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Between Nb2O5 and sugarcane biomass: valorization of brazilian natural resource

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Between Nb_2O_5 and sugarcane biomass: valorization of brazilian natural resources

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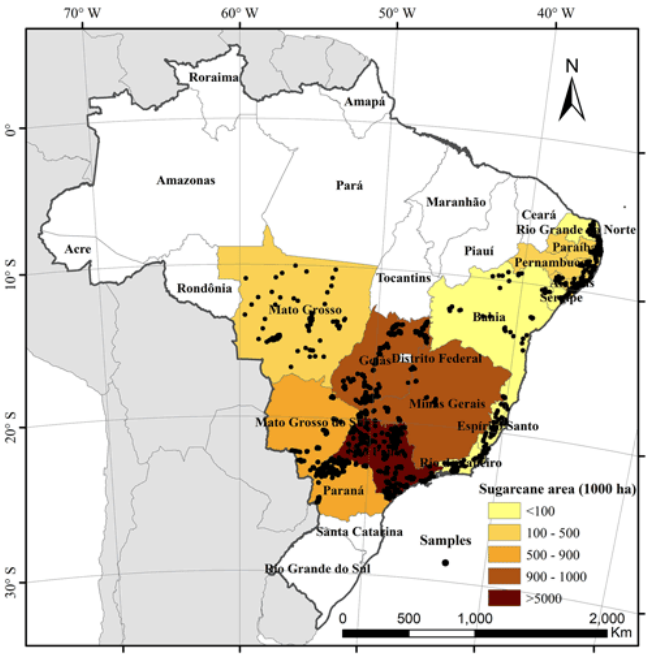
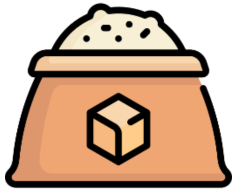
Sugarcane biomass in Brazil



Sugarcane production areas (2020)

Harvest 2023: 661x10^6 metric tons

Ethanol



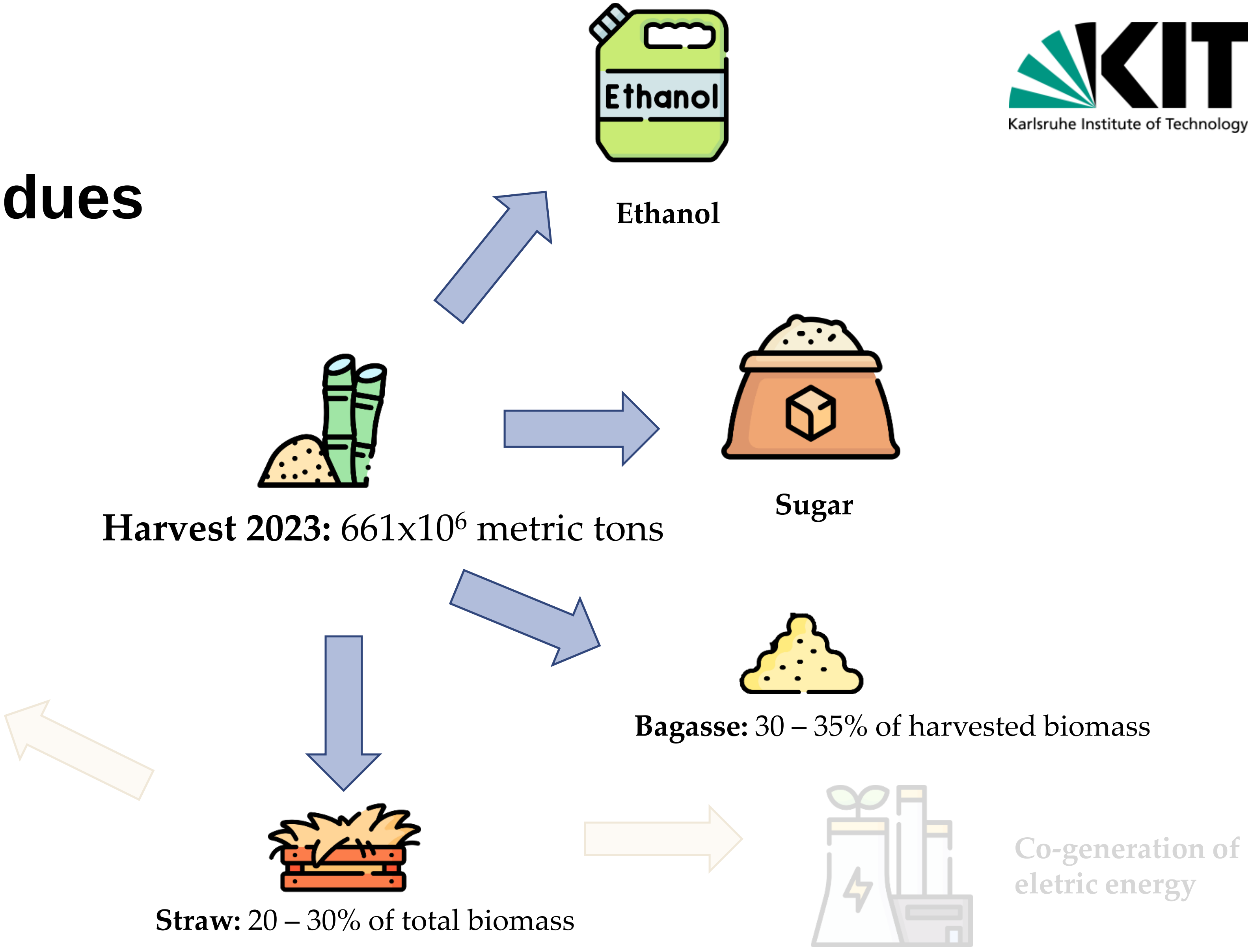
Sugar

Bagasse: 30 – 35% of harvested biomass

Straw: 20 – 30% of total biomass

Co-generation of eletric energy

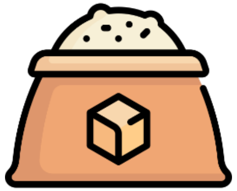
Sugarcane residues



Hofzetz and Silva, 2012 - Brazilian sugarcane bagasse: Energy and non-energy consumption

