Sustainable production of Cellulose-based products and additives to be used in SMEs and rural areas
Funded from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 101007733.

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Integrated biorefinery for the valorization of Colombian cocoa wastes

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CELISE Symposium

Warsaw, Tuesday, 25 July 2023

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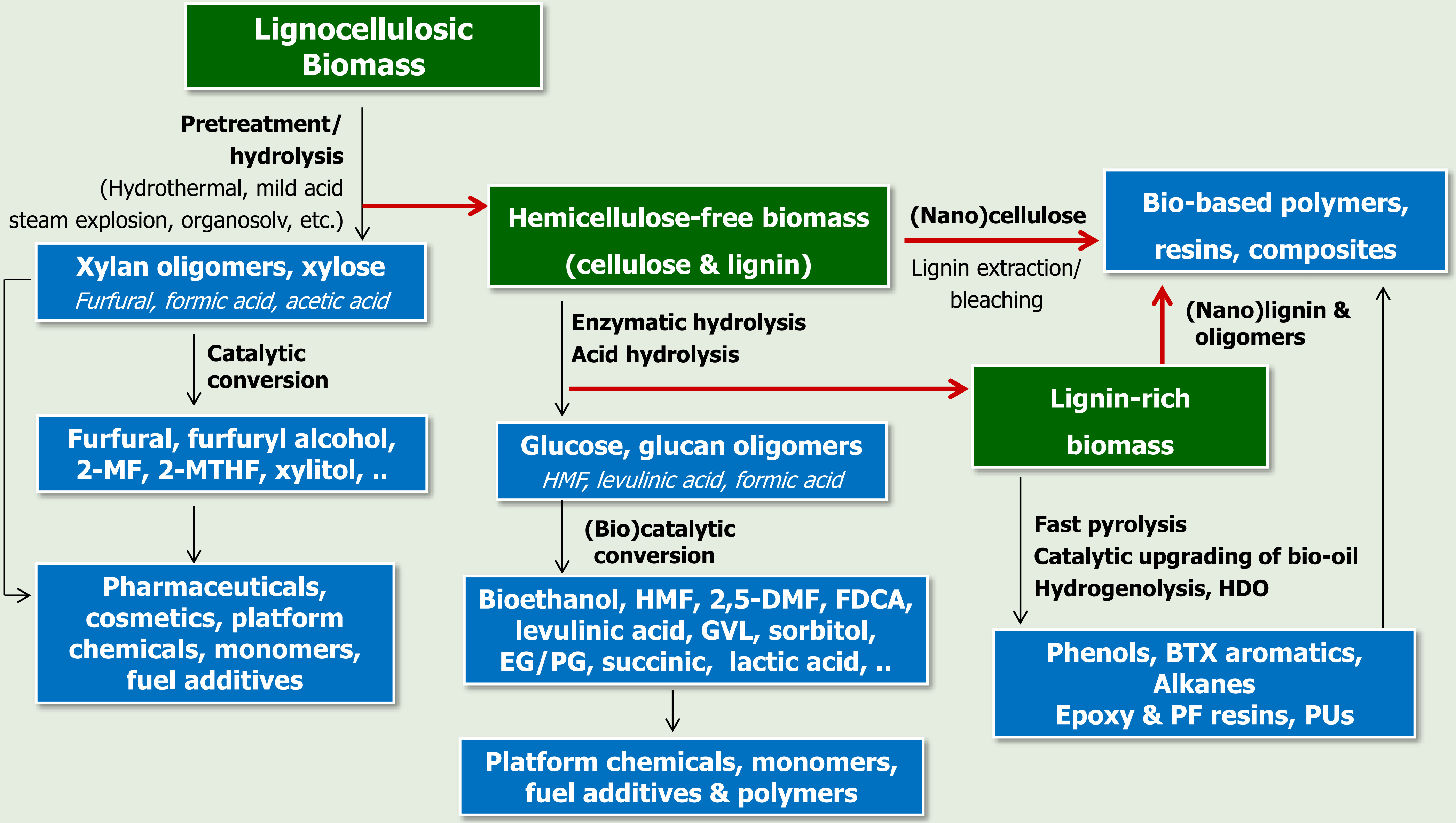
Integrated Biorefinery at AUTH – Valorization of “whole biomass”



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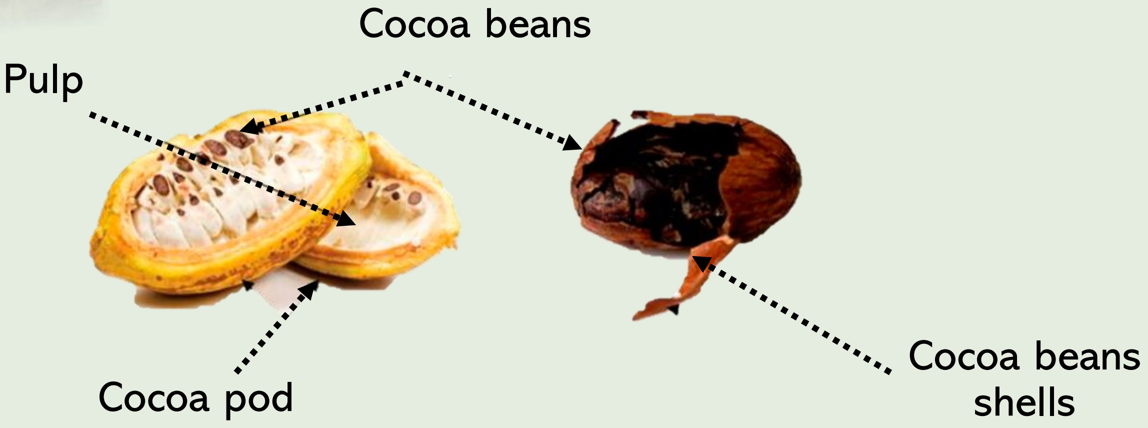
Cocoa bean shells

Samples provided by Universidad Cooperativa de Colombia (Prof. F. Colmenares) and Prof. J.C Colmenares (Poland)



Integrated Biorefinery of cocoa bean shell wastes

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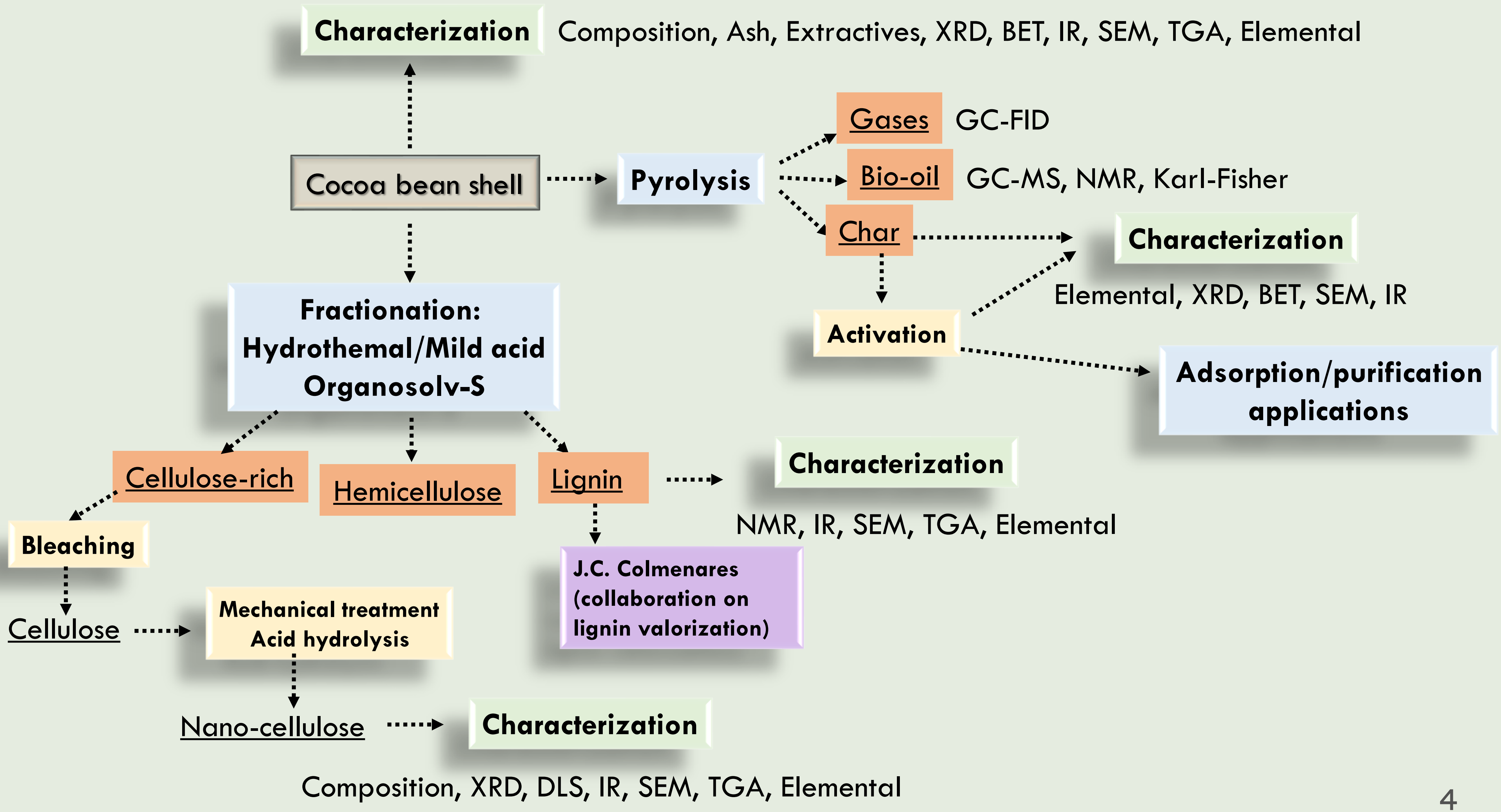

