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Thermochemical conversion of sugarcane bagasse and catalytic upgrading of fast pyrolysis bio-oil as a potential conversion route sugarcane refineries

Caroline Carriel Schmitt

Renata Moreira

Renato Cruz Neves

Danirel Richter

Axel Funke

Klauss Raffelt

Jan-Dierk Grunwaldt

Nicolus Danhmen

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A série "Comunicação Técnica" compreende trabalhos elaborados por técnicos do IPT, apresentados em eventos, publicados em revistas especializadas ou quando seu conteúdo apresentar relevância pública.



3. Exploiting the concept of biorefineries

3.2 Technologies of biorefineries

Thermochemical conversion of sugarcane bagasse and catalytic upgrading of fast pyrolysis bio-oil as a potential conversion route in sugarcane refineries

Carriel Schmitt, Caroline¹; Moreira, Renata²; Cruz Neves, Renato³; Richter, Daniel¹; Funke, Axel¹; Raffelt, Klaus¹; Grunwaldt, Jan-Dierk^{1,4}; Dahmen, Nicolaus¹

¹*Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology, Karlsruhe, Germany*

²*Fuels and Lubricants Laboratory, Instituto de Pesquisas Tecnológicas, São Paulo, Brazil*

³*Brazilian Bioethanol Science and Technology Laboratory, Campinas, Brazil*





3.2 Technologies of biorefineries

Sugarcane in Brazil

Brazil biggest producer worldwide



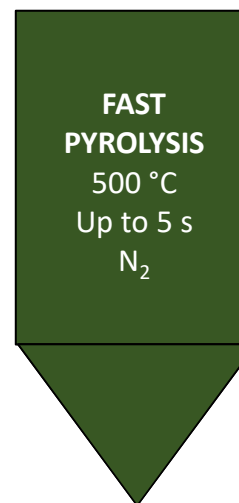
635.3 million tons
sugarcane
2018/2019



448 million tons
sugarcane bagasse
2018/2019



- ✓ Bioelectricity generation;
- ✓ 2G ethanol production;



ADVANTAGES THERMOCHEMICAL ROUTE:

- Sugarcane bagasse already centrally collected;
- ↑ [lignin] = 17-32 wt.%: interesting for thermochemical conversion: functionalized aromatic compounds;
- Expansion of the range of chemicals obtained in sugarcane refinery

