Upgrading of biocrude and valorisation of side streams

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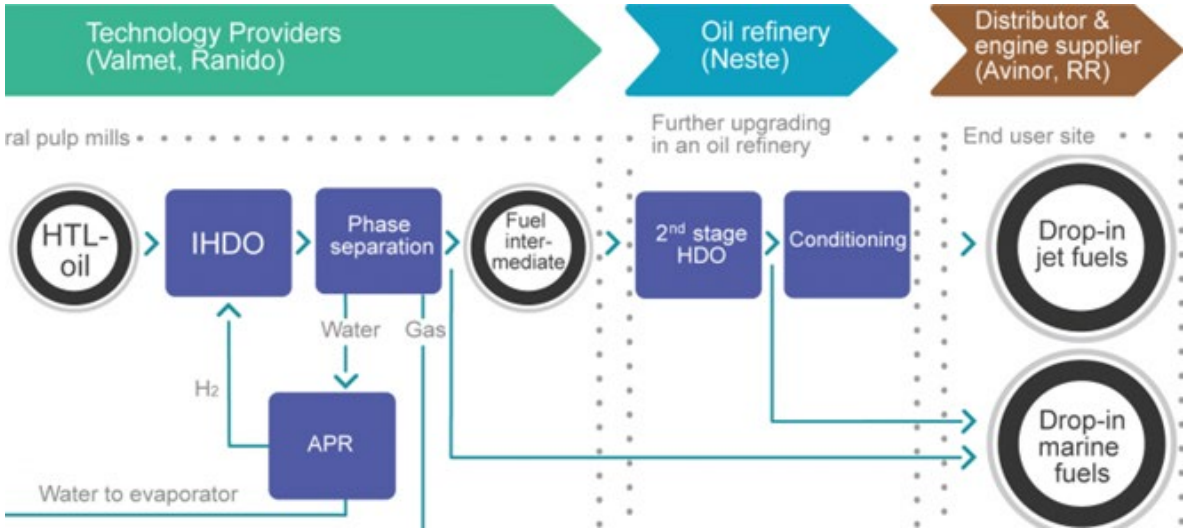
VTT

BL2F
Transforming Black Liquor to Biofuel

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

Valorisation of product streams from IHTL

- Upgrading of biocrude by two-stage hydrodeoxygenation
- Hydrogen production from aqueous phase by APR
- Treatment of sulfur-containing gases