Extractives, fractionation, pyrolysis

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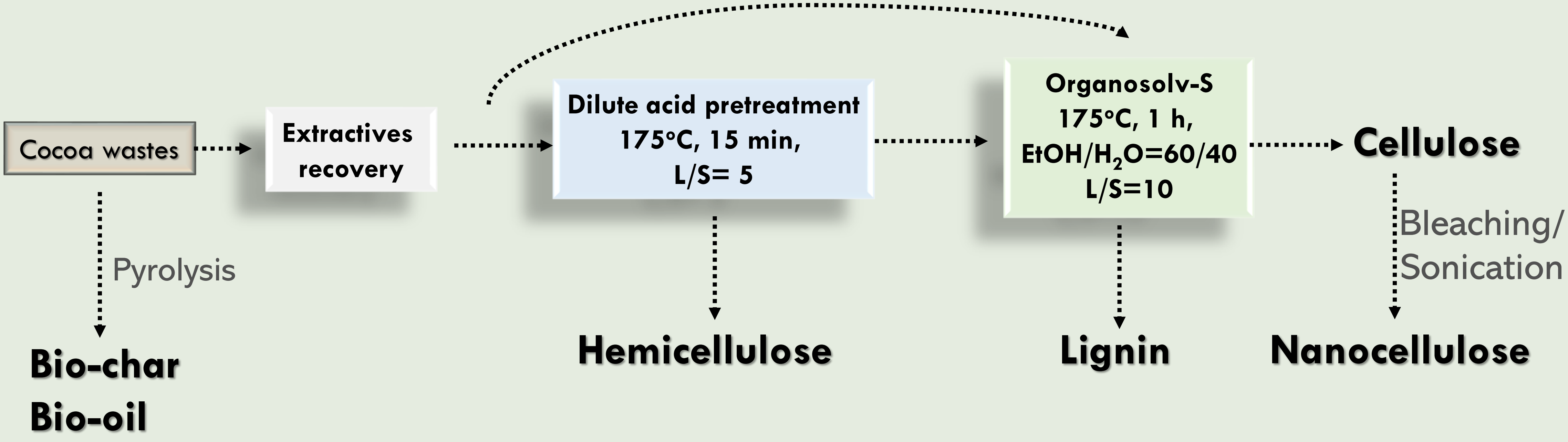

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Mechanical pretreatment

CCN-51

TCS-01

ICS-95

High shear blending

Sieving

150-1000 µm

CCN-51

TCS-01

ICS-95

<150 µm

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Chemical composition of initial samples

Sample	**CCN-51**	**TCN-01**	**ICS-95**
Glucan	16.9	16.6	15.9
Xylan	2.9	4.1	0.0
Galactan	8.5	10.1	11.1
Arabinan	0.0	0.0	0.0
Mannan	0.0	0.0	0.0
Acetyl units	0.6	0.8	1.7
Acid insoluble lignin	38.2	44.7	36.4
Acid soluble lignin	3.6	4.4	3.6
Ash	8.5	9.5	8.6
Total	**79**	**90**	**77**

- *Analysis was performed on as-received samples, containing extractives*
- *Low mass balance is attributed to the high protein content (to be determined)*

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Chemical composition of extractives-free biomass

	Extractives in H_2O	Extractives in EtOH
CCN-51	29.9%	23.0%
TCS-01	51.1%	20.2%
ICS-95	39.2%	16.3%

Sample	**CCN-51**	**TCN-01**	**ICS-95**
Glucan	27.1	24.2	29.0
Xylan	6.1	4.7	7.3
Galactan	12.5	8.5	15.2
Arabinan	0.0	0.0	0.0
Mannan	0.0	0.0	0.0
Acetyl units	1.9	0.7	1.8
Acid insoluble lignin	34.1	39.4	35.5
Acid soluble lignin	2.3	2.6	2.3
Ash	2.1	4.9	2.9
Total	**86**	**85**	**94**

Physicochemical properties of initial samples

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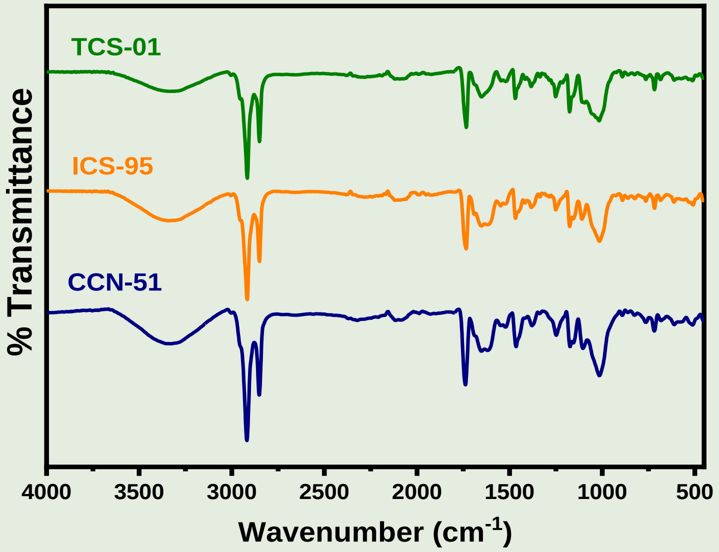
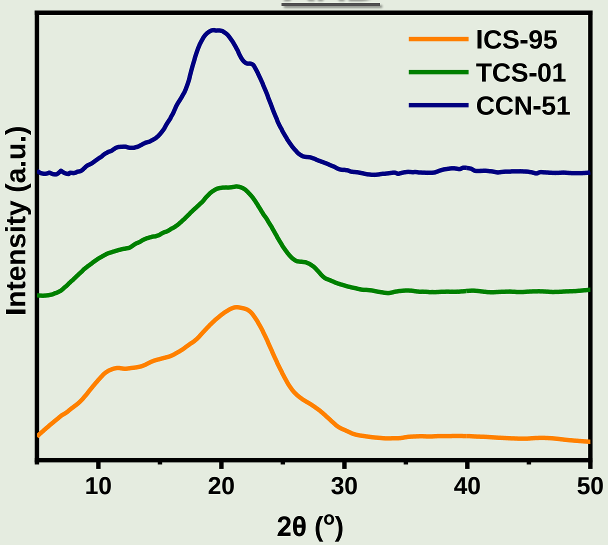
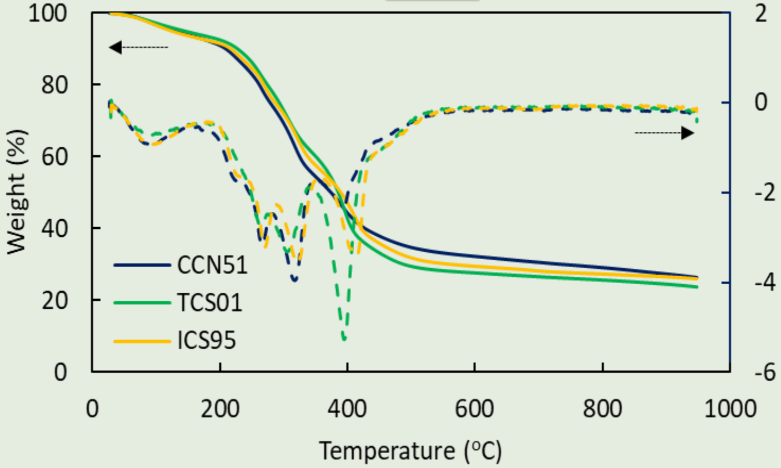