Sugarcane residues application

Ethanol

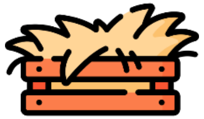


Sugar

Harvest 2023: 661x10^6 metric tons

Bagasse: 30 – 35% of harvested biomass

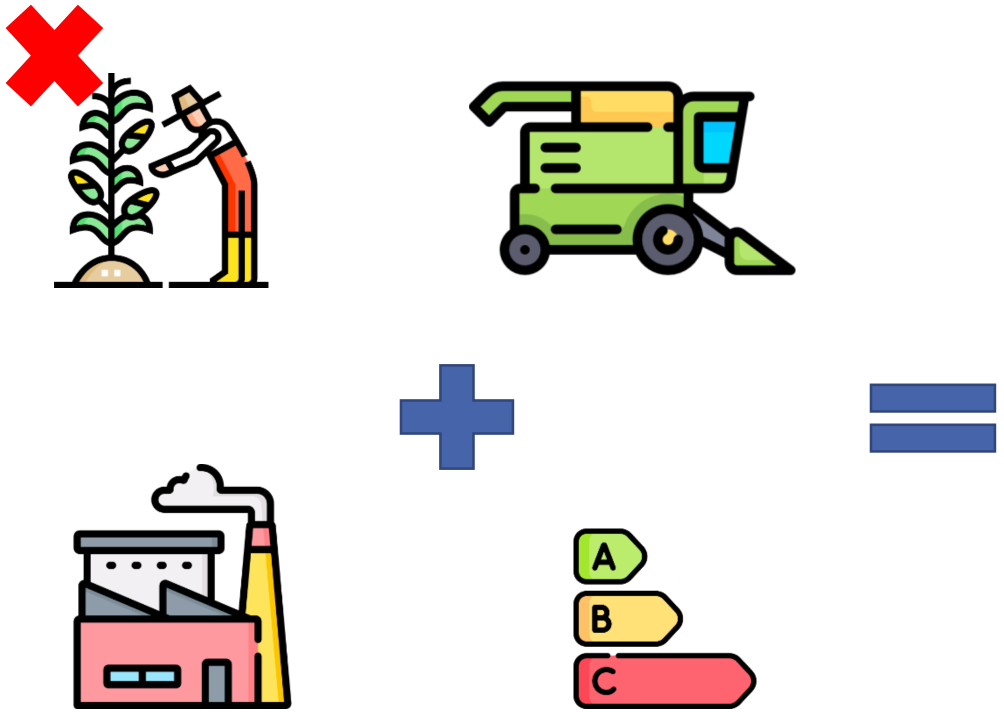
Straw in the field: soil protection

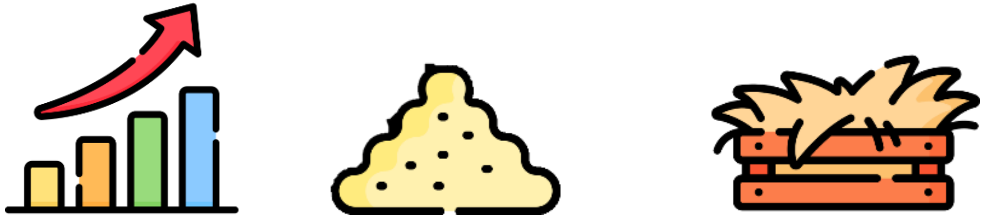


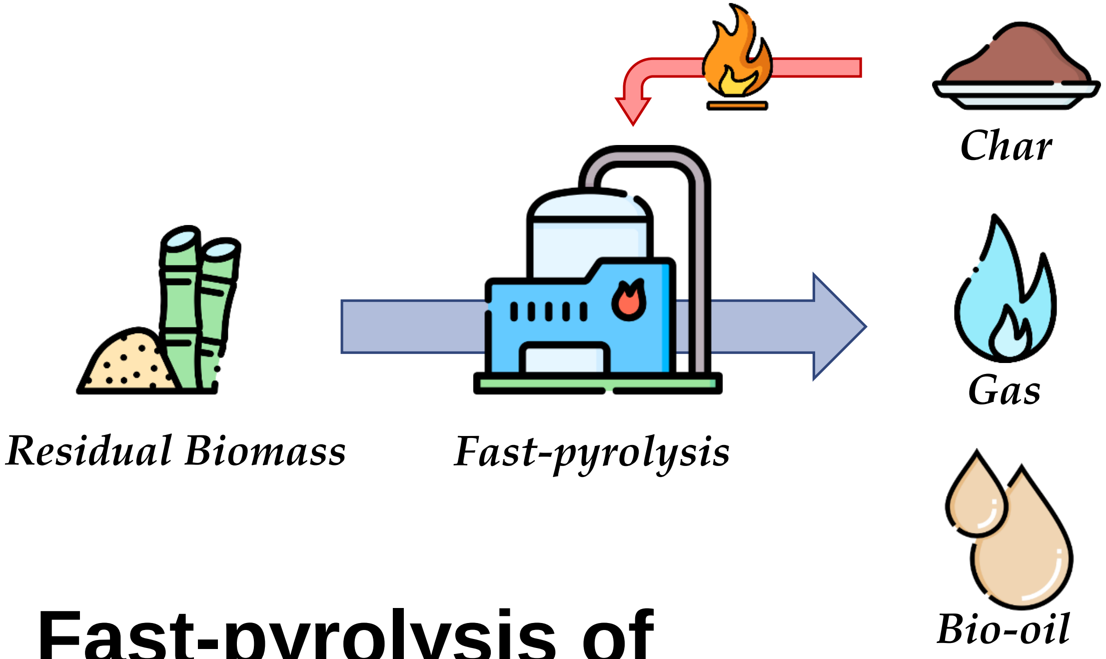
Straw: 20 – 30% of total biomass

Co-generation of eletric energy

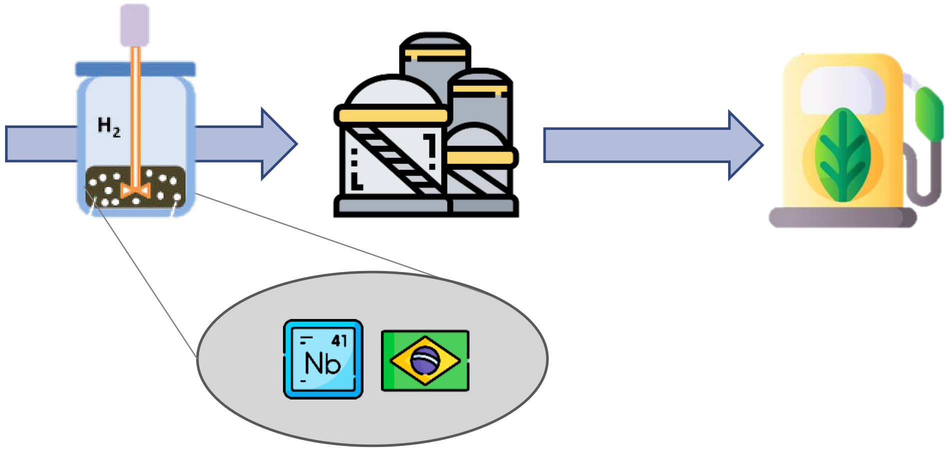
Expected increase of sugarcane residues







Bio-oil upgrading (Hydrotreatment)



Fast-pyrolysis of residual biomass

Content of this work

Production and hydrotreatment of sugarcane bio-oil from residual biomass

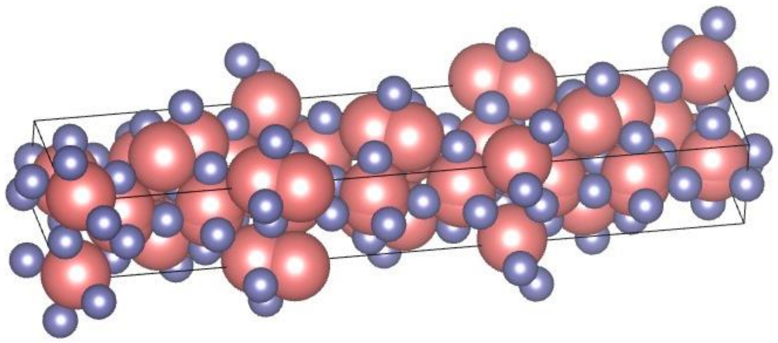
- Fast-pyrolysis of bagasse and straw with ethylene glycol or ethanol as quenching media
- Hydrotreatment of bio-oils with Nb_2O_5 supported catalysts