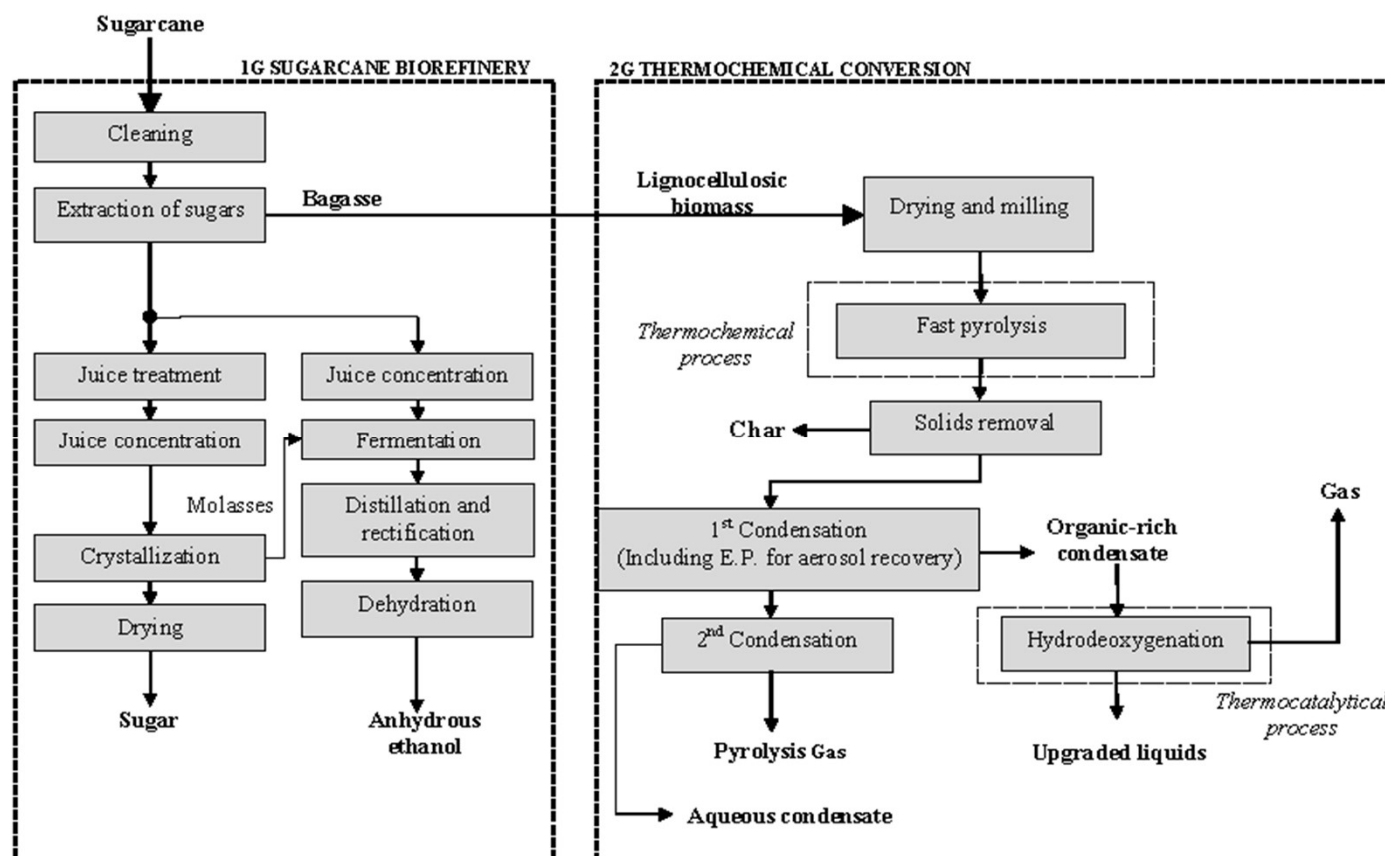


Fast pyrolysis bio-oil



3.2 Technologies of biorefineries

Integration 2G thermochemical conversion routes for sugarcane biorefinery





3.2 Technologies of biorefineries

AIM OF THE STUDY

The aim of this study is to present for the first time a comprehensive investigation from sugarcane bagasse characterization, fast pyrolysis and hydrotreatment to the final upgraded products.

This approach allows identification of the feedstock specific characteristics, advantages, and disadvantages of the whole process chain.



3.2 Technologies of biorefineries

MATERIALS and METHODOLOGY

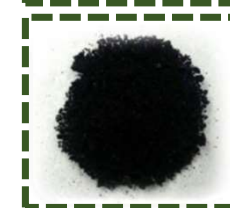
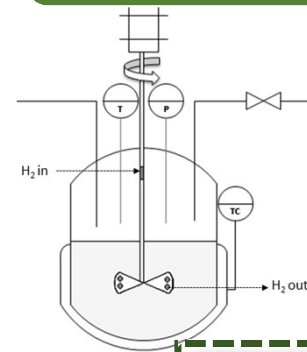
Sugarcane bagasse collection