XRD



TGA

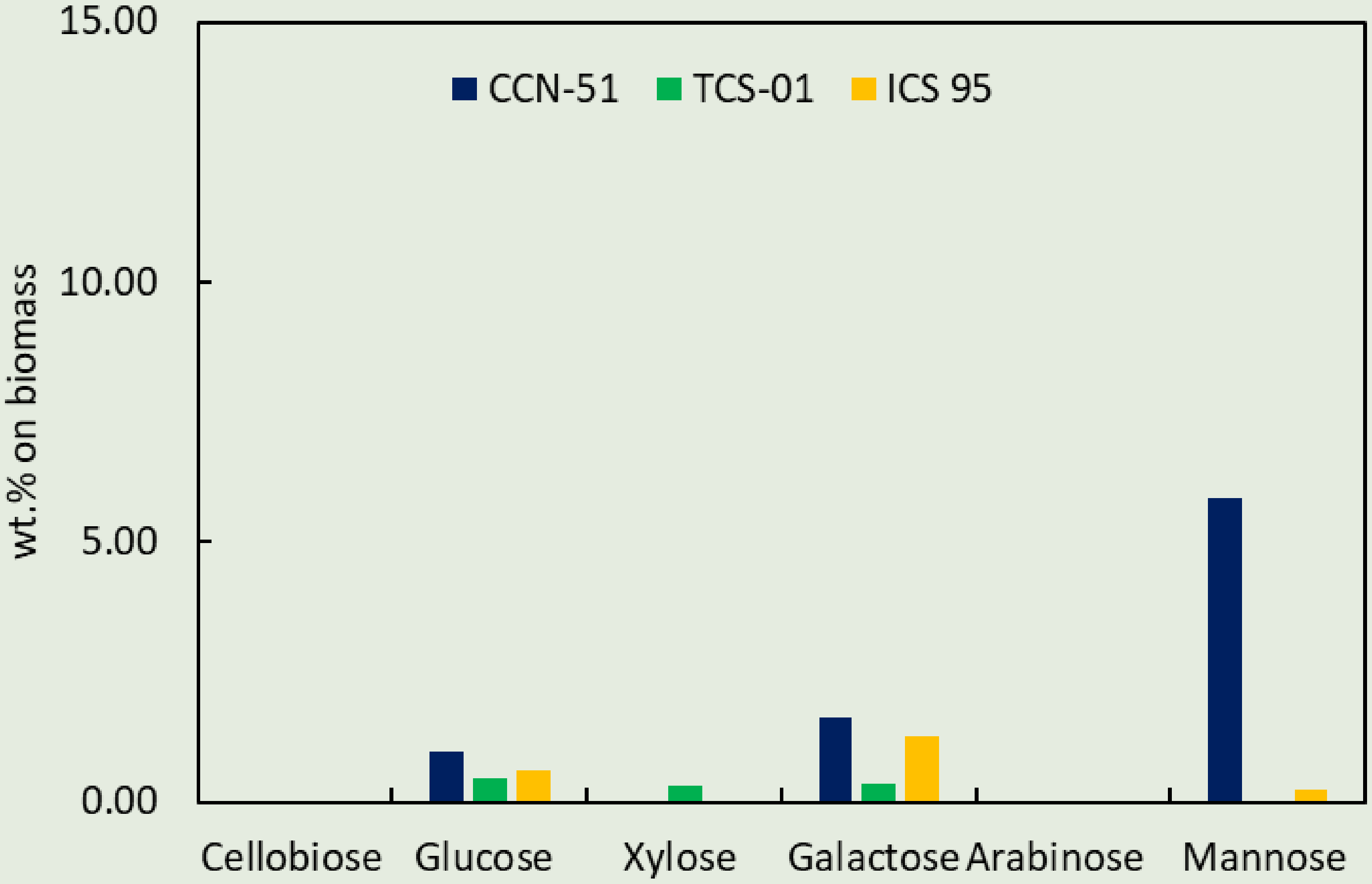


Elemental analysis

Sample	CCN-51	TCN-01	ICS-95
% C	41.8	44.2	43.4
% H	5.3	5.8	5.7
% N	3.0	3.6	2.6
% S	0.0	0.0	0.0
% O	49.9	46.4	48.3

Water soluble extractives recovery and analysis

Water soluble extractives by Soxhlet



Ethanol soluble extractives recovery and analysis

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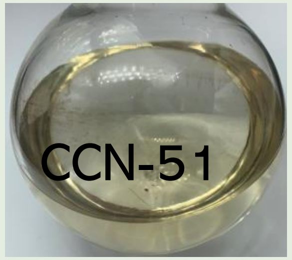
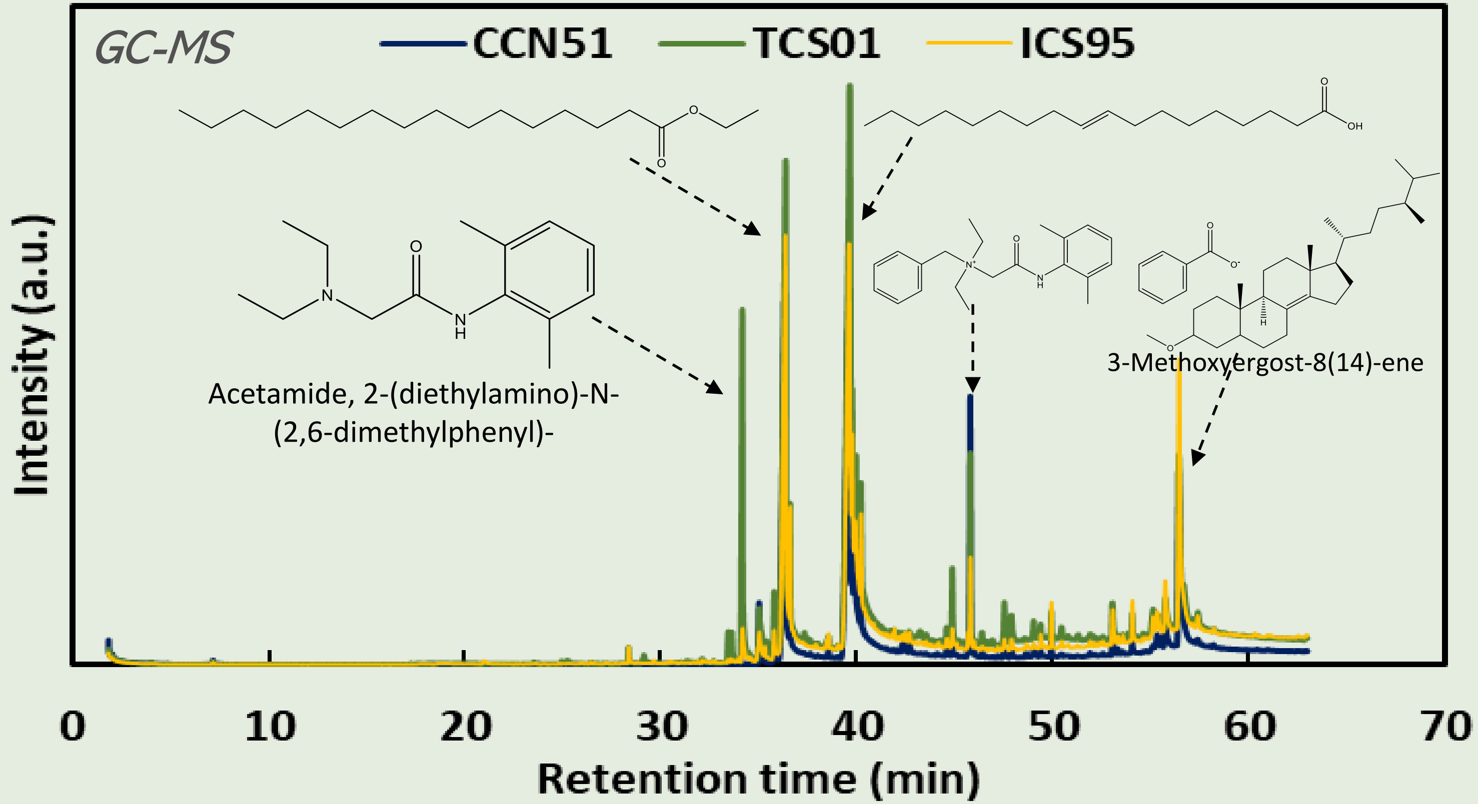


Ethanol soluble extractives by Soxhlet



- *Ethanol soluble extractives are mainly fatty acids/esters (C_{16}-C_{19}), sterols and tocopherols*