Nb_2O_5 as a catalyst

*“Niobium oxides remarkably **enhance** catalytic activity and **prolong** catalyst life when the small amounts are added to known catalysts. Moreover, niobium oxides exhibit a **pronounced effect** as supports of metal and metal oxide catalysts”*

Tanabe 1991

(Original Figure generated with Vesta 3)



- NbOx – catalyzes the cleavage of C-O bond
- Water resistant acid sites – catalyzes dehydration
- Synergism with active metals – hydrogenation ability
- Polymorphism – properties tunning

Tanabe 1991 – Niobium, a catalyst repair KIT.
Tanabe and Okazaki 1995 – Various reactions catalyzed by niobium compounds and materials
Tanabe 2003 – Catalytic application of niobium compounds

Nb_2O_5 as a catalyst

Karlsruhe Institute of Technology

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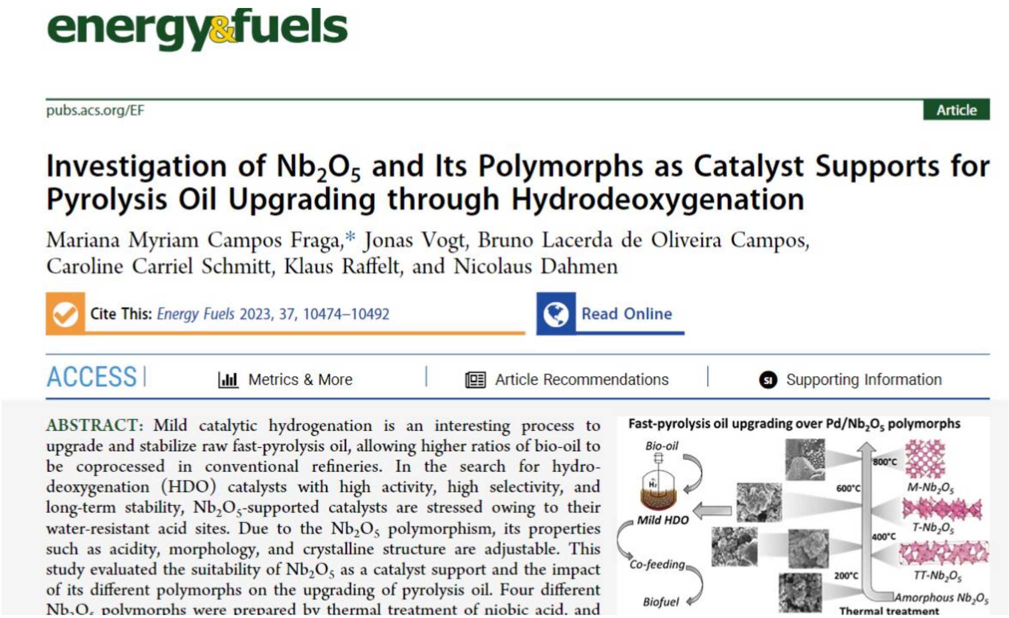
energy&fuels

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Investigation of Nb_2O_5 and Its Polymorphs as Catalyst Supports for Pyrolysis Oil Upgrading through Hydrodeoxygenation

Mariana Myriam Campos Fraga,* Jonas Vogt, Bruno Lacerda de Oliveira Campos, Caroline Carriel Schmitt, Klaus Raffelt, and Nicolaus Dahmen

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ABSTRACT: Mild catalytic hydrogenation is an interesting process to upgrade and stabilize raw fast-pyrolysis oil, allowing higher ratios of bio-oil to be coprocessed in conventional refineries. In the search for hydrodeoxygenation (HDO) catalysts with high activity, high selectivity, and long-term stability, Nb_2O_5-supported catalysts are stressed owing to their water-resistant acid sites. Due to the Nb_2O_5 polymorphism, its properties such as acidity, morphology, and crystalline structure are adjustable. This study evaluated the suitability of Nb_2O_5 as a catalyst support and the impact of its different polymorphs on the upgrading of pyrolysis oil. Four different Nb_2O_5 polymorphs were prepared by thermal treatment of niobic acid, and

- NbOx – catalyzes the cleavage of C-O bond
- Water resistant acid sites – catalyzes dehydration
- Synergism with active metals – hydrogenation ability
- Polymorphism – properties tunning

Tanabe 1991 – Niobium, a catalyst repair KIT.
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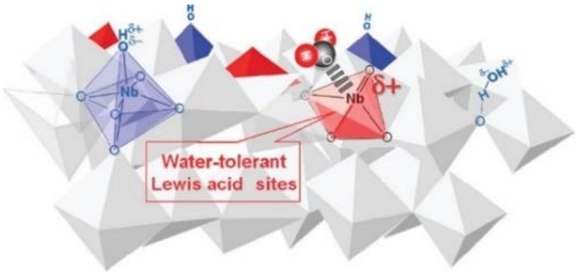
Methodology – Catalyst preparation



500 °C, 4 hours

Mixtures of:

TT-Nb_2O_5

T-Nb_2O_5

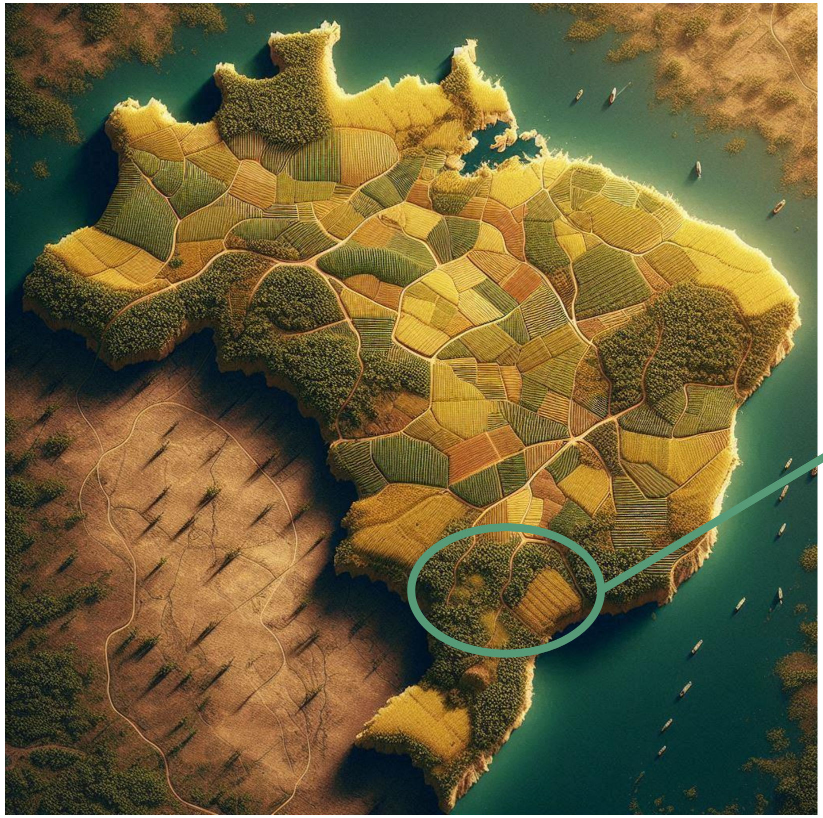
Wet impregnated with $Pd(NO_3)_2$ - Pd (1 wt.%)