Sugarcane bagasse preparation and characterization

Fast pyrolysis

Hydrotreatment

Characterization





3.2 Technologies of biorefineries

Sugarcane bagasse collection, preparation and characterization

COLLECTION



São Paulo, Brazil

PREPARATION



Dried to moisture content below 10 wt.% and milled to $\leq 2\text{mm}$

CHARACTERIZATION

ELEMENTAL ANALYSIS



MOISTURE CONTENT



ASH CONTENT



VOLATILE MATTER



HHV



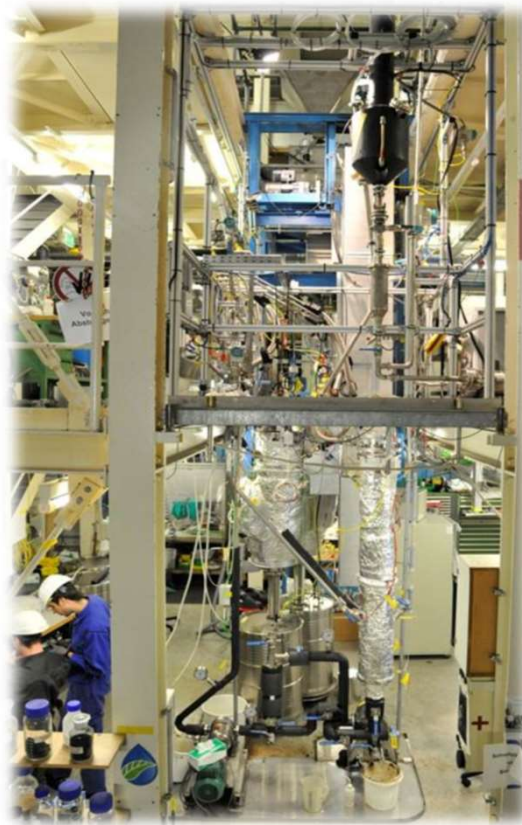
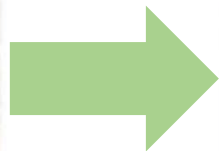
INORGANIC COMPOSITION



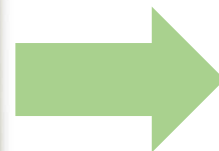
3.2 Technologies of biorefineries

Thermochemical conversion: Fast Pyrolysis

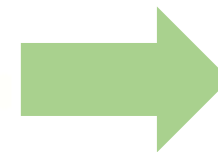
Sugarcane bagasse
 ≤ 2 mm



Phyton unit (10 Kg/h)
500 °C up to 3 s
FPBO condensated at 90 °C



Fast pyrolysis
bio-oil (FPBO)
main product



CHARACTERIZATION

ELEMENTAL
ANALYSIS



H₂O CONTENT



HHV



pH value



GC-MS/FID



INORGANIC
COMPOSITION



MOLECULAR
WEIGHT



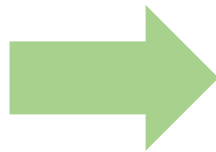
3.2 Technologies of biorefineries

Thermocatalytic treatment of fast pyrolysis bio-oil: Hydrotreatment with two Ni-based catalysts

Fast pyrolysis
bio-oil (FPBO)
main product



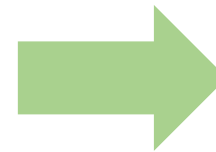
- Low pH value;
- High [H₂O];
- High [O];



Hydrotreatment



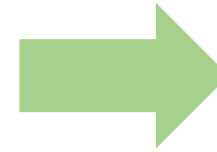
50 mL FPBO, 2.5 g catalyst
Catalysts: Ni/SiO₂ and Ni/Cr₂O₃-SiO₂
2 h, 325 °C, 90 bar of H₂
autoclave of 300 mL



