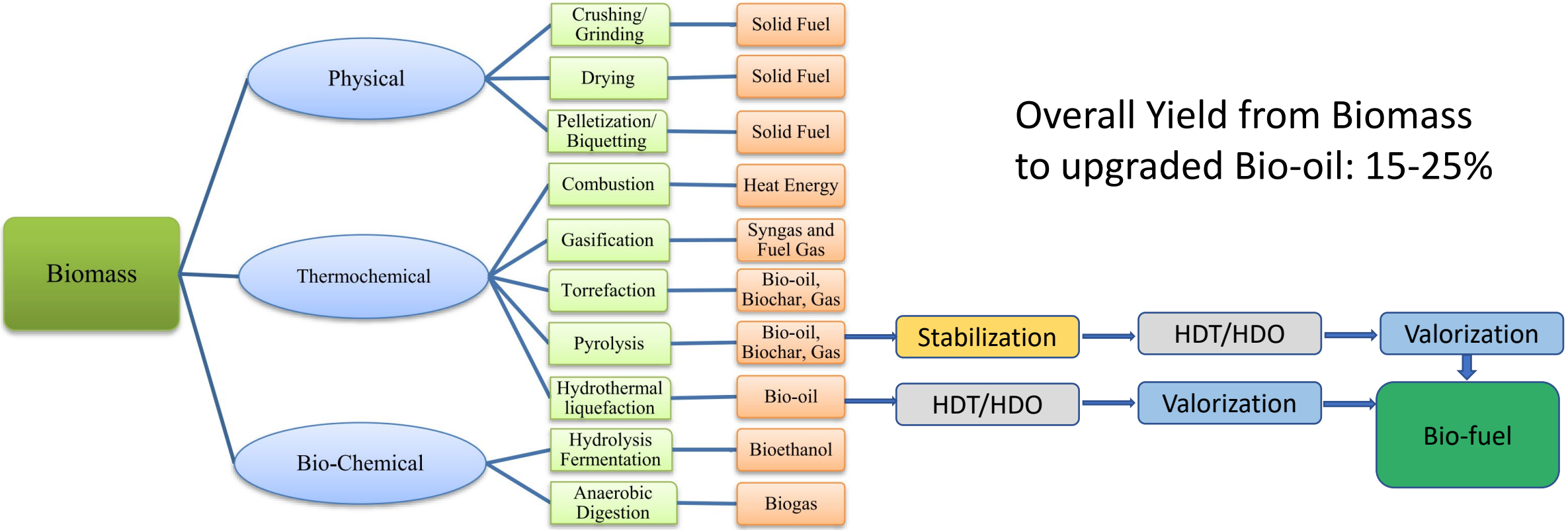
Biomass Conversion



Overall Yield from Biomass to upgraded Bio-oil: 15-25%

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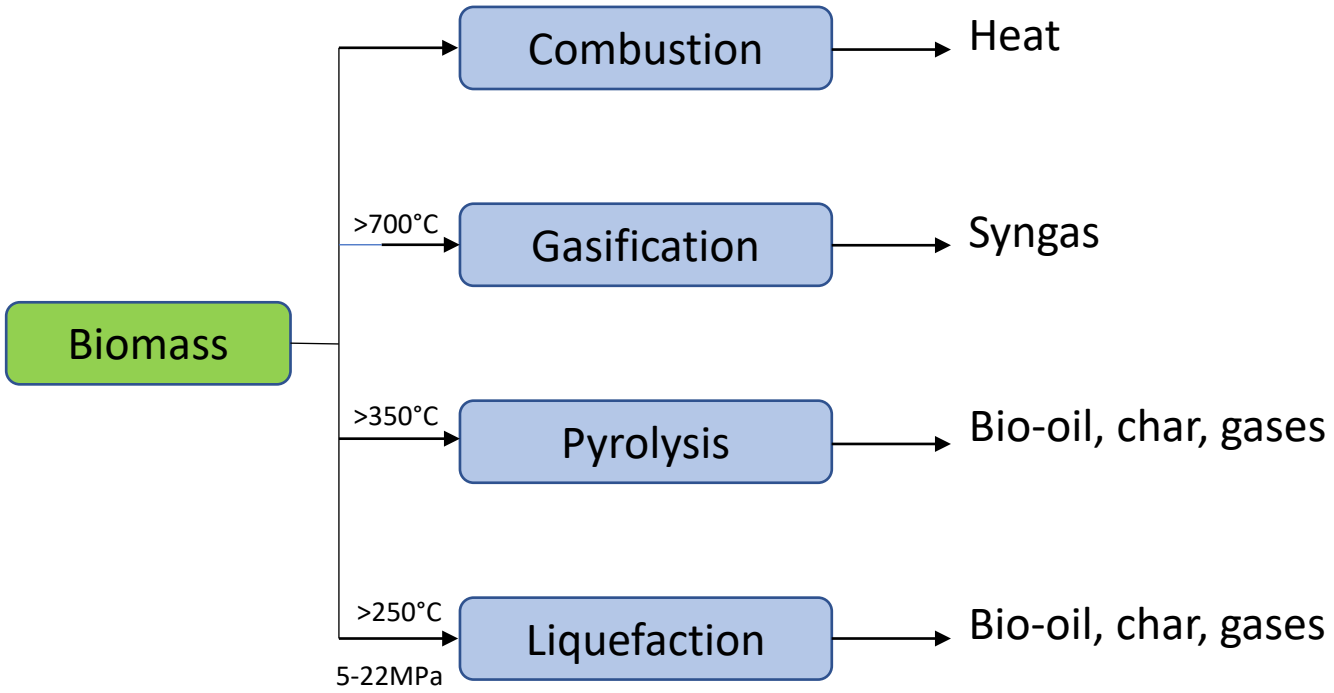
Source: Ong, Hwai Chyuan; et al., Renewable and Sustainable Energy Reviews, 113 (2019) 109266.

Thermochemical Conversion of Lignocellulosic Biomass



Composition of bio-oil:
Acids, Carbonyls, Furans, Phenols, Sugars, HCs, Others

Thermal pyrolysis: C 52%, H 6%, O 42%, HHV 19 MJ/kg

Catalytic pyrolysis: C 78%, H 9%, O 12%, HHV 37 MJ/kg
Catalysts: Na/K2CO3, Ca(OH)2, Zeolites (ZSM-5, HY, HBEA)

Hydrothermal liquefaction:
C 70-75%, H 6%, O 15-20%, HHV 30-32 MJ/kg
Catalysts: Homogeneous/Heterogeneous: Alkali salts (K2CO3, Na2CO3, NaOH, KOH), sulphides, ZrO2

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Hydrothermal Liquefaction

Advantages: suitable for wet feedstocks, unique properties of SC water, water acts as solvent, accelerates acid-based reactions, **produces stable bio-oil**

Mechanism: hydrolysis, alkylation, repolymerization; separation of WSO (incl. polar cmpd: acids, ROH)

Catalyst effects: promotion of WGS reaction, stabilization of intermediate products, prevention of char formation

Challenges: deactivation by salt residues and low stability of heterogeneous catalysts under sub- or supercritical water conditions