Batch mode isolation of extractives

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Biomass

H_2O (L/S=33) — Stirring 40ºC, 24 h

Filtration

Solid after H_2O extractives removal

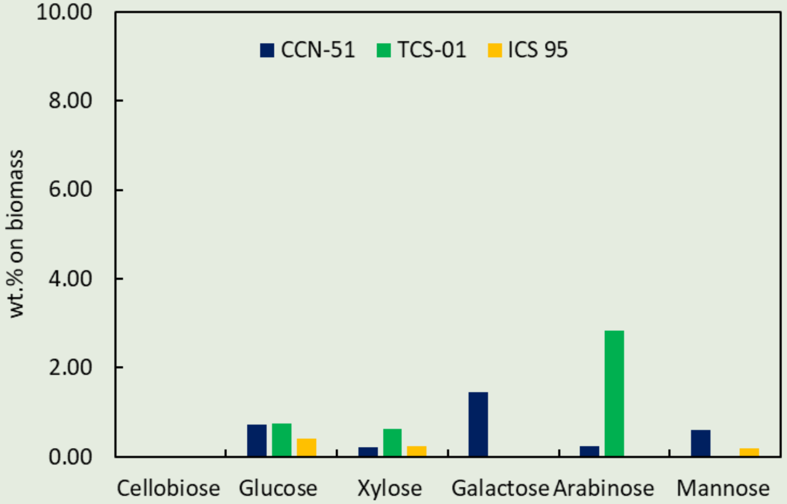
EtOH (L/S=20) — Stirring 40ºC, 9 h

Filtration

Recovered Liquids

	H_2O	EtOH
CCN-51		
TCS-01		
ICS-95		

Water soluble extractives



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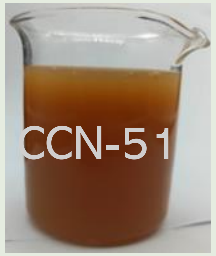
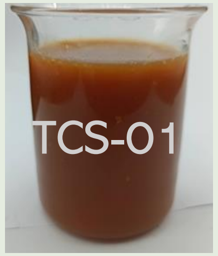
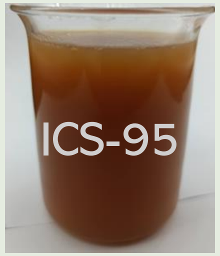
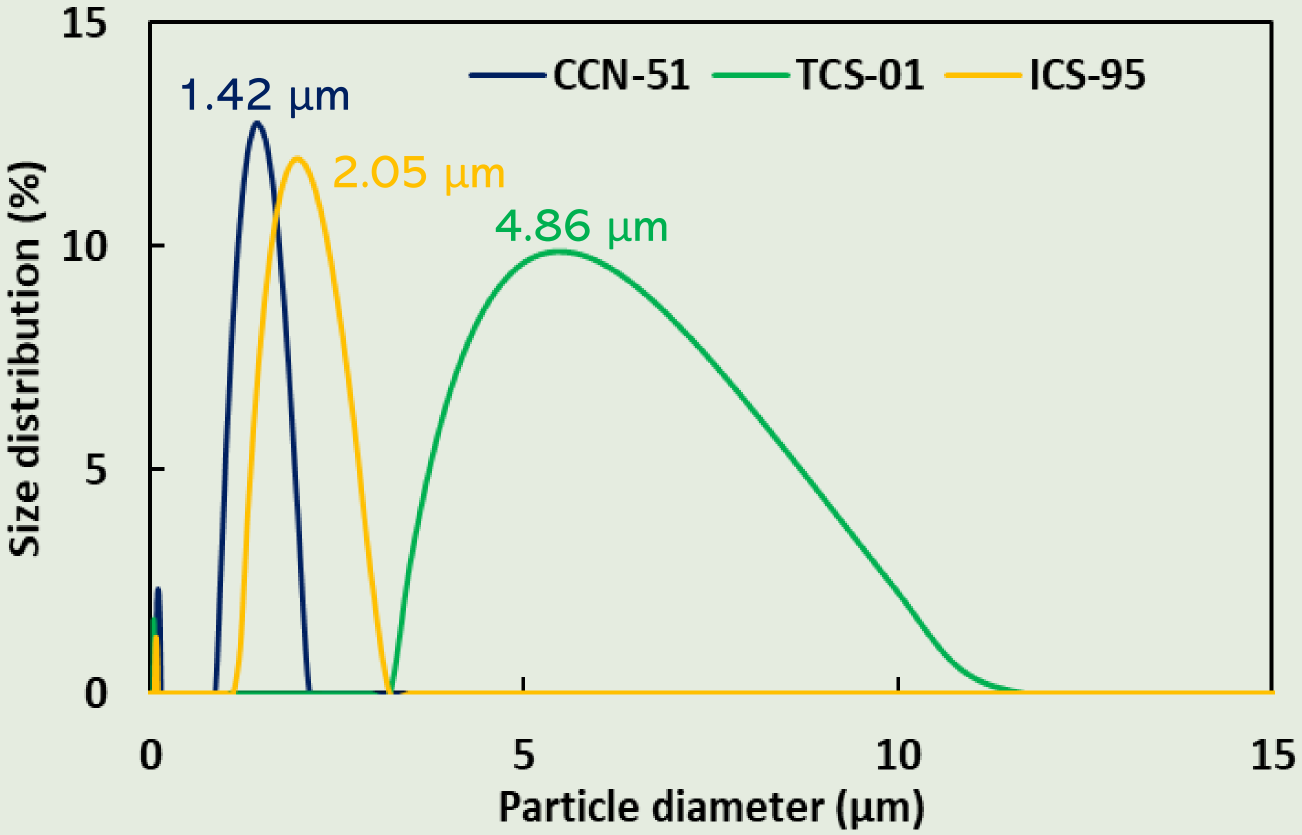
Particle size distribution (DLS) of water extractives suspensions







Solids: ≈ 3 wt.%



- *Stable colloidal suspensions recovered by batch water-soluble extractives isolation, possibly of fibrous nature (to be characterized further)*

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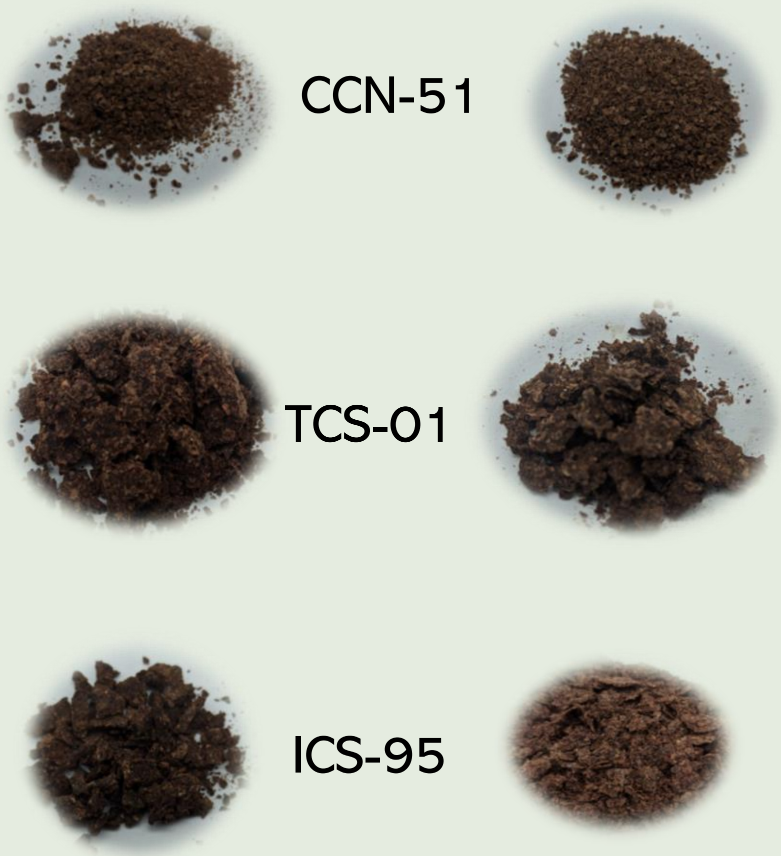
Characterization of extractives-free biomass (batch)

Solids after extraction in:

H_2O EtOH



Sample	CCN-51	TCN-01	ICS-95
Glucan	19.9	15.4	18.4
Xylan	5.9	6.4	5.9
Arabinan	12.6	12.8	12.7
Galactan	0.0	0.0	0.0
Mannan	0.0	0.0	0.0
Acetyl units	1.8	0.8	1.3
Acid insoluble lignin	54.4	57.0	42.0
Acid soluble lignin	2.9	2.8	2.9
Ash	5.3	3.5	3.3
Total	**103**	**99**	**87**

- *Glucan has been solubilized more effectively under batch treatment in water compared to Soxhlet*
- *Thus, lignin concentration is higher in batch treated samples*

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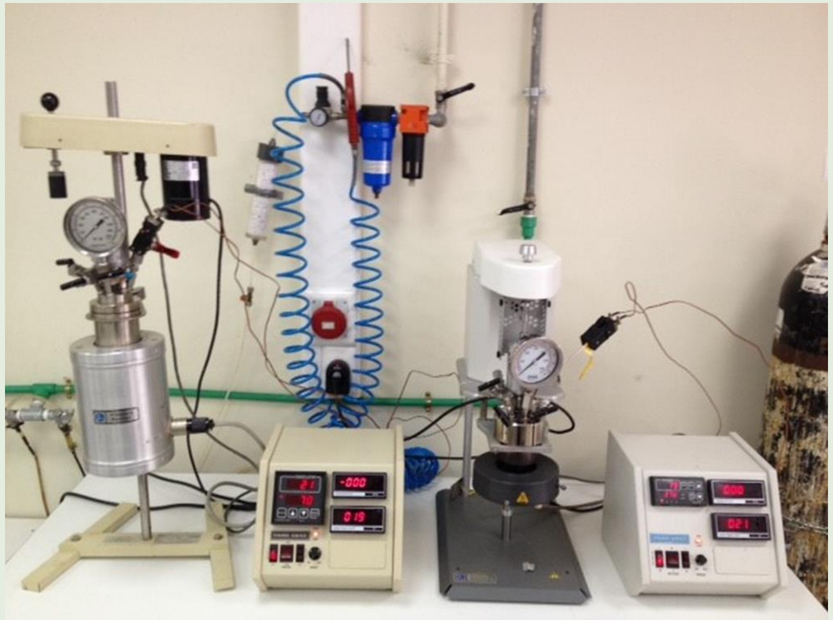
WP1 - Biomass pretreatment/fractionation

<u>Task 1.2.</u>: Novel and sustainable hydrolysis processes as pre-treatment

- Integrated biorefinery for the valorization of wastes
- Mild acid, autohydrolysis and organosolv pretreatment towards the isolation of biomass components (cellulose, hemicellulose, lignin)