Gas fraction



Upgraded oil +
upgraded light phase

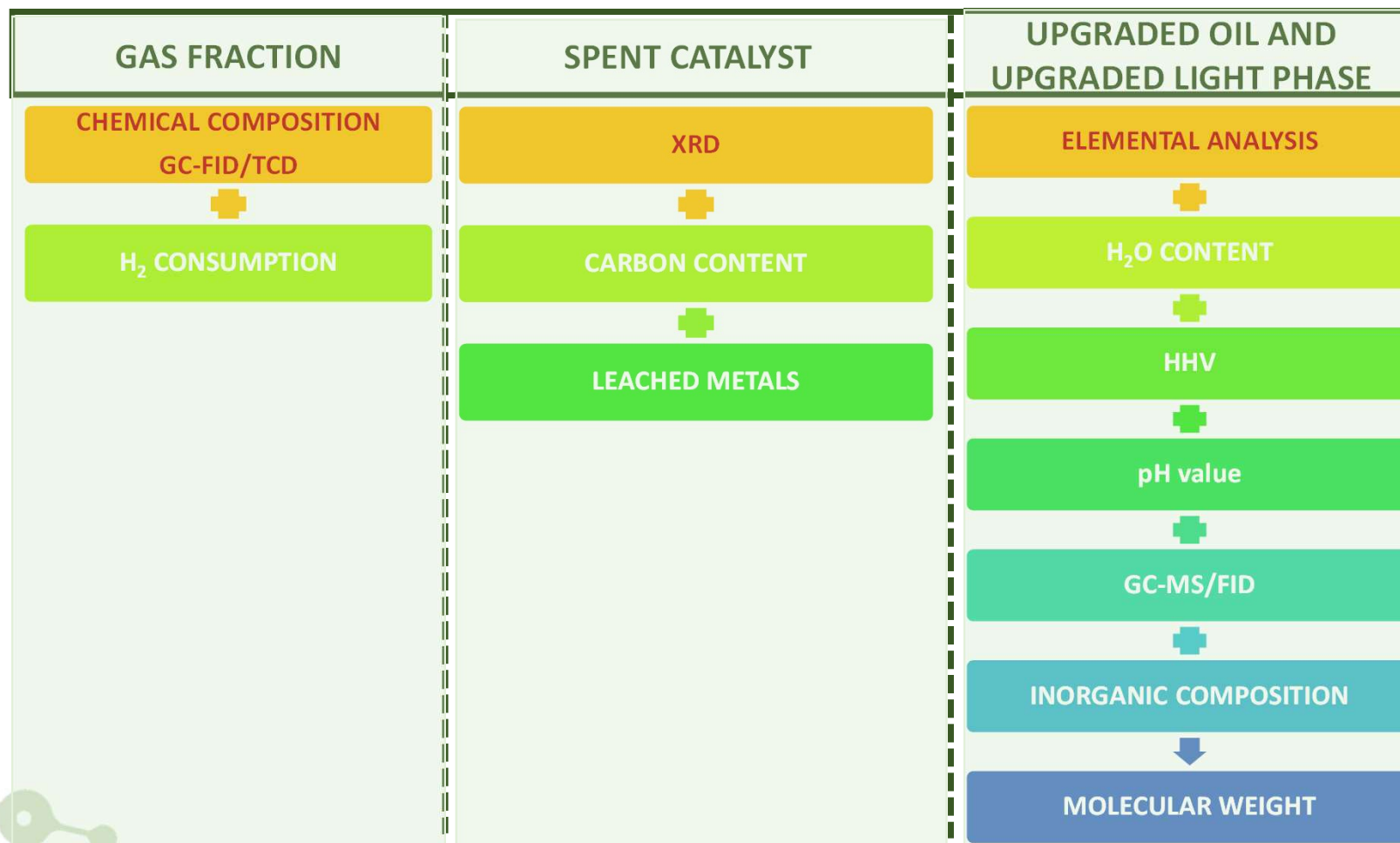


Spent catalyst +
solid residue



3.2 Technologies of biorefineries

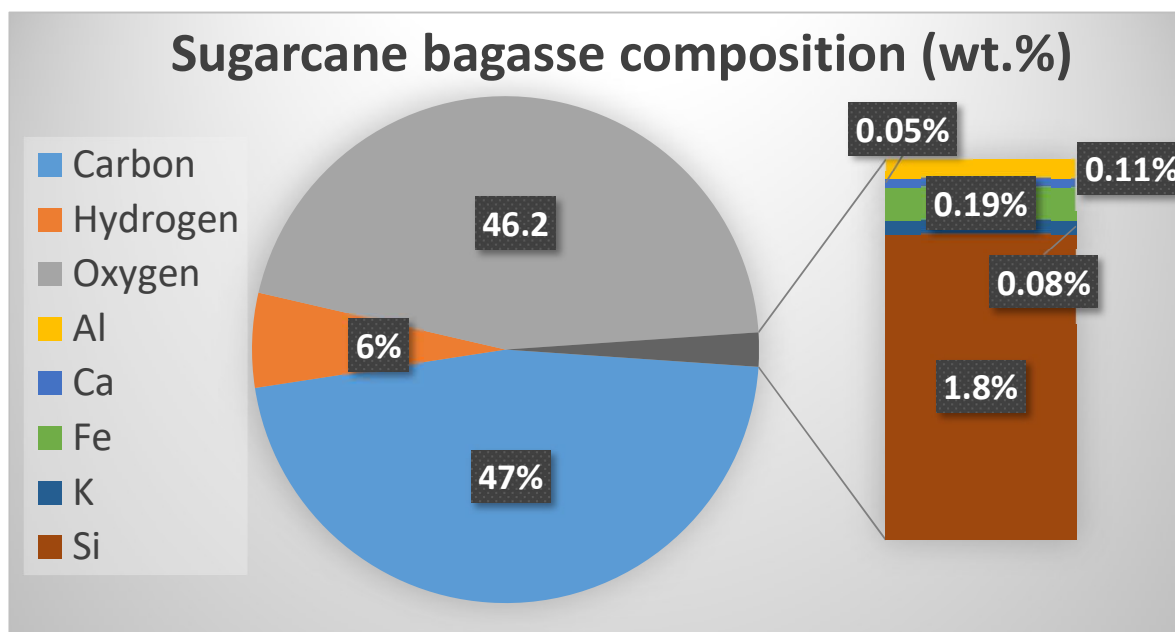
Hydrotreatment products: Characterization





3.2 Technologies of biorefineries

Results: Sugarcane bagasse characterization



↑ ash content!