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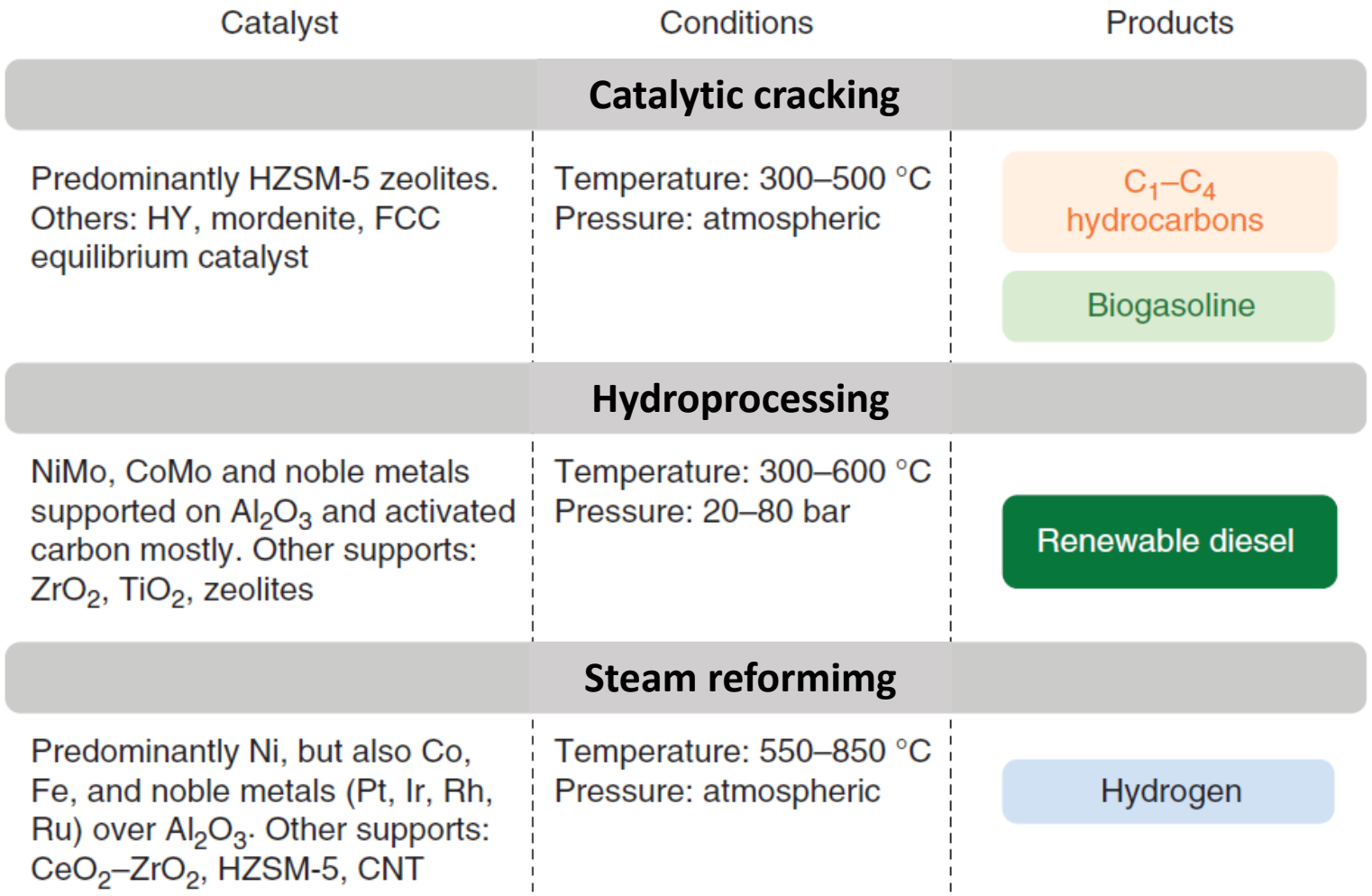
Catalytic upgrading of bio-oils



Catalyst	Conditions	Products
Catalytic cracking		
Predominantly HZSM-5 zeolites. Others: HY, mordenite, FCC equilibrium catalyst	Temperature: 300–500 °C Pressure: atmospheric	C_1–C_4 hydrocarbons Biogasoline
Hydroprocessing		
NiMo, CoMo and noble metals supported on Al_2O_3 and activated carbon mostly. Other supports: ZrO_2, TiO_2, zeolites	Temperature: 300–600 °C Pressure: 20–80 bar	Renewable diesel
Steam reformimg		
Predominantly Ni, but also Co, Fe, and noble metals (Pt, Ir, Rh, Ru) over Al_2O_3. Other supports: CeO_2–ZrO_2, HZSM-5, CNT	Temperature: 550–850 °C Pressure: atmospheric	Hydrogen

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Oyedun et. Al, Chemical Catalyst for Biomass upgrading, Ed. M. Crocker, Wiley VCH, 2020, 35.