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Fractionation of cocoa wastes

Step 1: Hydrothermal/dilute acid pretreatment

Biomass

Solvent: H_2O (LSR=5)

Temperature: 175 °C

Time: 15 min

Catalyst: 2.3 wt.% H_2SO_4

Severity factor (logRo)

$$R_0 = t \cdot \exp\frac{(T-100)}{14.75}$$

Combined Severity factor (logR')

logR'=logRo-|pH|

Liquid enriched in hemicellulose components

Cellulose and lignin

Step 2

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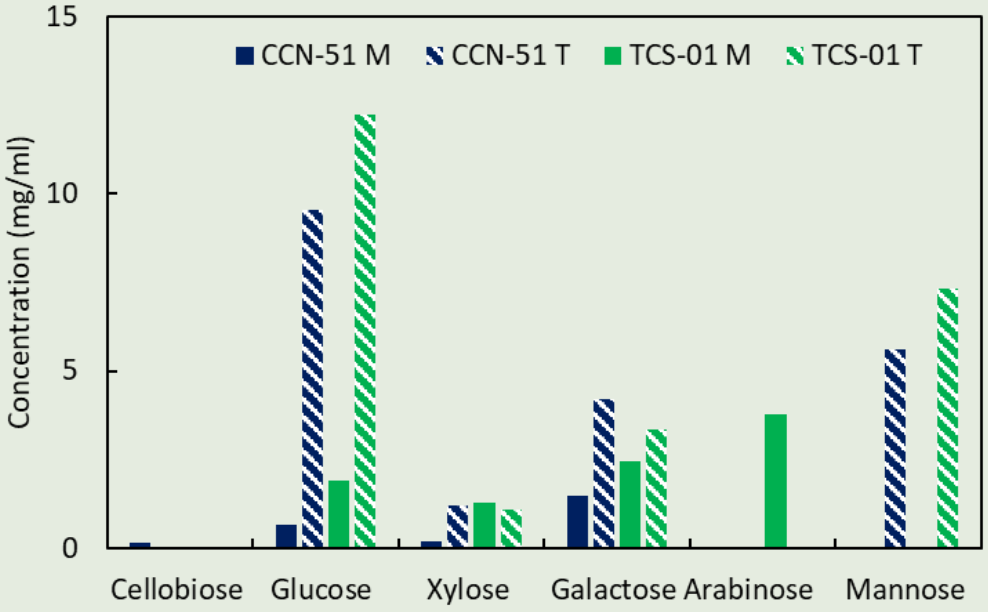
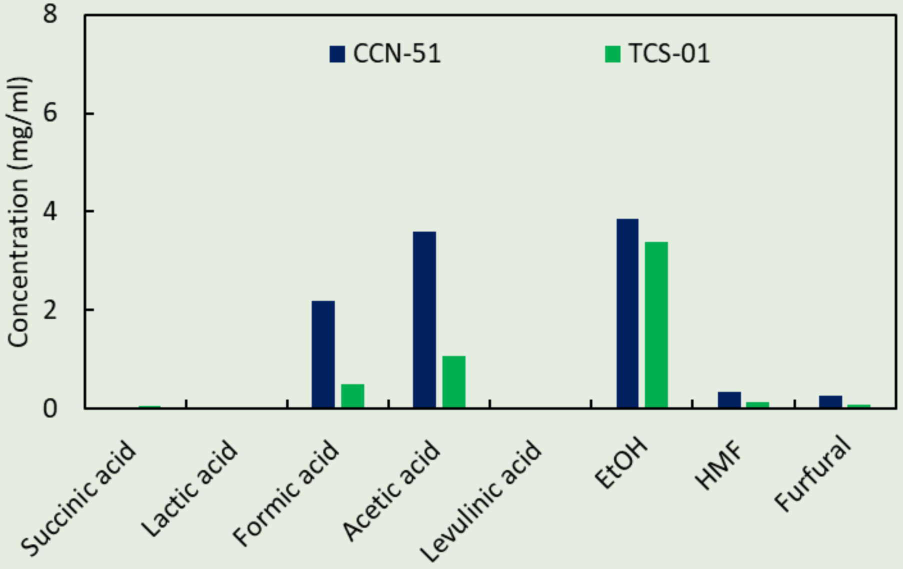
Characterization of liquid streams

CCN-51

TCS-01





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Characterization of solid streams

CCN-51

TCS-01

Sample	CCN-51	TCN-01
Glucan	26.1	16.1
Xylan	3.6	2.2
Galactan	5.7	0.0
Arabinan	0.0	3.3
Mannan	0.0	0.0
Acetyl units	0.3	0.0
Acid insoluble lignin	62.1	65
Acid soluble lignin	1.7	1.1
Ash	0.7	1.4
Total	**100**	**89**

- *Lignin and glucan enriched solids have been recovered*

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Fractionation of cocoa wastes

Step 2: Organosolv pretreatment (lignin/glucan enriched biomass)

Solid from step 1

Solvent: EtOH/H_2O=60/40 (LSR=10)

Temperature: 175 ^oC

Time: 1 h

Catalyst: 2.9 wt.% H_2SO_4

Liquid enriched in (remaining) hemicellulose components

Lignin

Cellulose

Analysis of organosolv liquids

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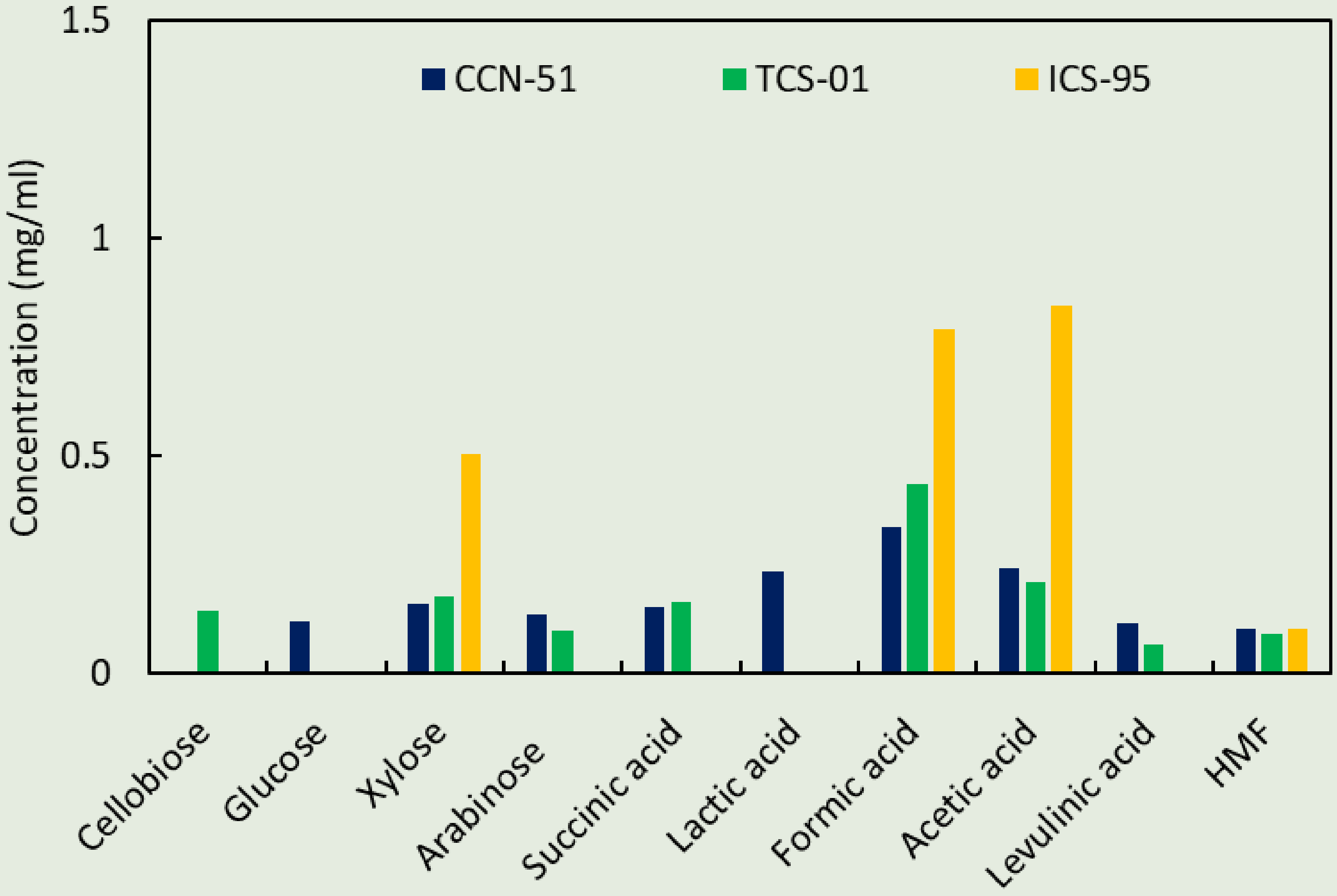