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Biocrude upgrading

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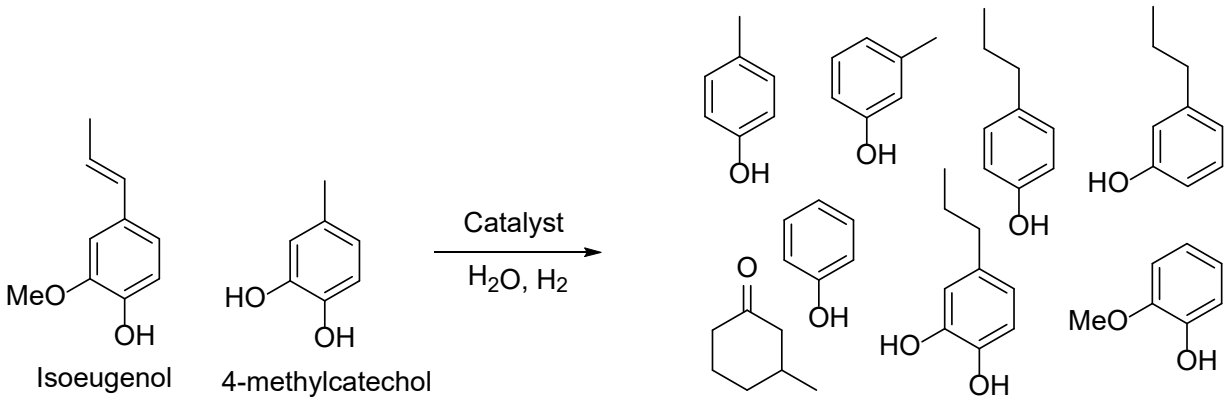
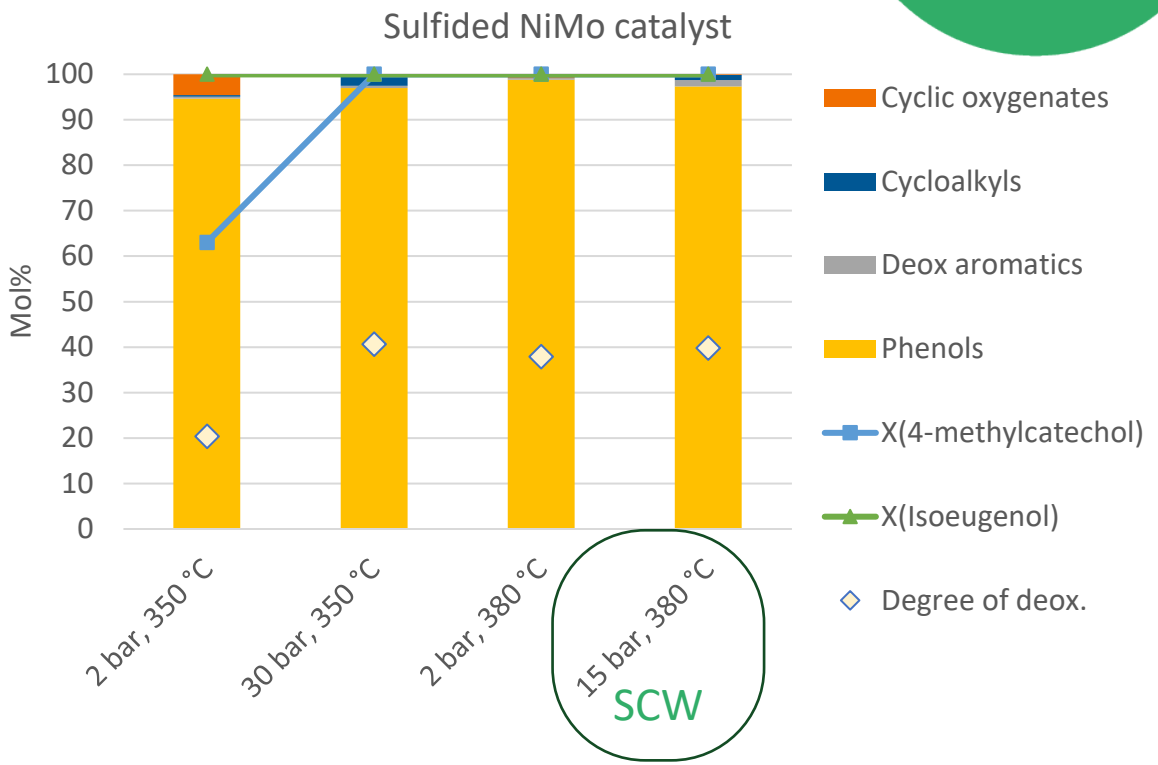
Hydrothermal hydrodeoxygenation

- Hydrodeoxygenation of model compounds was studied in batch and continuous-flow experiments in sub- and supercritical water
- Batch experiments focused on NiMo catalysts on various supports
- Up to 40% deoxygenation was achieved, even though phenols were the main products



Isoeugenol 4-methylcatechol



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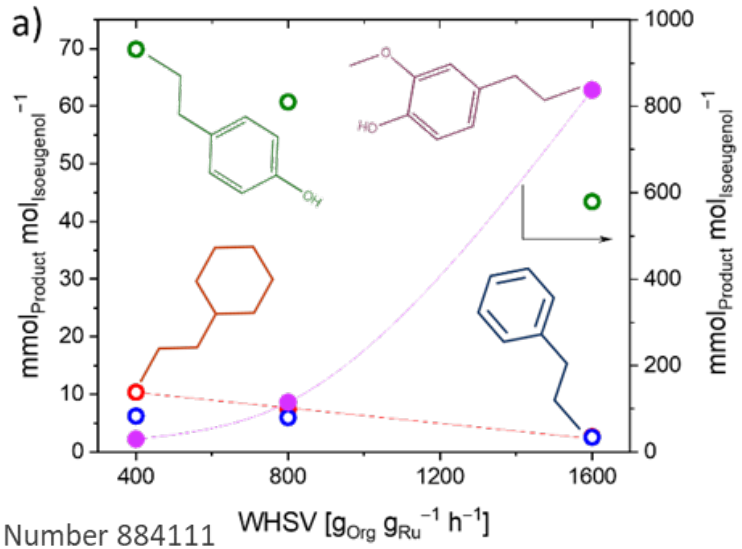
Hydrothermal hydrodeoxygenation