↓ potassium content! (0.08 wt.%)!

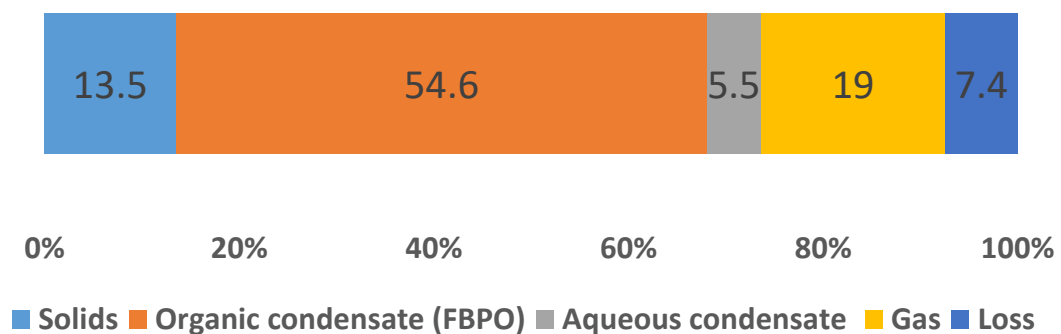
	SCB*
Residual moisture (wt. %)	2.80
HHV (MJ/kg)	18.51
Proximate analysis	
Ash (wt.%)	6.75
Volatile matter (wt.%)	80.32
Fixed carbon (wt.%)	10.14



3.2 Technologies of biorefineries

Results: Fast pyrolysis of sugarcane bagasse

Fast Pyrolysis products distribution (wt.%)



↓ potassium content (catalytic effect) ↑ FPBO yield!

Physicochemical properties and elemental analysis FPBO (dry basis)

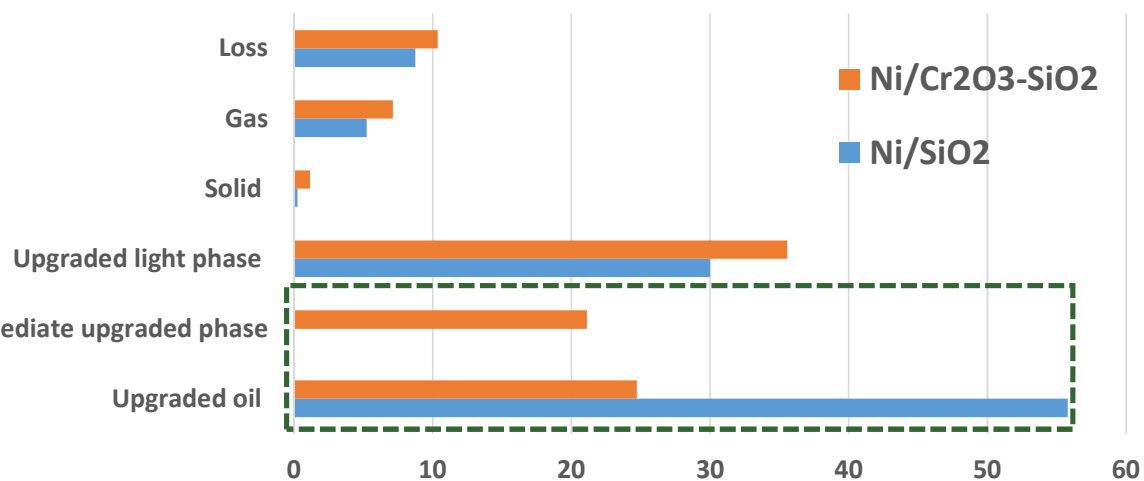
Solid (wt.%)	0.8
pH value	2.9
H ₂ O (wt.%)	20.9
Density (g/cm ³)	1.18
HHV (MJ/kg)	23.79
Carbon (wt.%)	56.89
Hydrogen (wt.%)	6.55
Oxygen (wt.%) ^{**}	36.56
Nitrogen (wt.%)	<0.2