Pd - ΔT 350 °C

Pd/Nb_2O_5

ΔT+ H_2/N_2

Methodology – Straw and bagasse collection



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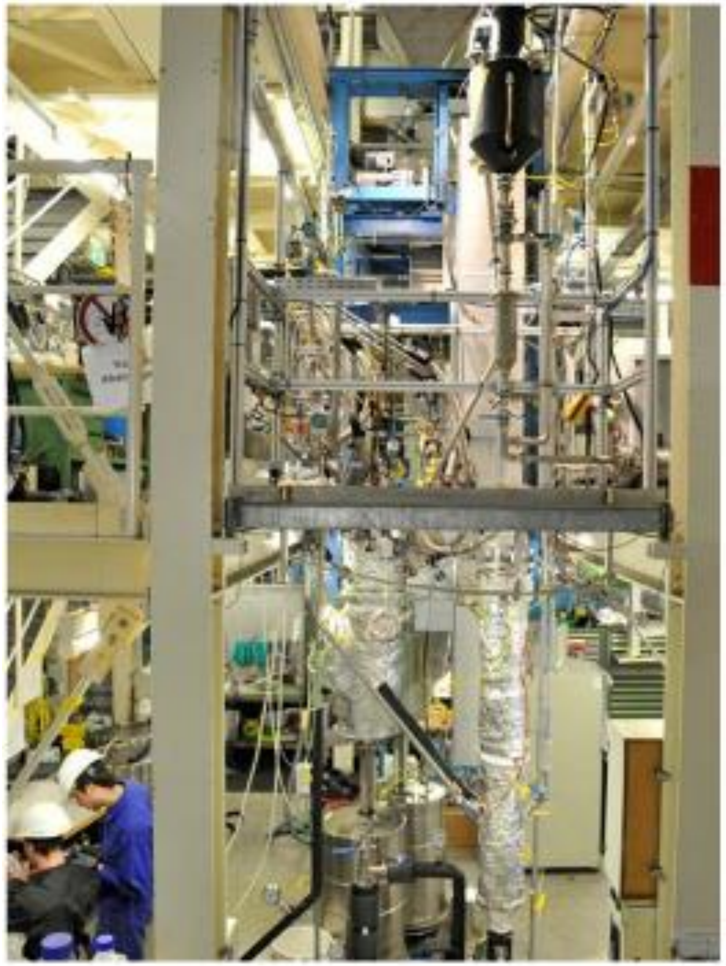
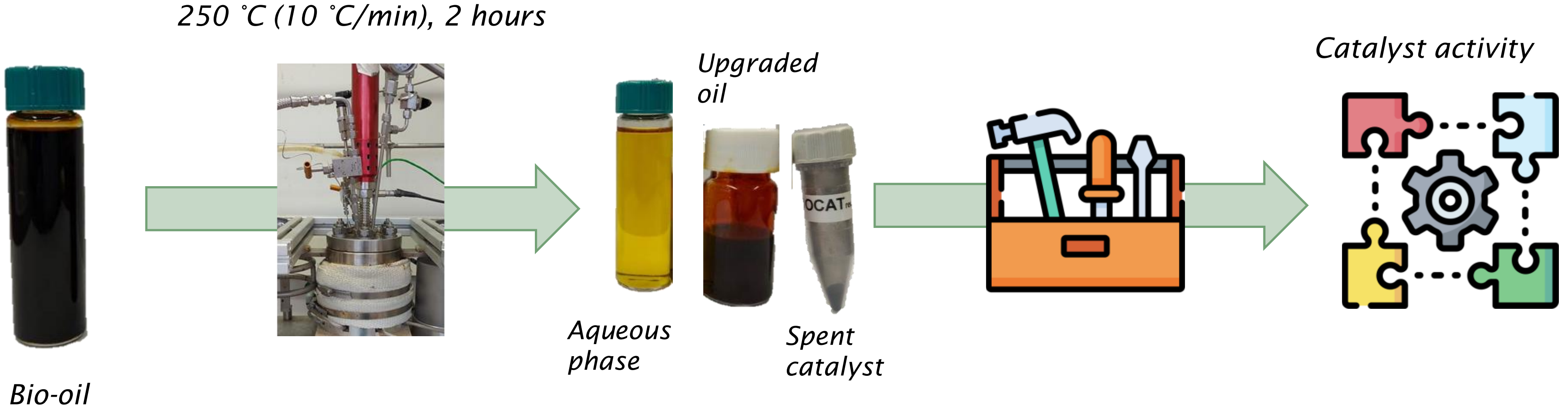
Methodology – Fast-pyrolysis



Python - KIT

Biomass	Pyrolysis quenching	Abbreviation
Bagasse	Ethylene glycol	BG-EG
Bagasse	Ethanol	BG-ET
Straw and Bagasse	Ethylene glycol	BS-EG
Straw and Bagasse	Ethanol	BS-ET