- *Liquids CCN-51 and TCS-01 derived from Organosolv of extractives-free and HLW/mild acid treated biomass*
- *Direct organosolv on extractives-free biomass (sample ICS-95) increases the hemicellulose components in liquid stream*

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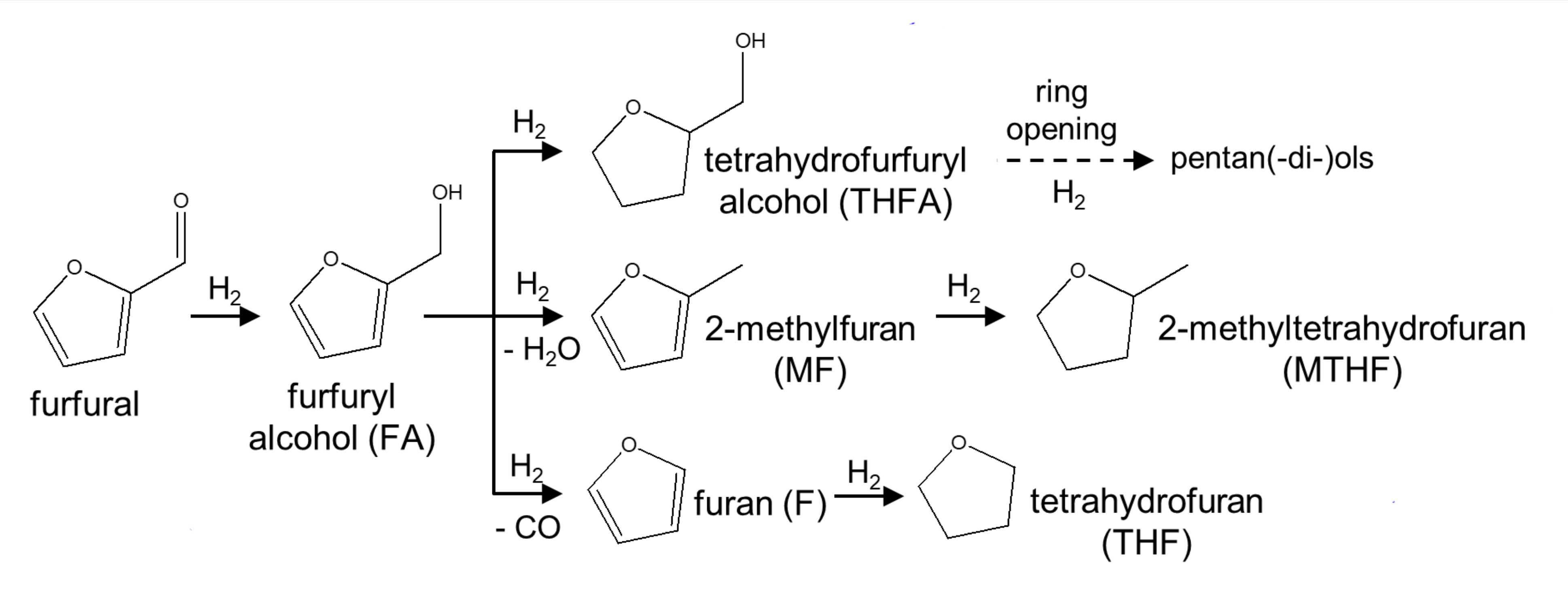
Catalytic hydrogenation of furfural: General reaction mechanism – possible routes



- **Dominant pathways/products depend on catalyst type, reaction parameters and solvent (acting or not as H-donor for inducing transfer hydrogenation)**

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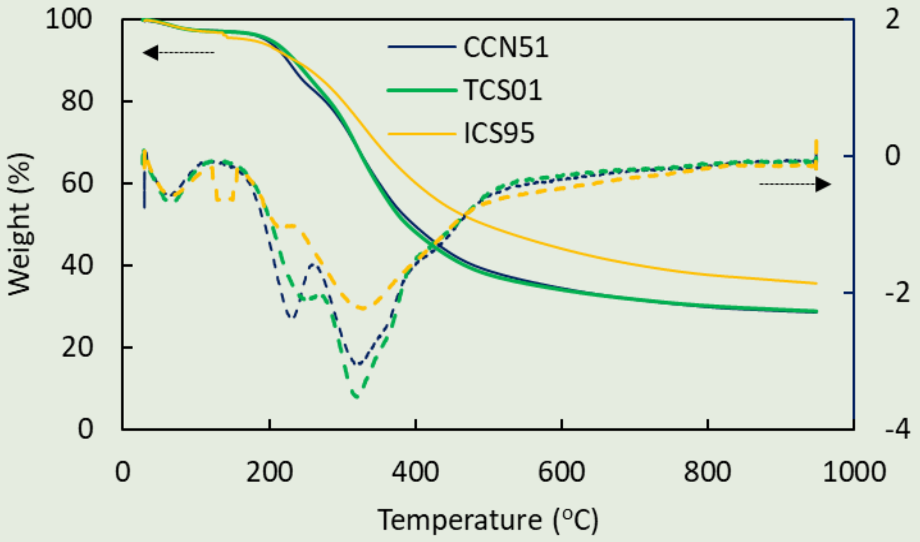
Characterization of lignins

CCN-51

TCS-01

ICS-95

TGA



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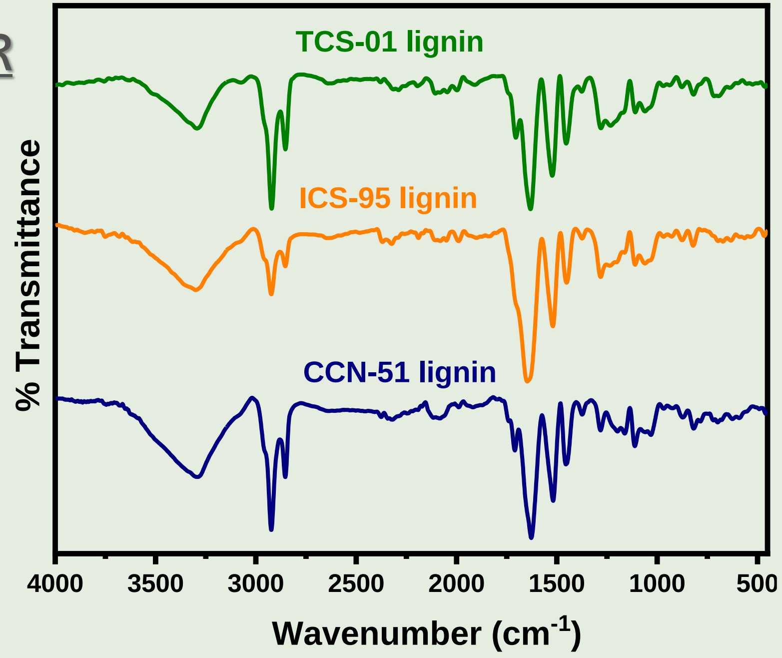

Sample	% C	% H	% N	%S	%O	Residual mass(%)
CCN-51	69.4	7.9	6.6	0.0	16.1	28.6
TCS-01	61.6	7.3	6.8	0.8	23.5	28.9
ICS-95	57.6	5.8	7.0	0.9	28.6	35.7