3.2 Technologies of biorefineries

Results: Hydrotreatment of fast pyrolysis bio-oil

Products distribution of hydrotreatment with Ni/SiO₂ and Ni/Cr₂O₃-SiO₂



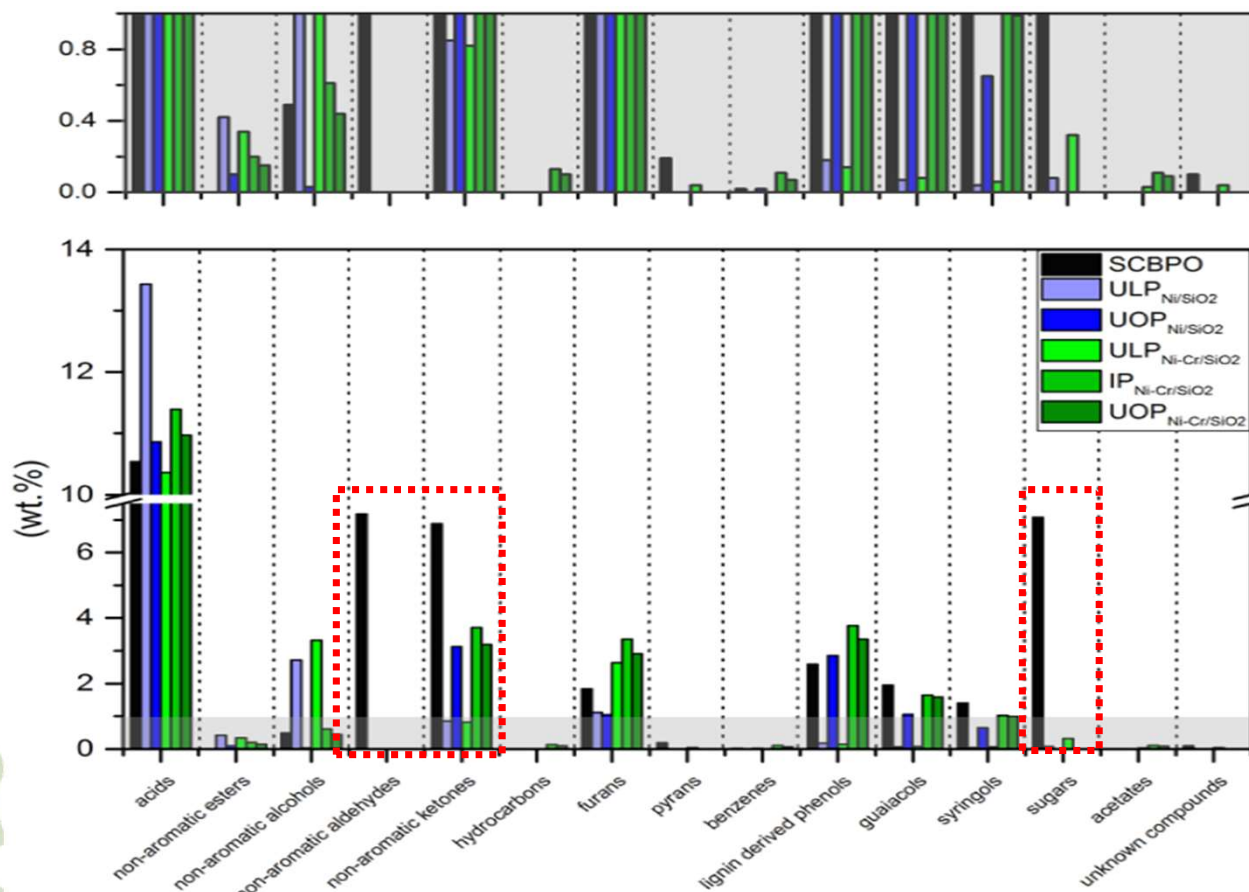
	FPBO	UOP _{Ni/SiO2}	IUP _{Ni-Cr/SiO2}	UOP _{Ni-Cr/SiO2}
H ₂ O (wt.%)	20.9	8.3	8.8	8.6
pH value	2.9	-	3.8	-
HHV (MJ/kg)	23.79	31.89	31.73	30.42
Carbon (wt.%)	56.89	71.1	68.31	66.63
Hydrogen (wt.%)	6.55	7.83	8.69	8.25
Oxygen (wt.%)**	36.56	20.74	22.67	24.79
Nitrogen (wt.%)	<0.2	0.33	0.33	0.33
DOD (%)*	-	43.3	38.0	32.2