Methodology – Upgrading of bio-oils



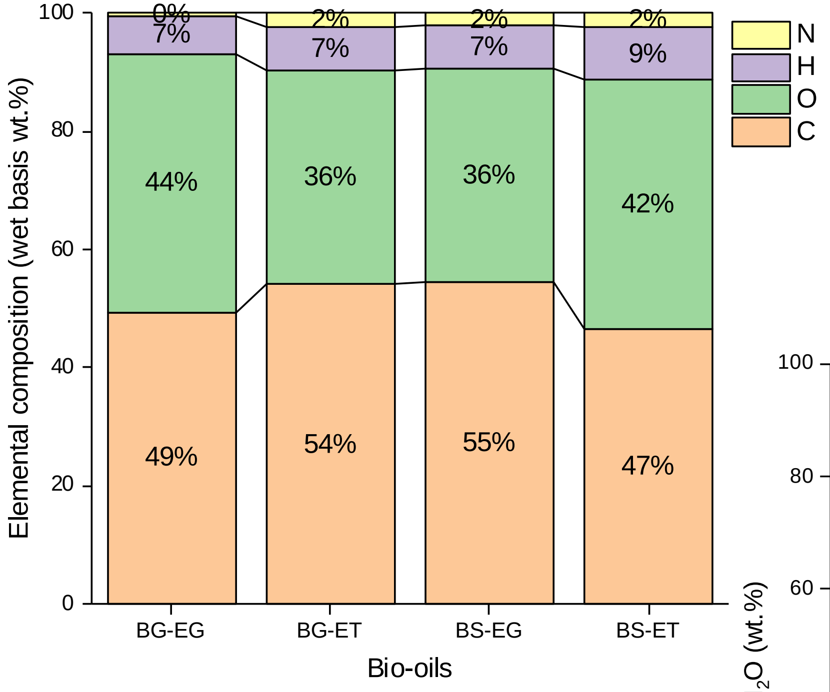
Batch reactor

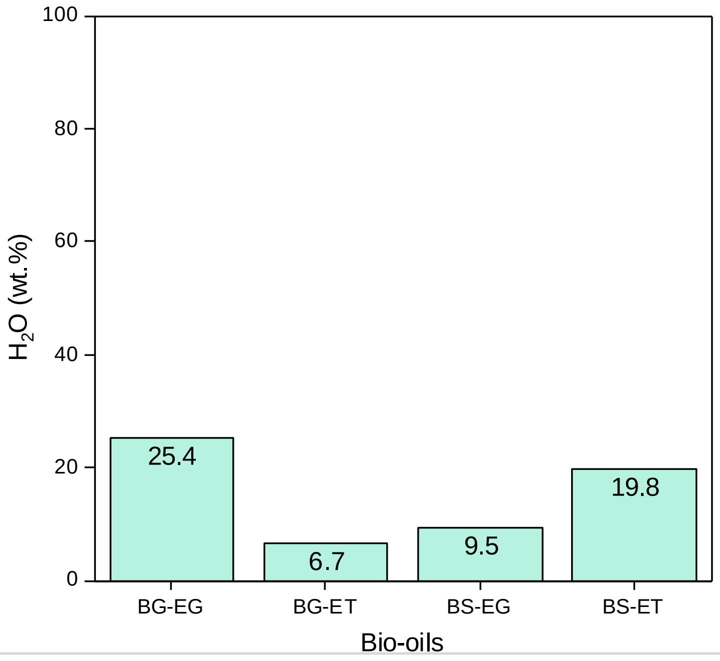
200mL
P_{max} 360 Bar
T_{max} 400 ˚C

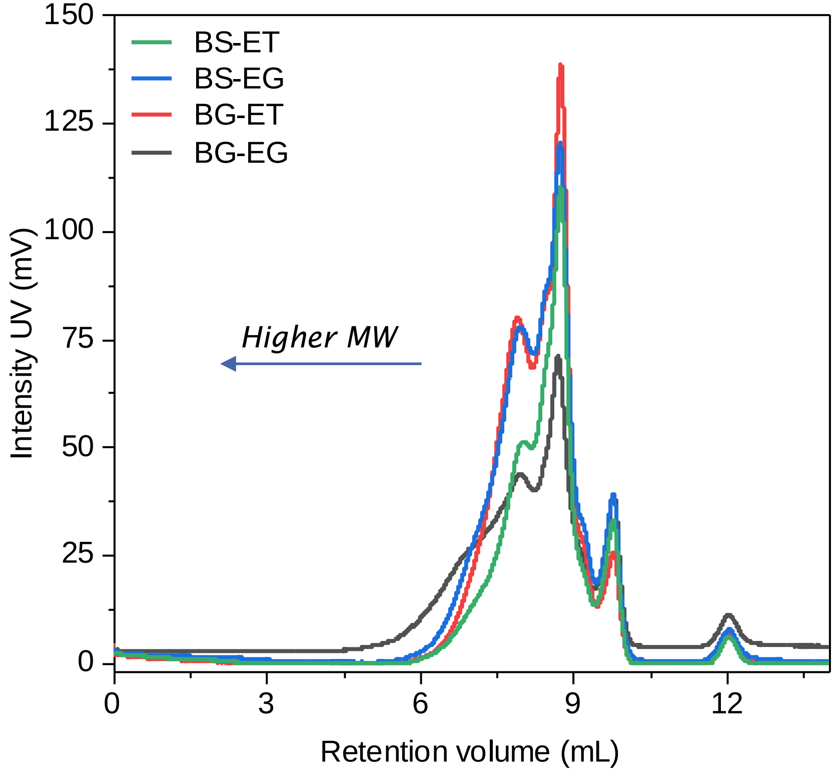
- Complexity of feedstock: HDO parameters
  - H_2 uptake
  - Generated gases
  - Polymerization degree
  - Functional groups via ^{1}H-NMR
  - Chemical compounds via GC-MS/FID