- Catalyst stability was thoroughly tested in supercritical water in both batch and continuous flow systems
- Even though stable in batch mode, the NiMo catalysts were unstable in continuous flow due to leaching of the active metals
- Promising results were obtained with sulfided Ru/AC; the catalyst was stable and active in deoxygenation of isoeugenol using isopropanol as hydrogen source
- Due to lack of BL-based feed, hydrothermal HDO was studied using pine HTL biocrude from Aarhus Univesity
- S-Ru/AC yielded 24-63 wt% of upgraded biocrude with high amounts (up to 40%) of coke



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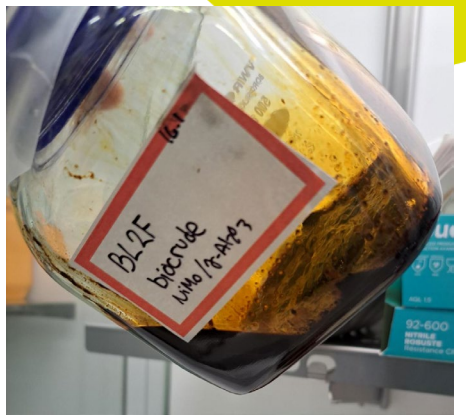
Upgrading of black liquor-based biocrude

- Small sample of purified HTL biocrude was hydrotreated in a batch experiment using a NiMo catalyst
- Oxygen content of the biocrude decreased from 18% to under 10%
- Sulfur content decreased from 2% to under 0.2%



- Direct hydrotreatment is a promising method for upgrading of the black liquor-based HTL biocrude

Sample	Elemental composition (wt%)				Water (wt%)	TAN (mg KOH/g)
	C	H	S	O		
Biocrude	70.18	6.87	**2.00**	**18.49**	4.38	96.7
Top product	85.62	12.18	**0.07**	**3.7**	<0.5	3.6
Bottom product	81.17	8.47	**0.18**	**9.8**	<0.5	13.1

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Valorisation of side streams

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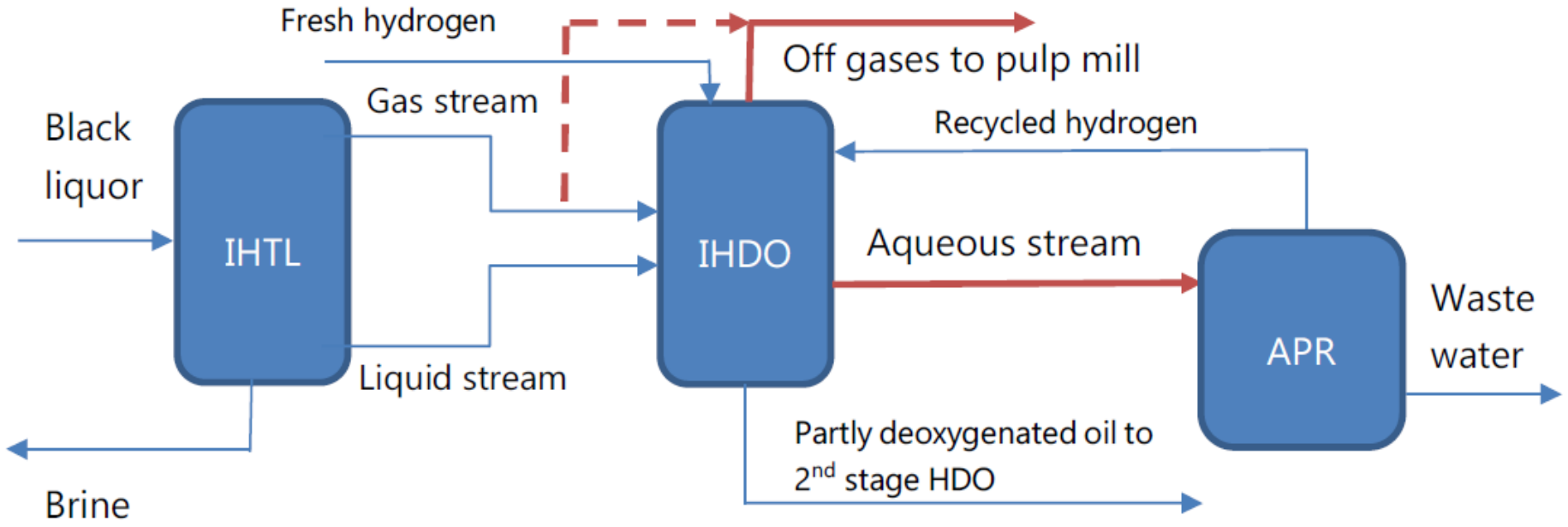
Utilization of side streams in the integrated BL2F concept