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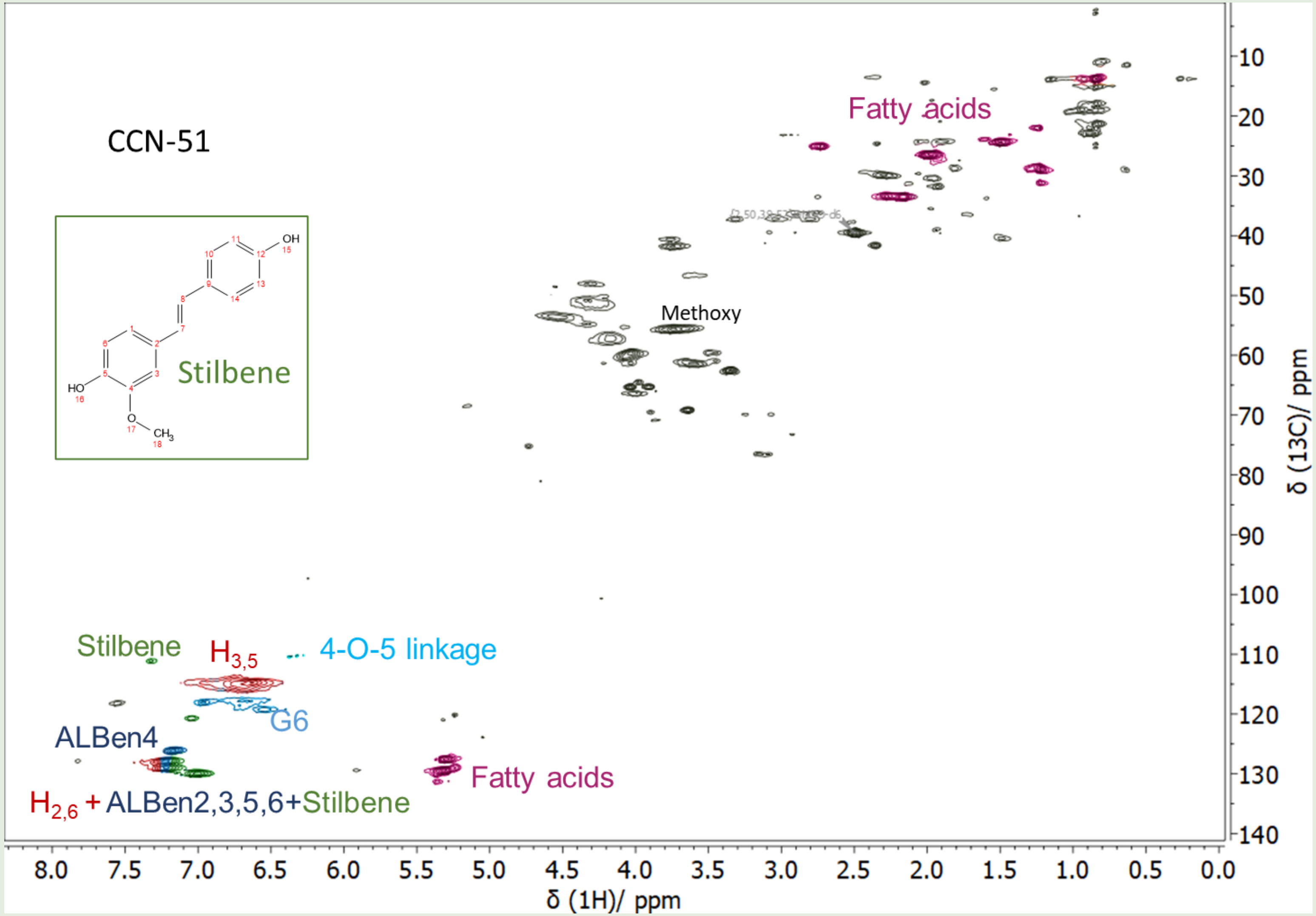
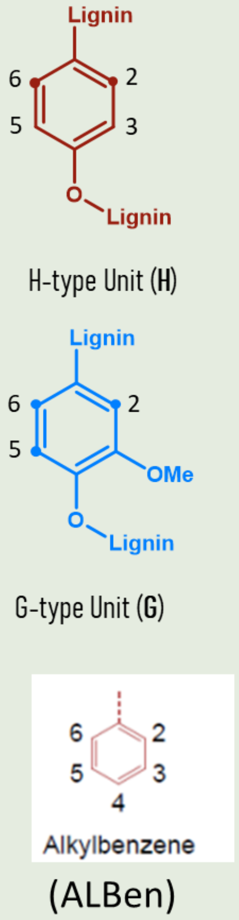
2D HSQC NMR of lignins: structure and composition of lignins





2D HSQC NMR of lignins: structure and composition of lignins

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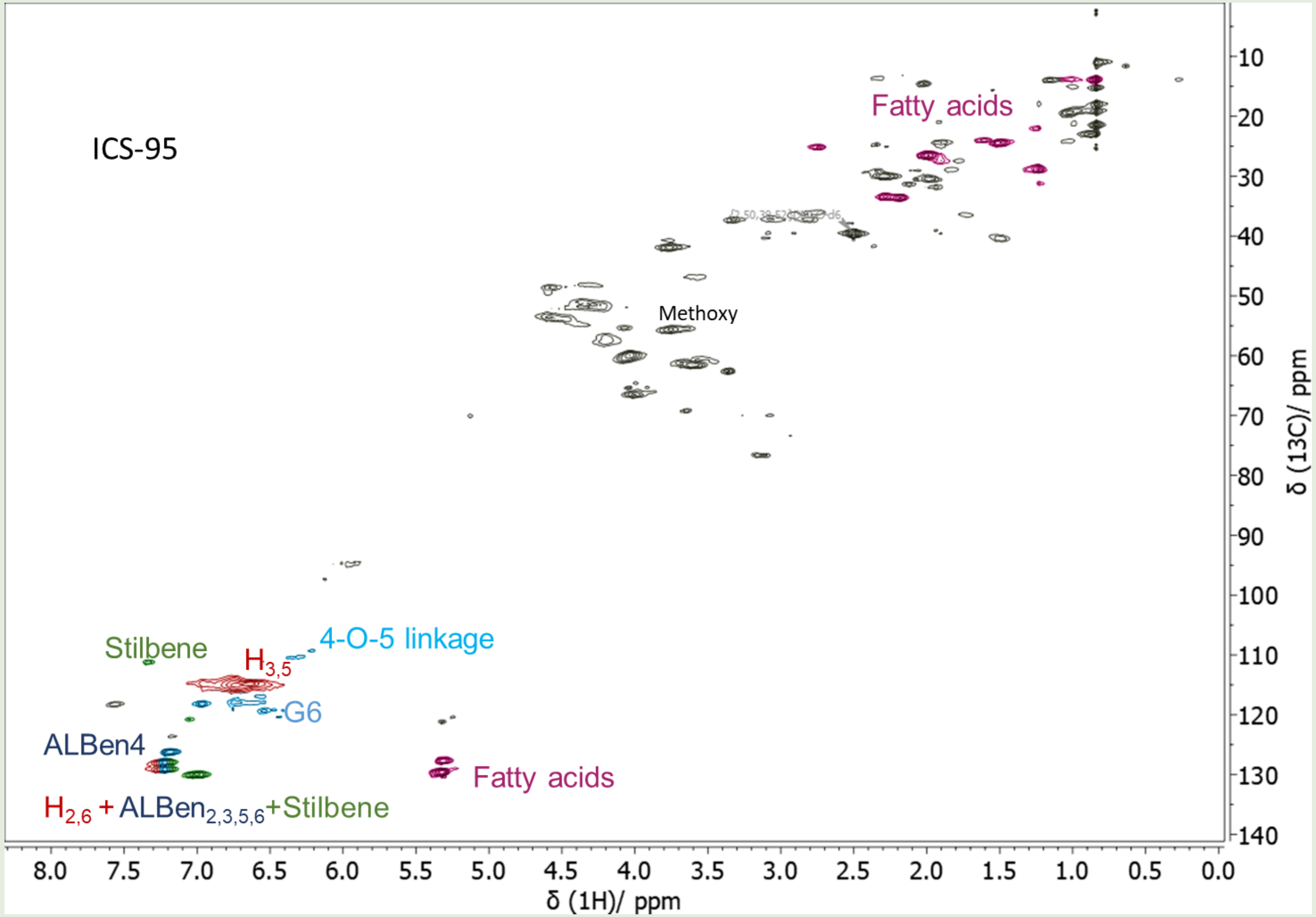

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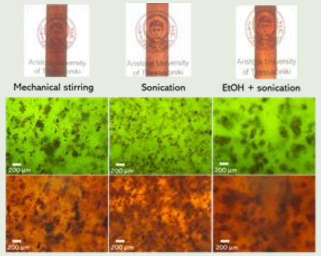
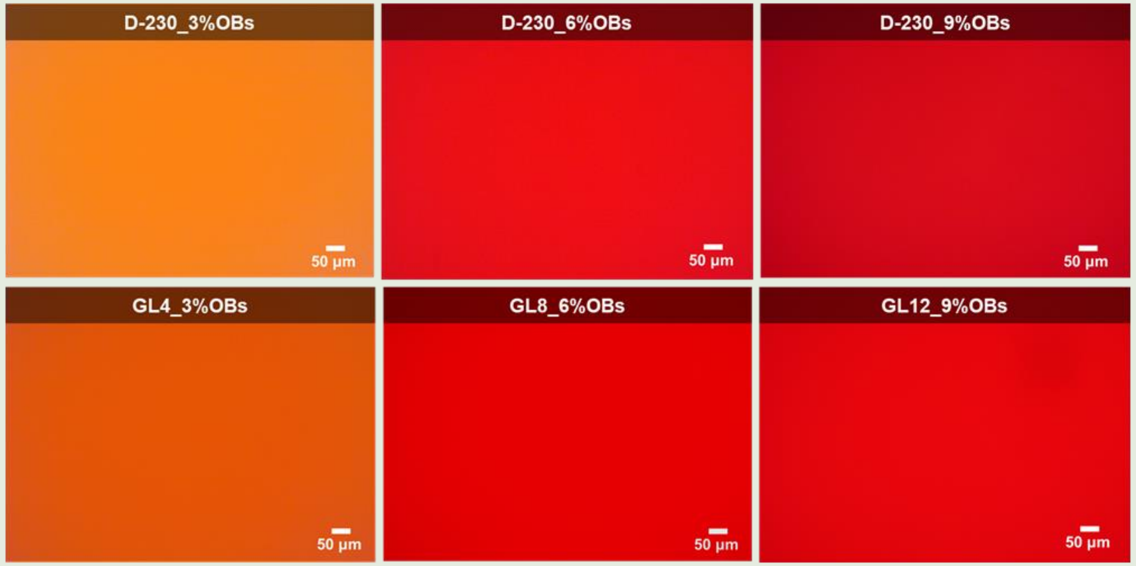
EPOXY - LIGNIN COMPOSITES - LIGNIN DISPERSION

Organosolv Lignin - Epoxy Composites



Kraft-epoxy composites



Images of OBs-epoxy composites, obtained using ***Optical Microscopy***

Mixture of OBs lignin with Epoxy resin pre-polymer and curing agent D-230, prior curing → ***NO lignin particles***