R&D Projects

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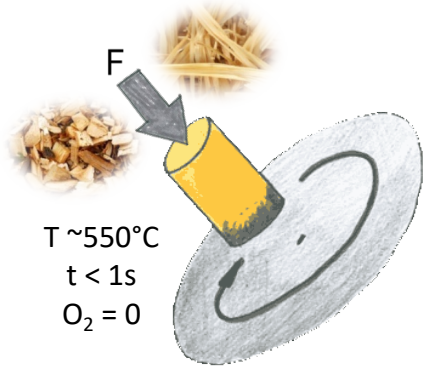
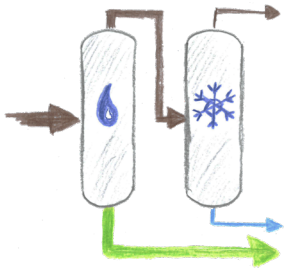
BioMates (Bio-based intermediates)





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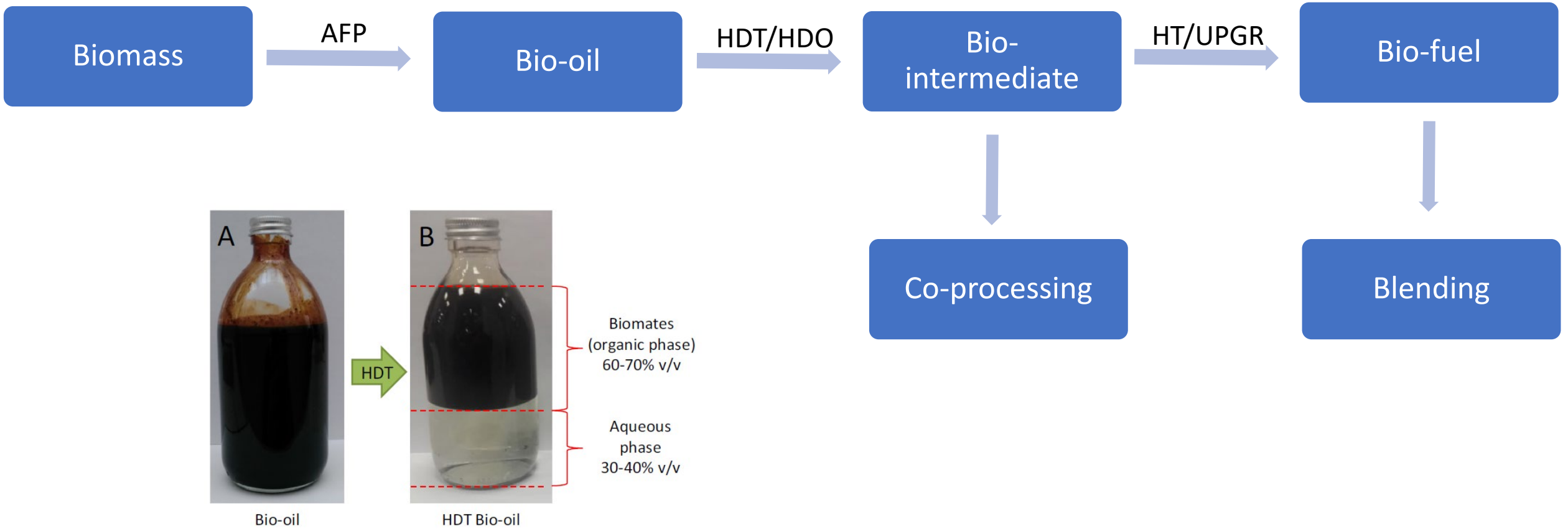