- Aqueous stream from IHDO is utilized in aqueous phase reforming (APR) to produce hydrogen
- Off gases are led to the pulp mill for treatments

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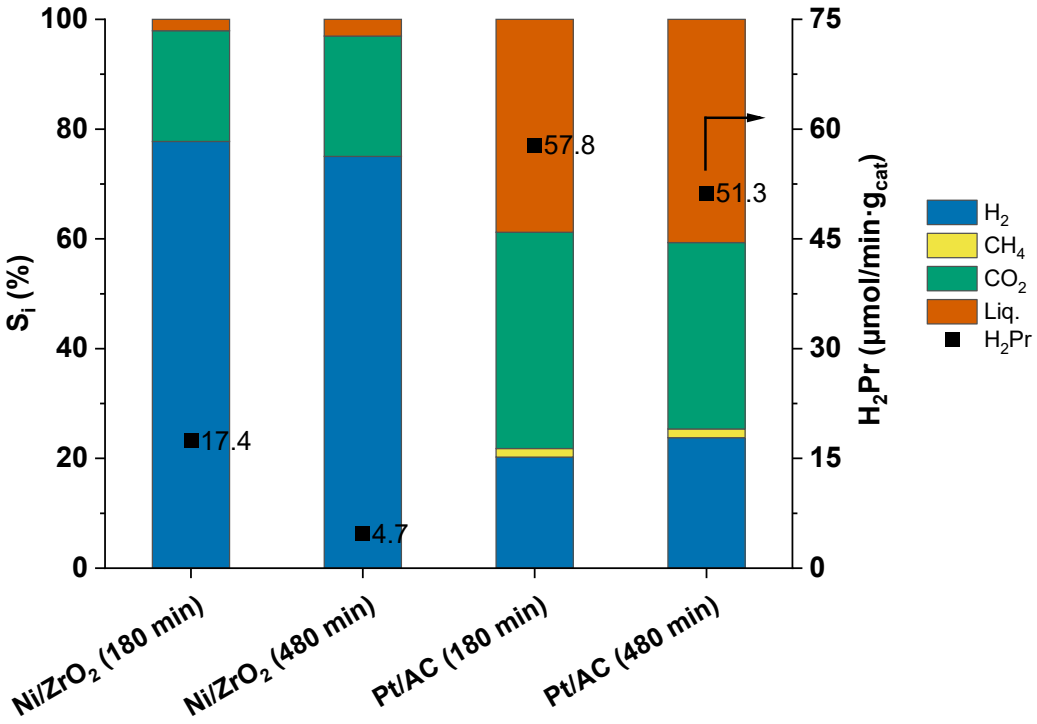
Aqueouos phase reforming

- Aqueous phase reforming (APR) is a catalytic technology to produce hydrogen from organics dissolved in diluted aqueous streams
- In BL2F, the target was to produce hydrogen to be used for integrated hydrodeoxygenation (IHDO) from aquoeous by-product streams obtained from the process
- Due to poor avaibility real process waters to be tested , our work focused on the APR of black liquor HTL aqueous product model compounds: acetic acid, methanol, phenol, 4-methylcathecol
- Six different supported metal catalysts either prepared at VTT or sourced elsewhere were studied for APR of those model compounds in a continuous high pressure fixed bed reactor system



Product selectivity (S_i) and H_2 production for Ni/ZrO_2 and Pt/AC in the APR of four model compound mixture.

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APR - Conclusions

- APR of compounds with aromatic structure seem to be challenging => low initial conversions and H_2
  - Such components are abundant in the aqueous phase of black liquor HTL product
- With methanol, relatively high and stable hydrogen production was observed ($Y(H_2)$ = 32%).
- With all other model compounds than methanol, fast catalyst deactivation was observed with all tested nickel-based catalysts
- Pt-based catalyst was observed to be more stable but less selective for hydrogen production
- The main reason for Ni catalysts deactivation was concluded to be metal leaching and blocking of active sites
- APR cannot supply enough hydrogen for IHDO. Furthermore, catalyst deactivation is a challenge to be solved.