Sugarcane bio-oils characterization

Elemental composition, water content and molecular weight



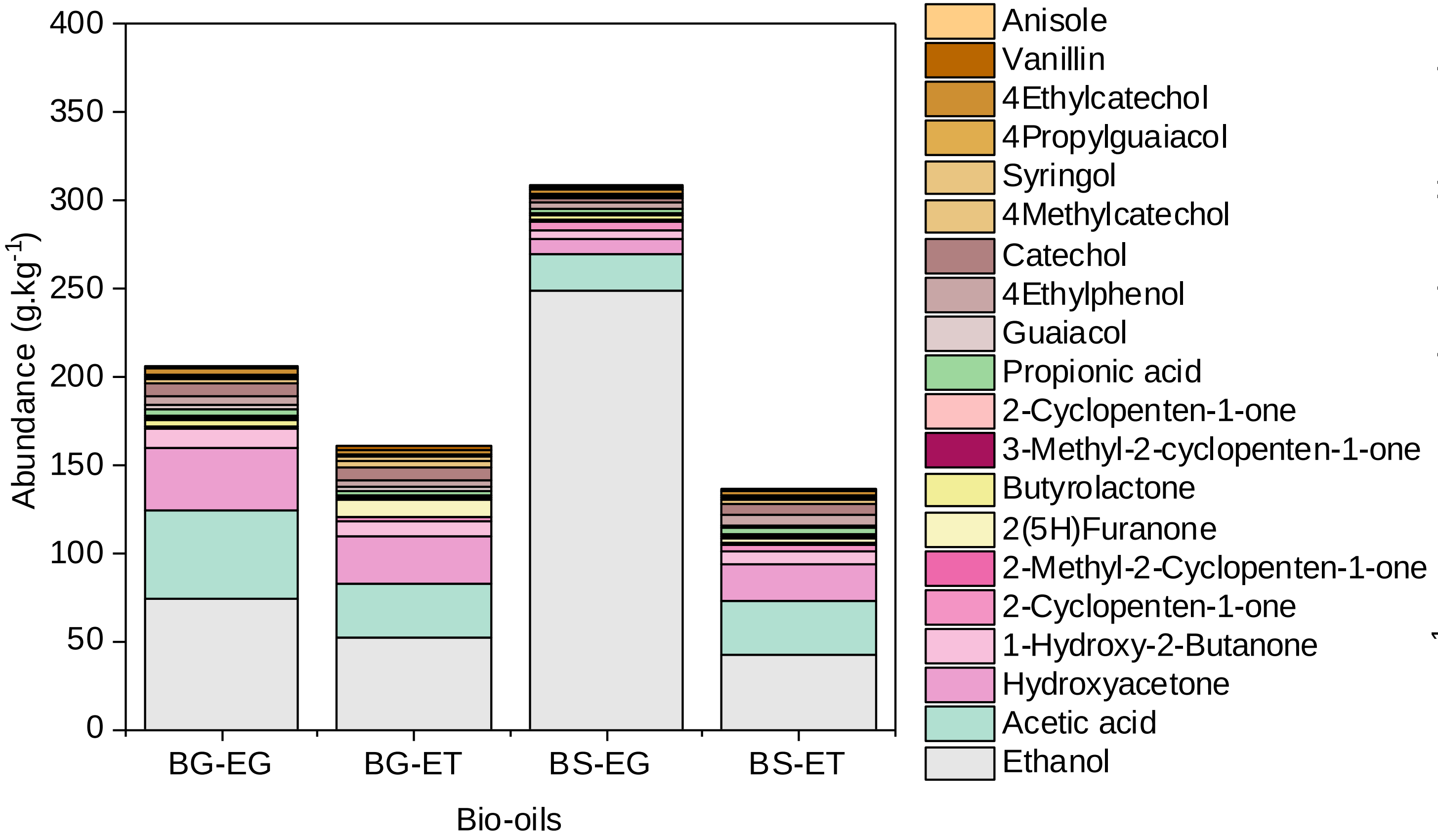




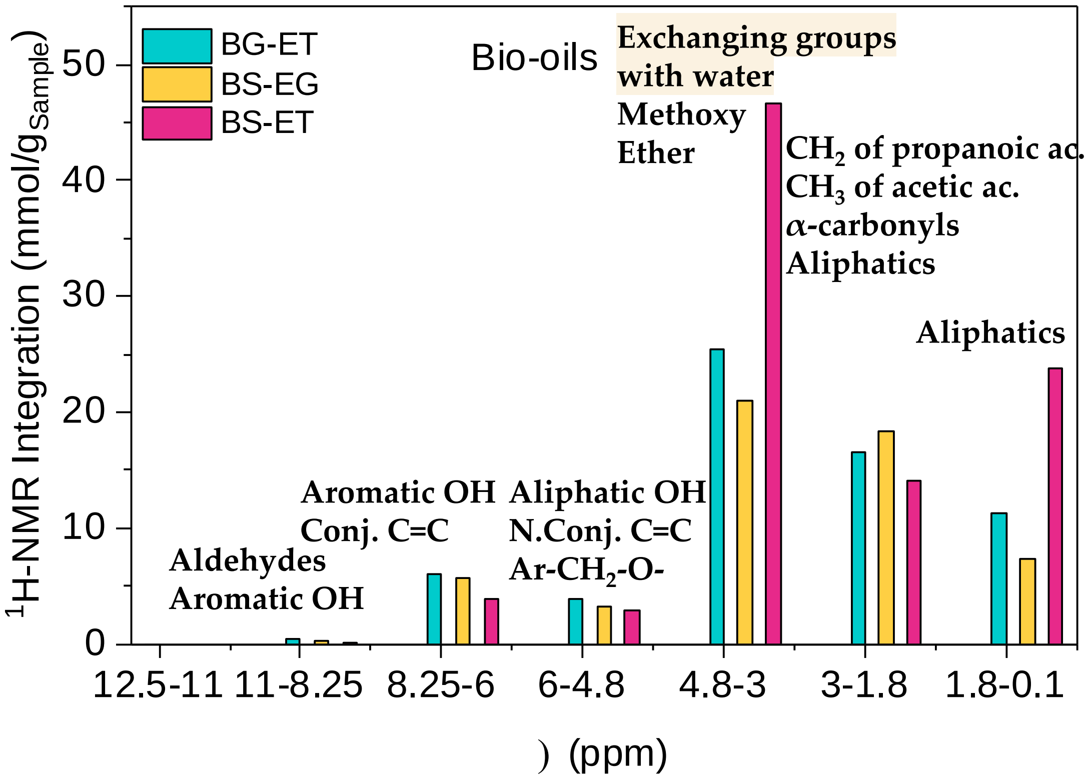
Sugarcane bio-oils characterization

Karlsruhe Institute of Technology

Chemical composition (GC-FID)



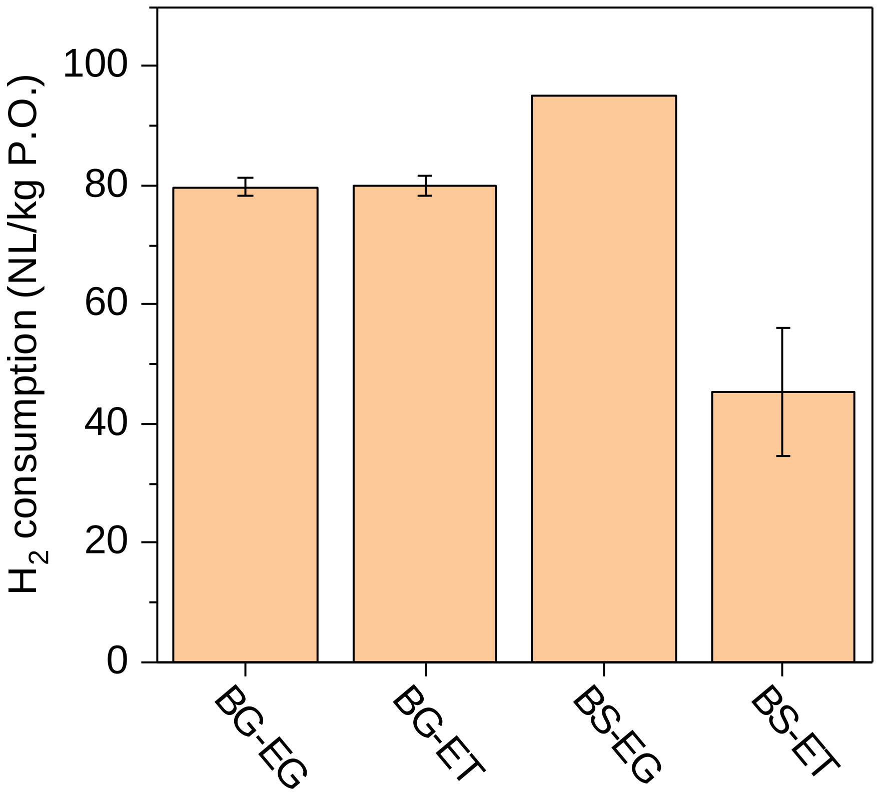
Chemical composition (¹H-NMR)