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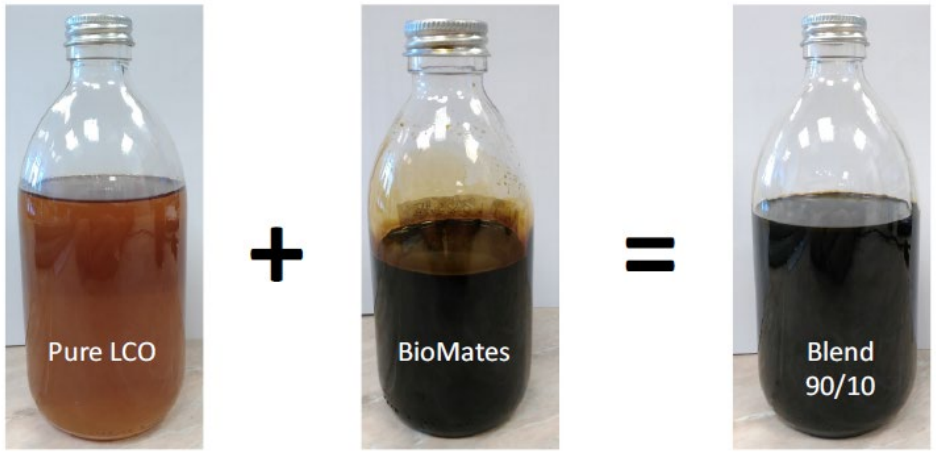
Co-processing of LCO with BioMates



CoMo/Al2O3

320-390°C
70 bar
LHSV 1 h-1

- Product: Diesel- and gasoline-range hydrocarbons with negligible water and oxygen content, low viscosity and TAN
- Normal operation with no ΔP build-up was observed during **the 37-days test period**, indicating negligible coke formation or process efficiency losses
- Reduced hydrogen consumption by up to 8.9% compared to standalone LCO hydroprocessing, thus not raising any economic concerns
- Inhibition in terms of HDS activity, can be overcome by increasing the reaction temperature