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Gas treatment concept studies

Gas treatment concepts studied

1. Separation of hydrogen from the gas stream and production of sulfuric acid from the rest of the gas after hydrogen separation
2. Sulfuric acid production without hydrogen separation
3. Separation of hydrogen and burning the non-condensable gases in recovery boiler

Concept & TEA studies

1. Aspen Plus simulation models were created for the three cases to obtain energy and mass balances and to estimate investment costs of the equipments (Aspen Economic Analyser)
2. OPEX & CAPEX were calculated for the three cases and profitability analysis was performed for the two best cases

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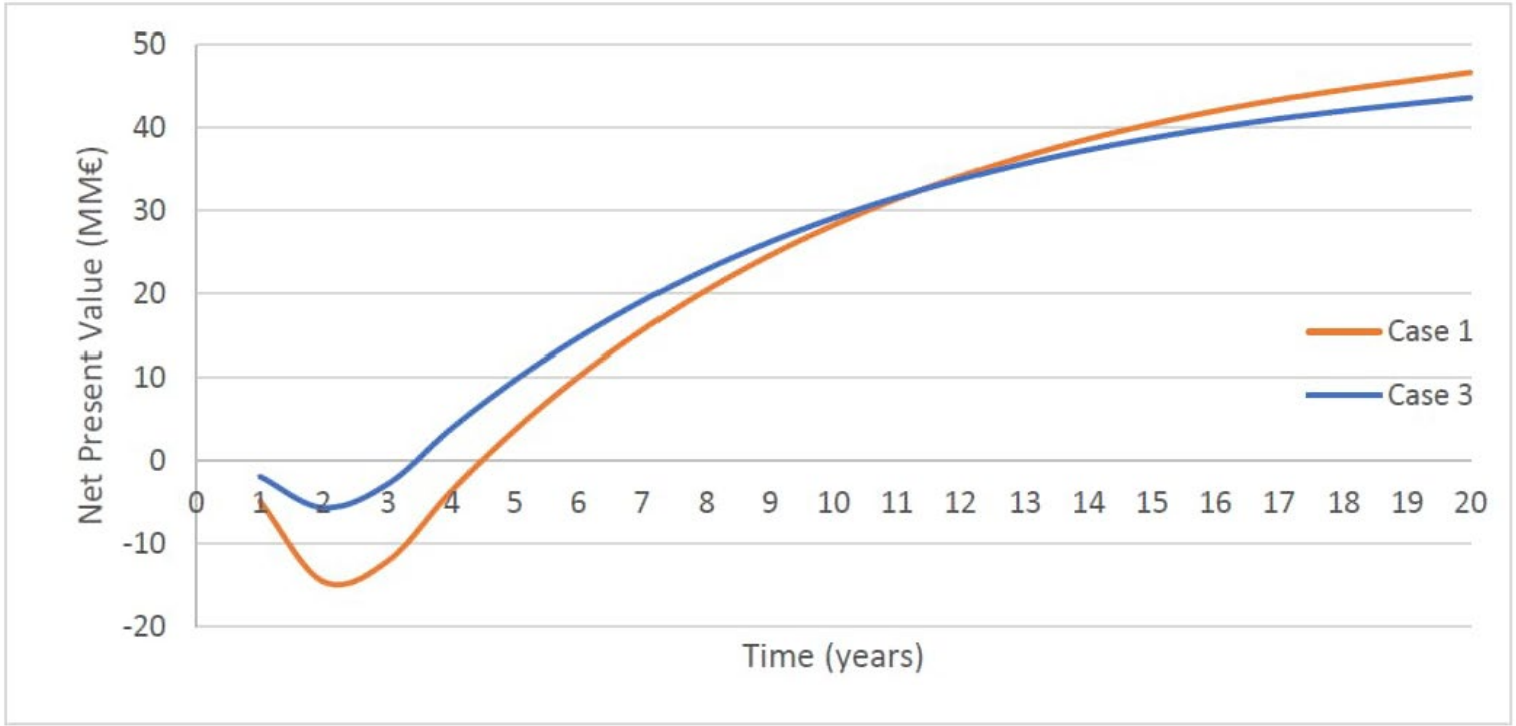
Gas treatment - Profitability analysis

- Good profitability was observed for the cases 1 & 3 with short payback times 1.4 and 0.7 years
- The main income would be hydrogen sales
- The most sensitive parameter affecting the profitability is the hydrogen sales price



Saad, M., 2023, Utilization of Sulphur Containing Gases from Hydrothermal Liquefaction Process,Master's Thesis in Chemical Engineering and Processing, Lappeenranta–Lahti University of Technology LUT.

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Acknowledgements

Jasmiina Palo, Kristian Chen, Pouya Sirous-Rezaei, Tyko Viertiö, Niko Vuorio (VTT)

Alexey Kurlov, David Baudouin (PSI)

Pavel Kukula, Luděk Meca (Ranido)

Ekaterina Sermyagina, Anja Leminen (Neste)

Mustafa Saad, Kristian Melin (LUT)

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Thank you!

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