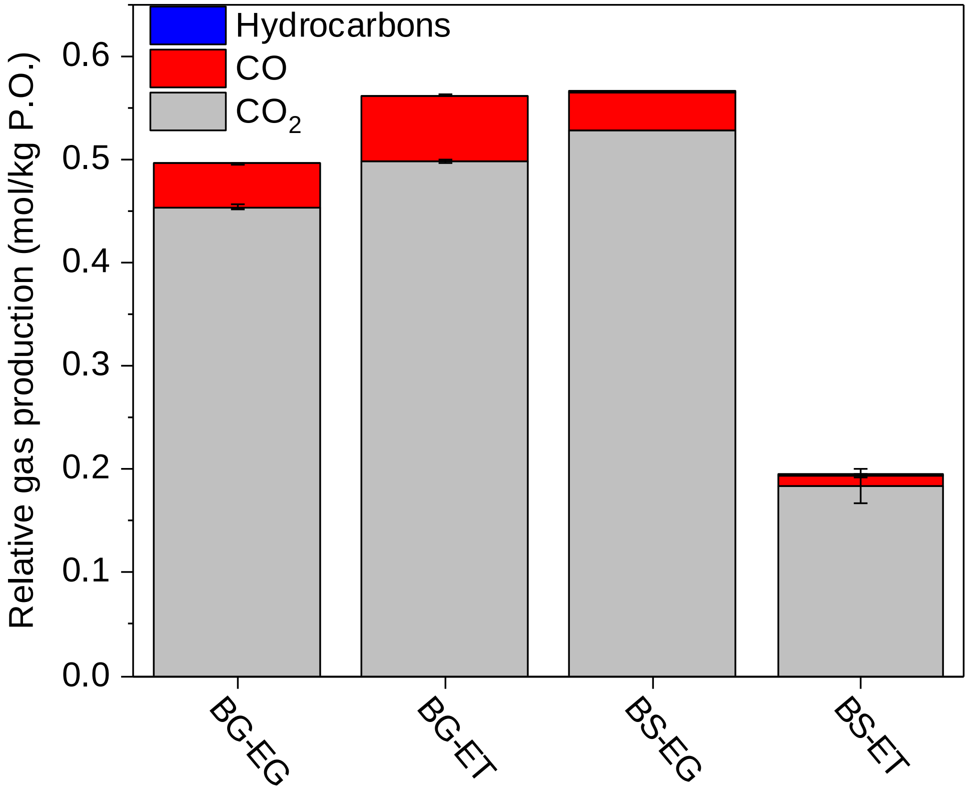


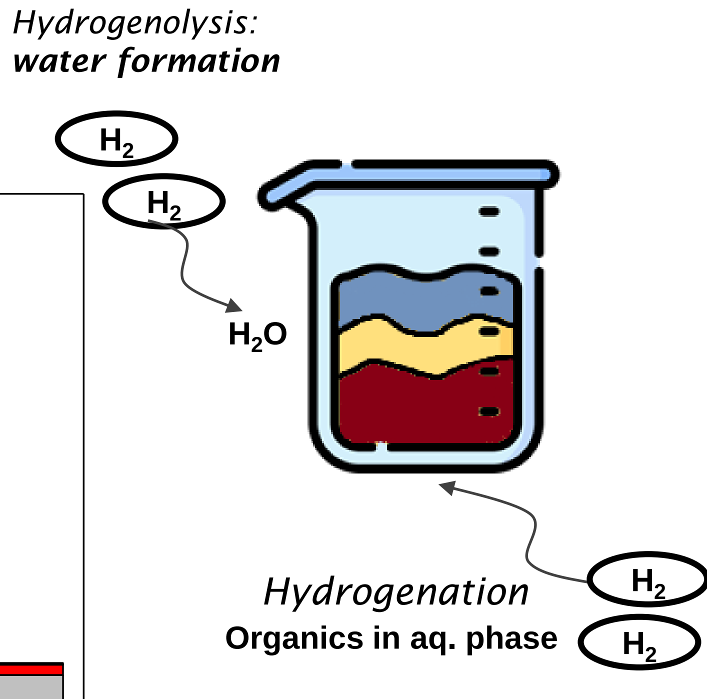
Bio-oils upgrading – Elemental content

		Wet basis (wt.%)					Dry basis (wt.%)			
		C	H	N	H_2O	O	C	H	N	O
BG-EG	Aq. phase	18.8	9.0	2.8	55.9	69.4	30.6	4.8	3.8	60.8
	Up. oil	60.1	7.4	0.5	11.1	32.0	67.6	6.9	0.6	24.9
BG-ET	Aq. phase	21.5	9.6	1.5	55.7	67.4	48.5	7.7	3.4	40.4
	Up. oil	61.5	7.8	0.5	9.6	30.4	68.0	7.4	0.5	24.1
BS-EG	Aq. phase	19.4	9.9	2.0	60.5	68.7	16.4	2.7	1.7	79.3
	Up. oil	63.4	7.3	0.6	8.8	28.7	69.5	6.9	0.7	22.9
BS-ET	Single phase	43.1	10.5	2.2	25.5	44.1	57.9	10.3	3.0	28.8

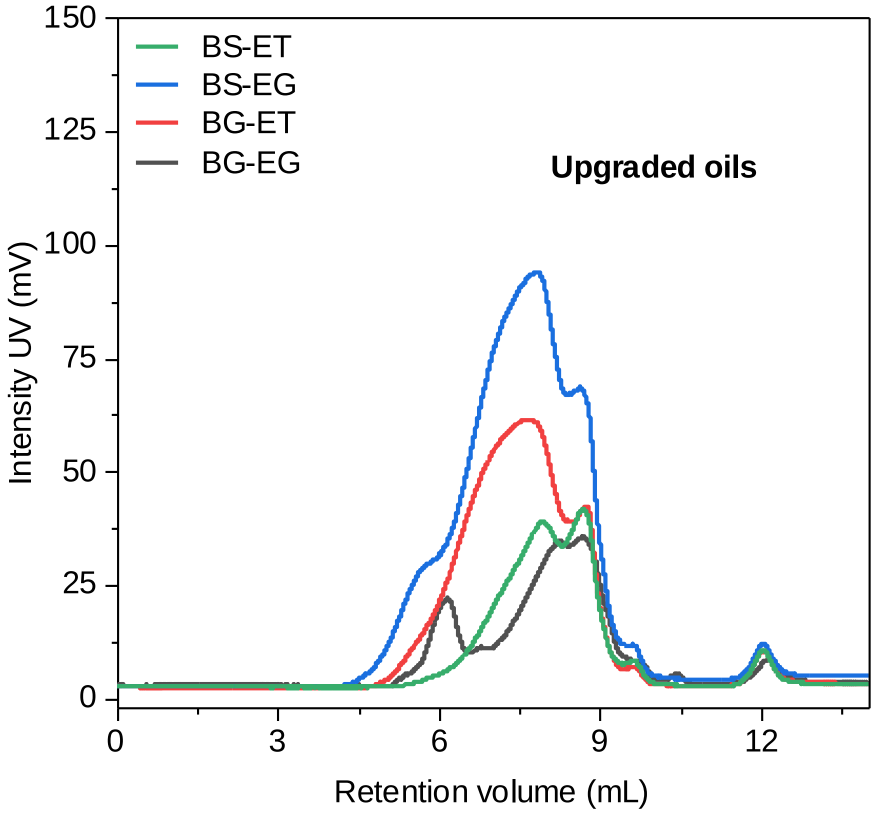
Bio-oils upgrading – H_2 uptake, Gas production