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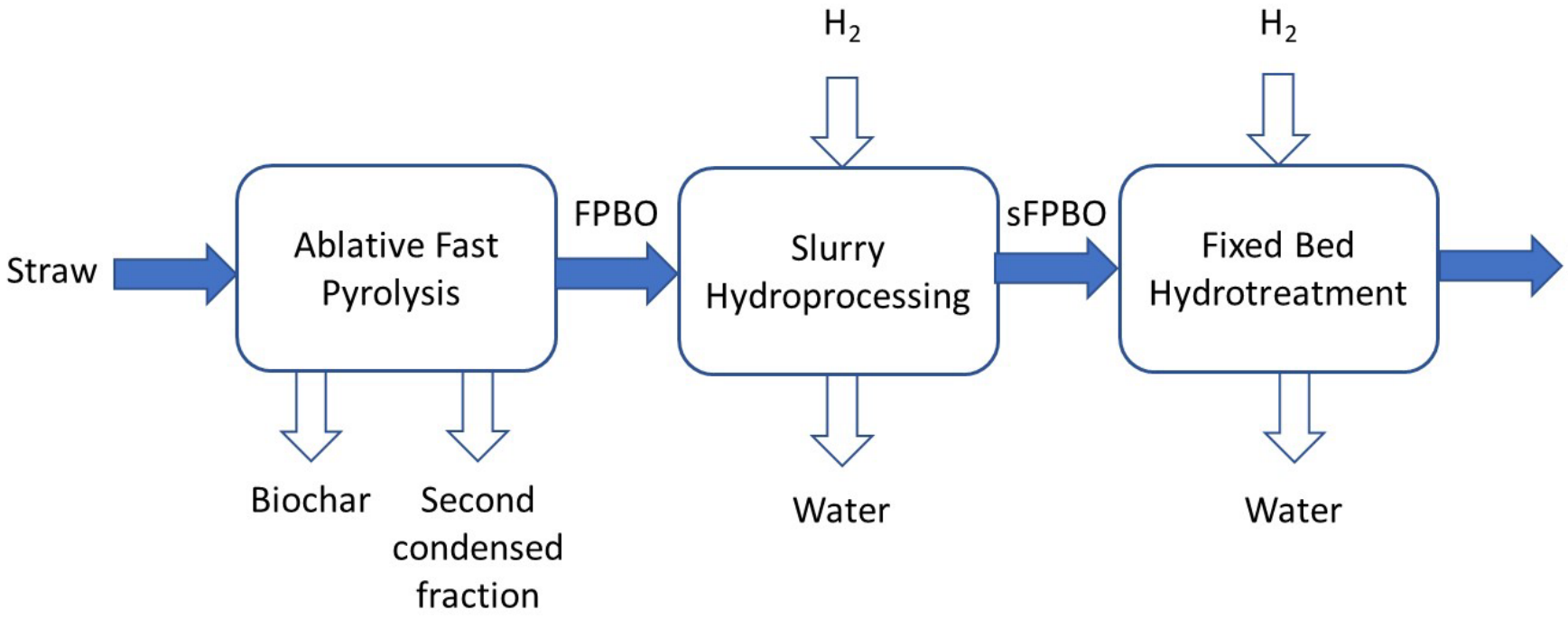
Dimitriadis et al., Fuel Processing Technology Volume 230 (2022) 107220.

BioMates Project

Fast pyrolysis of Straw followed by bio-oil upgrading



C 85%, H 12%, O 3%, S 72 ppm, H2O 0.38%
Density: 0.95 kg/L, Viscosity @313K: 17 mm2/s

Produced BioMates: 150 Liters
Overall mass yield: 20 wt.%
Overall carbon yield: 32 wt.%.

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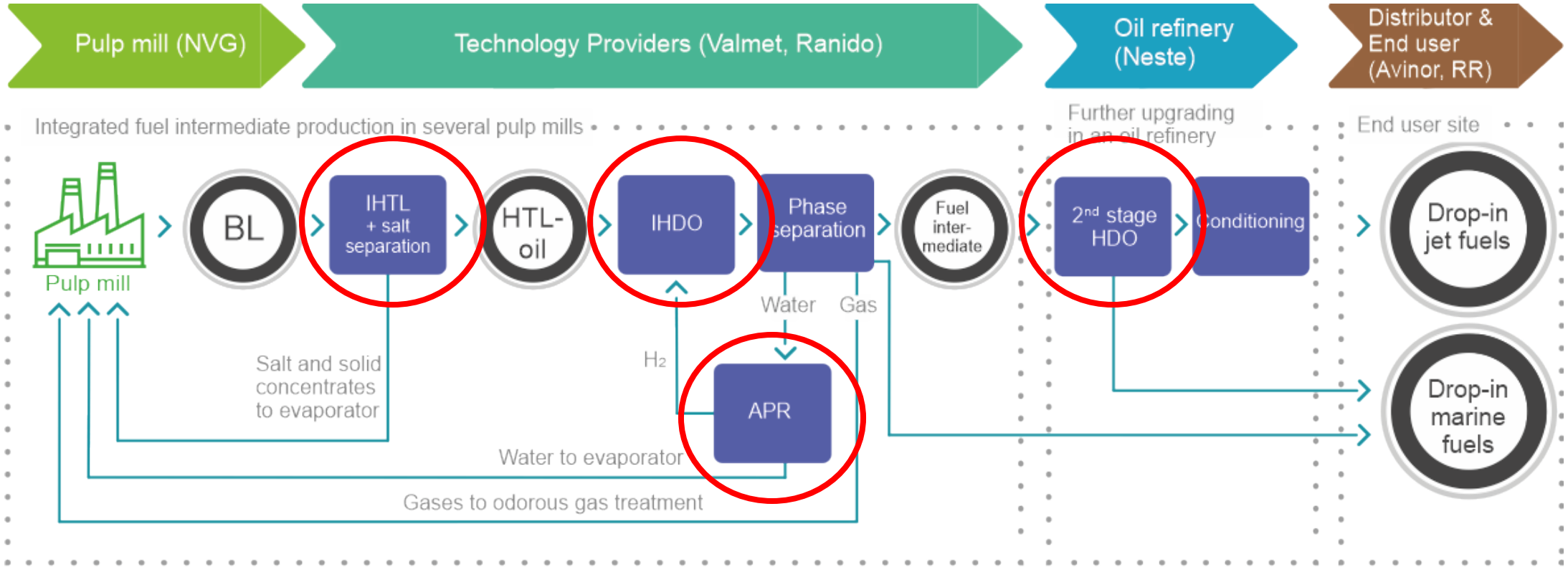
BL2F Project