*DOD: degree of deoxygenation



3.2 Technologies of biorefineries

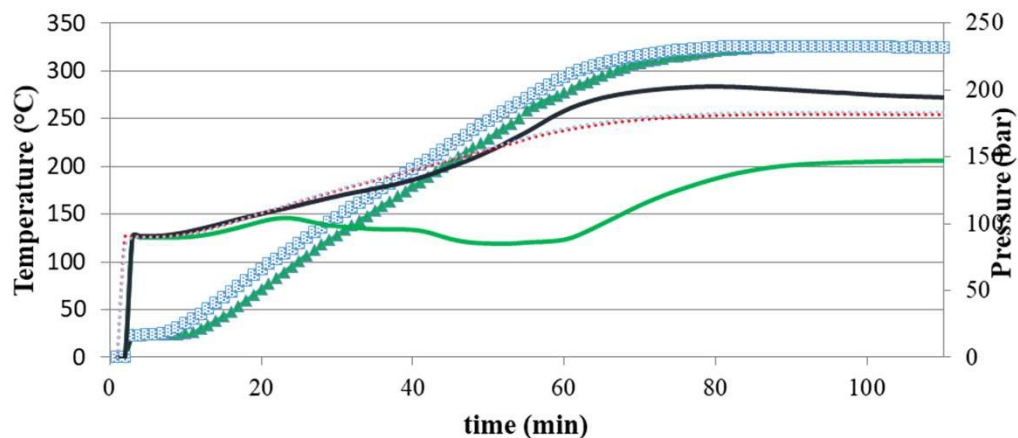
Results: Hydrotreatment of fast pyrolysis bio-oil



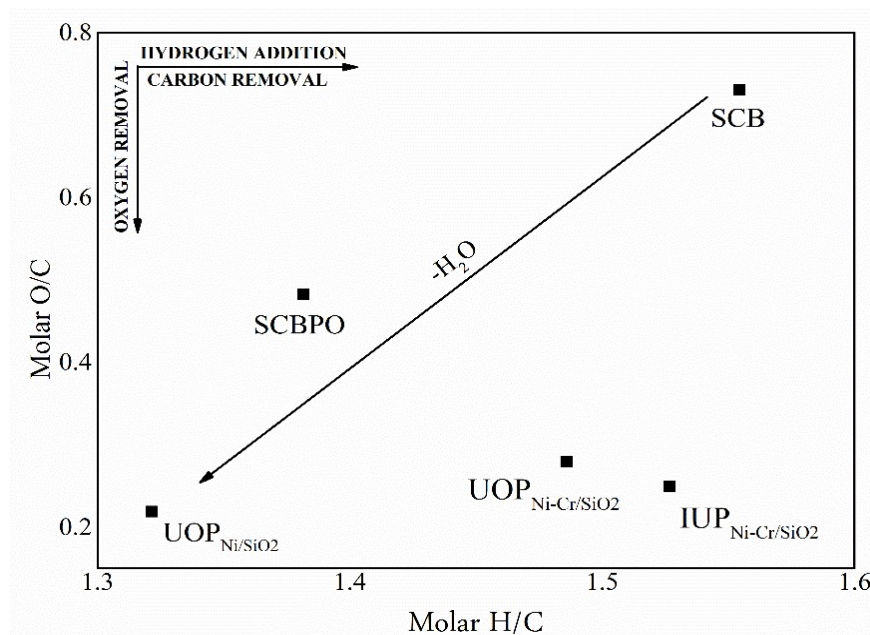


3.2 Technologies of biorefineries

Results: Hydrotreatment Fast pyrolysis bio-oil



- Internal Temperature Autoclave Ni-Cr/SiO₂
- Internal Temperature Autoclave Ni/SiO₂
- Pressure Ni-Cr/SiO₂
- Pressure Ni/SiO₂
- Autoclave theoretical pressure ideal gas equation
- Autoclave theoretical pressure soave redlich kwong equation