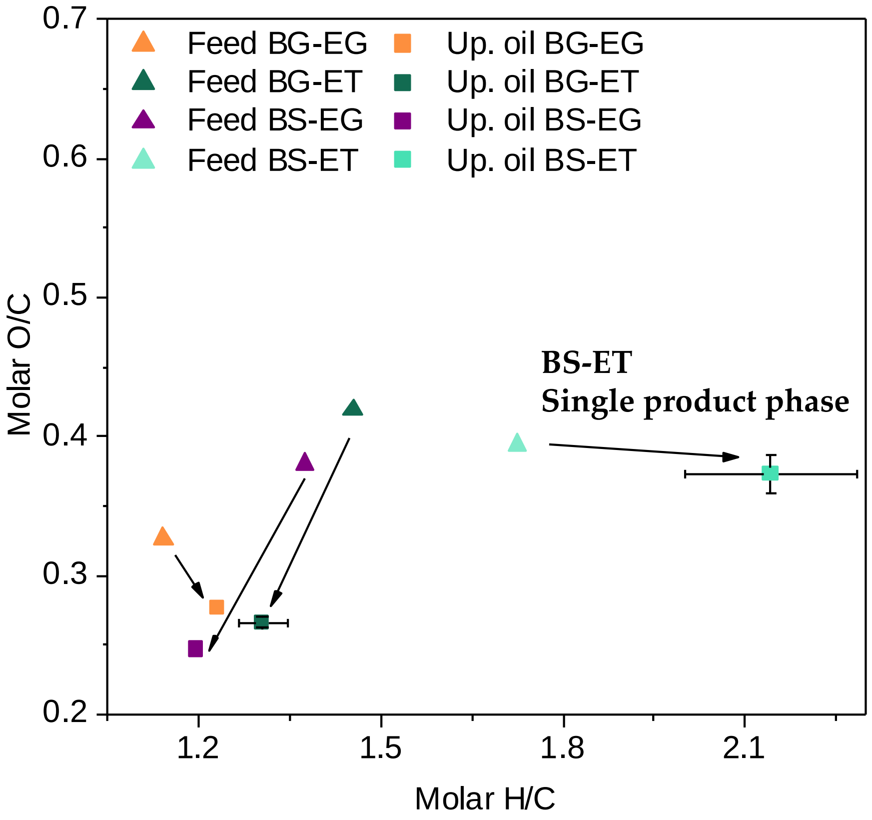






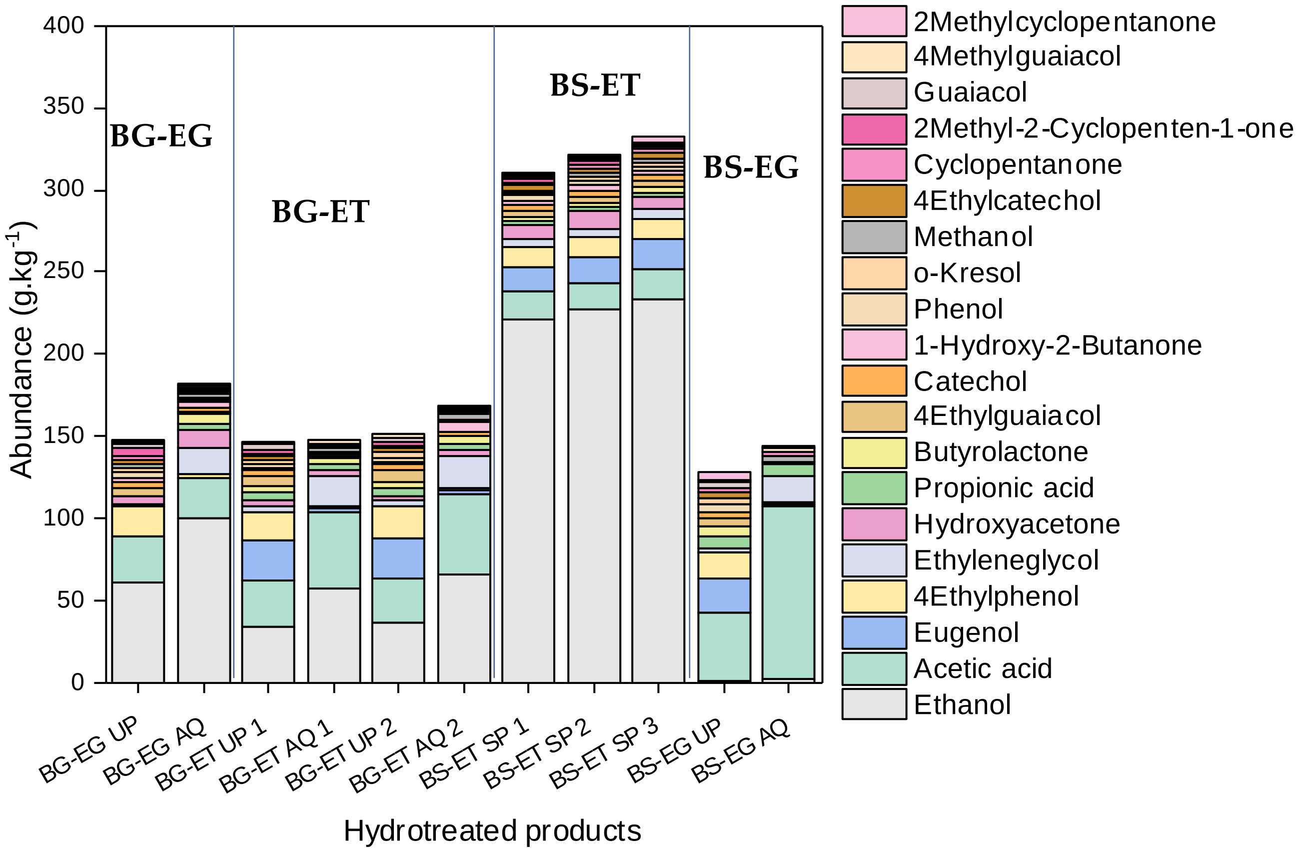
Bio-oils upgrading – Molecular weight, O/C & H/C



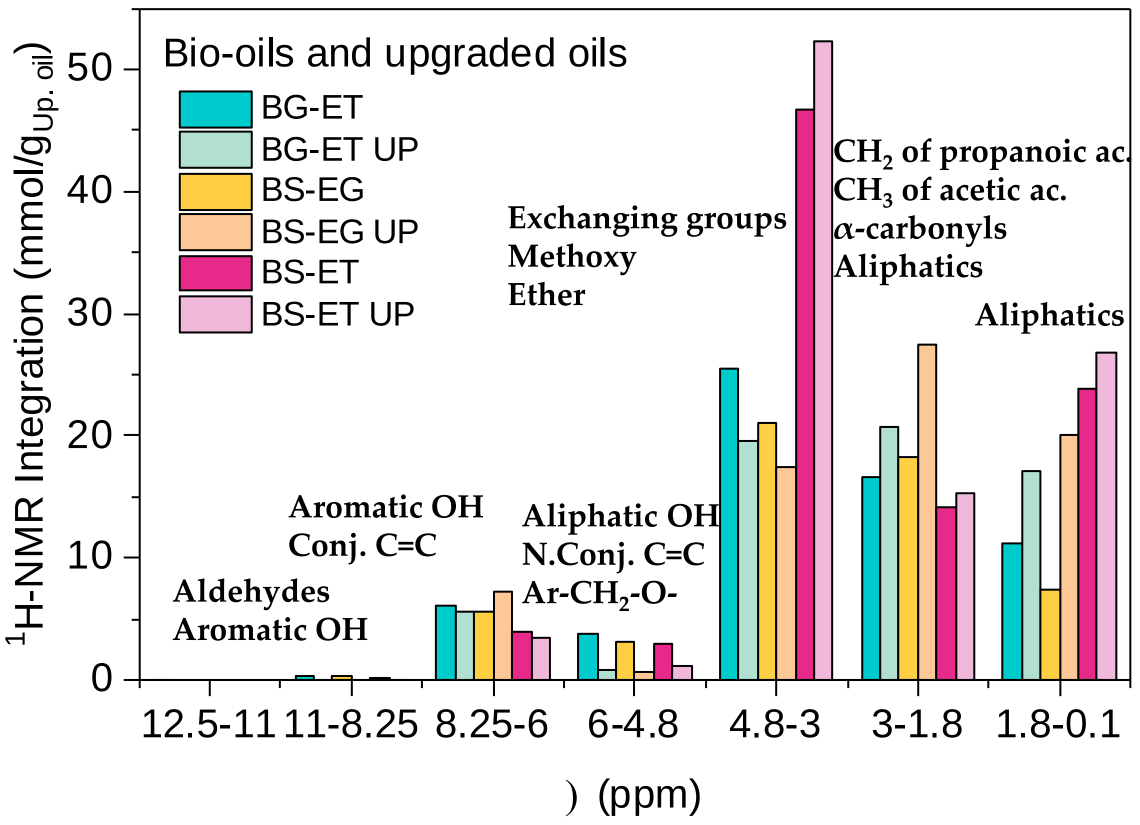


Upgraded oil characterization

Chemical composition (GC-FID)



Chemical composition (^{1}H-NMR)



Summary

- The quenching media directly affects the phase separation during pyrolysis and hydrotreatment.
- The phase separation has a strong influence on the HDO sucess and on controlling viscosity.
- Ethanol as a quenching media helped with viscosity issues.
- Ethanol was one of the main components, in almost all cases. Independent of the quenching media used.
- The catalyst was successful on reducing the O/C ratio for all four tested bio-oils.

Icons from Freepik, Flaticon. https://www.flaticon.com/freepik

Ackownledgments

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Thank you!

Questions?