Four catalytic steps: 1) IHTL, 2) IHDO, 3) APR, 4) HDO/upgrading @refinery

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BL2F - Catalysts

- **IHTL – Integrated Hydrothermal Liquefaction**
  Alkali salts: K_2CO_3, Na_2CO_3, NaOH, KOH, sulphides, ZrO_2

- **IHDO – Integrated Hydrodeoxygenation**
  NiMo, CoMo, NiW, Mo /SCW stable support (TiO_2, ZrO_2, C)

- **APR – Aqueous Phase Reforming**
  Ni/water stable support, VTT catalyst

- **HDO/upgrading @refinery**
  commercial or tailor-made catalysts for Hydroprocessing (HT, HC, HI)

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BL2F – Catalyst for IHDO

- Stability under SCW conditions
- Good Activity & Selectivity
- Low sensitivity to impurities / by-products
- Life-time (suppressed deactivation)

Sample	SCW stability	BET (m^2/g)		Comment
		Before	After SCW	
Corundum extrudate – alpha-Al2O3	yes	1.81	2.22	
Rutile extrudate – TiO2	yes	3.57	3.71	
Monoclinic zirconia extrudate – ZrO2	(yes)	56.4	47.2	(yes) = minor changes in spec. area
Monoclinic zirconia extrudate – ZrO2	no	102	47.3	extrusion additive not SCW stable
Monoclinic zirconia extrudate – ZrO2	no	65.1	46.1	extrusion additive not SCW stable
Beta silicon carbide extrudate – SiC	yes	27.3	28.4	
Activated carbon granulate - C	yes	890	798	micropores before: 771, after: 662 m^2/g

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Summary and Outlook

- Complex composition of bio-feedstocks challenges development of new catalytic systems that have to be universal and should operate under broad range of reaction conditions.
- Catalytic Pyrolysis and Hydrothermal Liquefaction are currently the most promising processes for biomass conversion to liquid fuels.
- Further catalytic upgrading of bio-oils by hydrotreating is necessary in order to produce intermediates that can be used for coprocessing in the refinery or as bio-fuel additives for blending.
- Integrated hydrodeoxygenation (IHDO) process requires a robust, very stable catalyst that needs to be tolerant to impurities and has to be stable under supercritical water conditions.

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BL2F Partners:

Tampere University

Brunel University London

KIT Karlsruhe Institute of Technology

SINTEF

PAUL SCHERRER INSTITUT PSI

VTT

THE NAVIGATOR COMPANY

Valmet

NESTE

Ranido

LGi sustainable innovation

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Thank you!

Get in touch with the project:

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