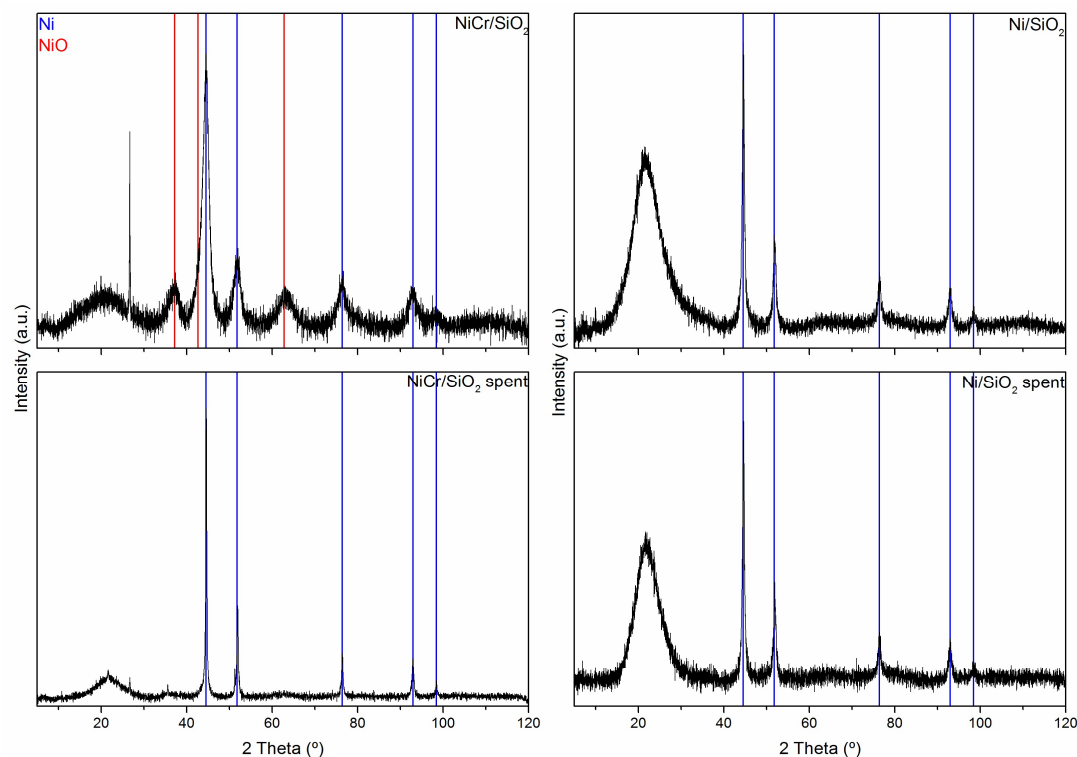
	Ni/SiO ₂	Ni-Cr/SiO ₂
Hydrogen consumption (NL/Kg feed)	199.43	326.2
Gas composition		
Carbon dioxide (mol/kg feed)	1.146	1.263
Carbon monoxide (mol/kg feed)	0.041	0.058
Methane (mol/kg feed)	0.016	0.718



3.2 Technologies of biorefineries

Results: Catalyst characterization

	Ni/SiO ₂	Ni/Cr ₂ O ₃ -SiO ₂
Carbon (wt.%)	0.36	18.5
Leached metal to ULP (wt.%)	Ni: 0.73	Ni: 0.054 Cr: <0.09



Crystalite size

Ni/SiO₂: 17.7 nm before and after reaction;

Ni/Cr₂O₃-SiO₂: 4.4 nm (before) to 38.2 nm after reaction → sintering



3.2 Technologies of biorefineries

Conclusions

A comprehensive study from sugarcane bagasse characterization to upgraded products after treatment was presented.

- Low moisture and low K content in the sugarcane bagasse were reflected in the high yield of FBPO **OUTSIDE** the range expected for residual biomass;
- Hydrotreatment with both catalysts resulted in upgraded oils with around 30% less O and approx. 43% less water in comparison to the FPBO;
- **Ni/Cr₂O₃-SiO₂** showed higher **hydrogenation** activity whereas **Ni/SiO₂** showed higher **hydrodeoxygenation** activity;
- Sugarcane bagasse proved to be an attractive feedstock for 2G biorefineries with overall yield of 30.5 wt.%;
- Further studies will target higher FPBO yields (fast pyrolysis) and upgraded oils with lower oxygen content.



3.2 Technologies of biorefineries

Thank you!