Completely transparent lignin-containing composites
WITHOUT ANY SOLVENT or OTHER TREATMENT

"Sub-Micro Organosolv Lignin as Bio-Based Epoxy Polymer Component: A Sustainable Curing Agent and Additive", Christina P. Pappa, Stylianos Torofias, Konstantinos S. Triantafyllidis
https://doi.org/10.1002/cssc.202300076

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Characterization of cellulose “enriched” solids

CCN-51

TCS-01

ICS-95

Sample	**CCN-51**	**TCN-01**	**ICS-95**
Glucan	30.3	16.0	34.2
Xylan	3.3	2.3	3.2
Galactan	4.5	2.7	0.0
Arabinan	0.0	0.0	0.0
Mannan	0.0	0.0	0.0
Acetyl units	0.0	0.2	0.6
Acid insoluble lignin	19.2	36.7	56.1
Acid soluble lignin	0.8	0.6	1.1
Ash	0.8	0.8	1.8
Total	**52**	**59**	**97**

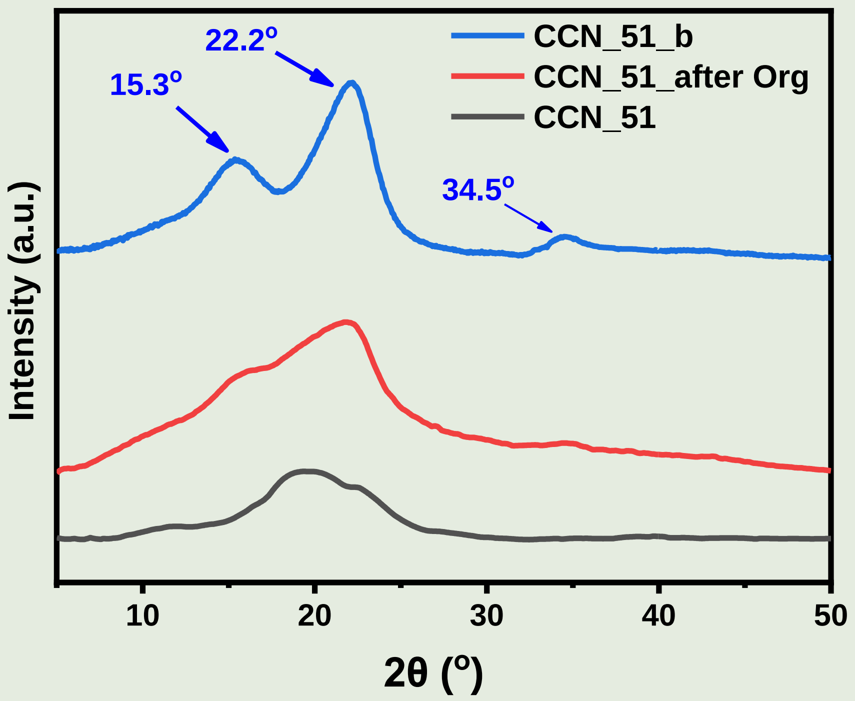
- *Delignification by organosolv needs to be improved*

Isolation of crystalline cellulose

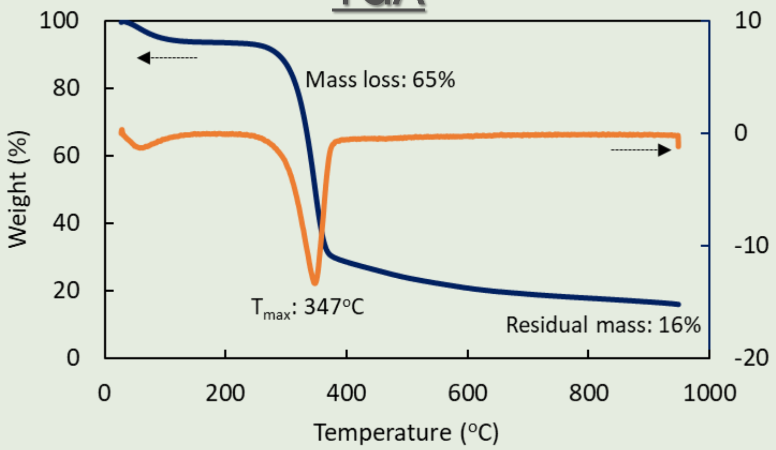
Solid after 2-step pretreatment

Bleaching

XRD



TGA



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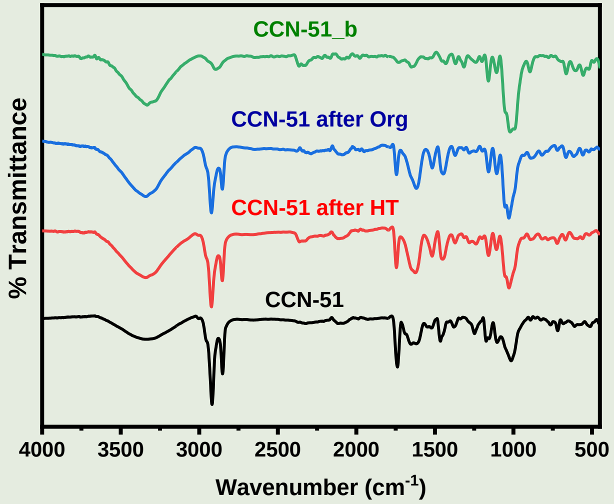

Cellulose

Sample	% C	% H	% N	%S	%O	Residual mass(%)
CCN-51	41.9	6.1	2.8	0.0	49.1	16.0

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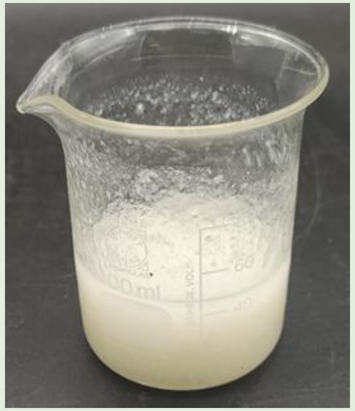
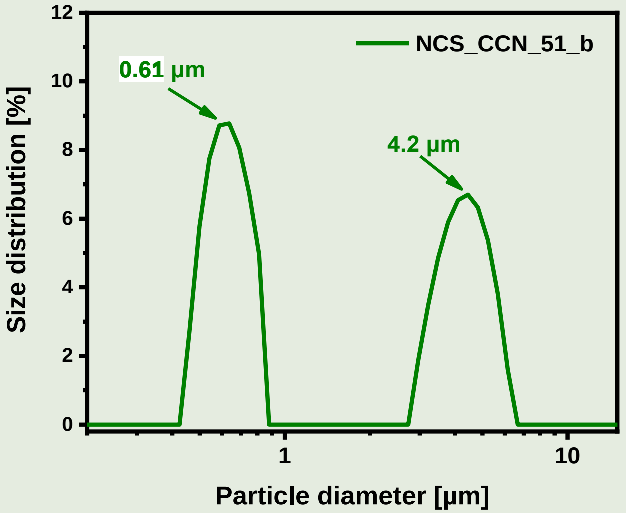
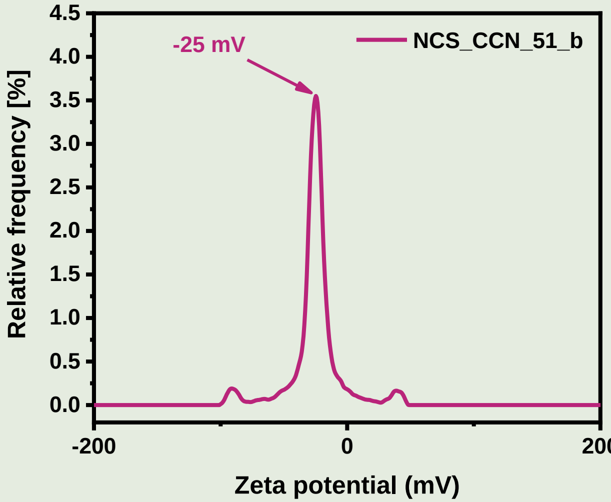
Nano/micro-cellulose production



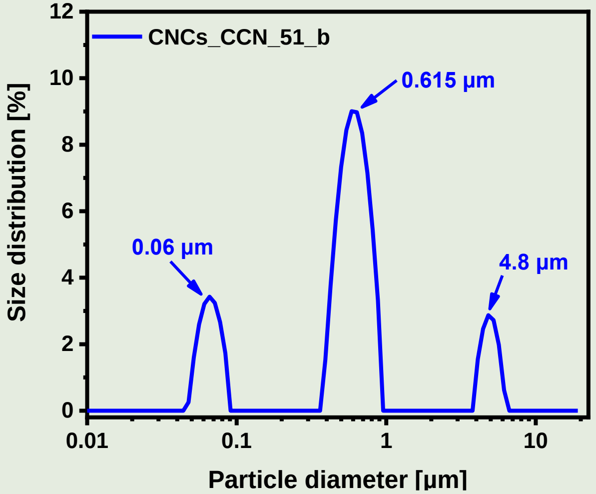
Sonication:
1 h,
50% ampl.
50% pulse

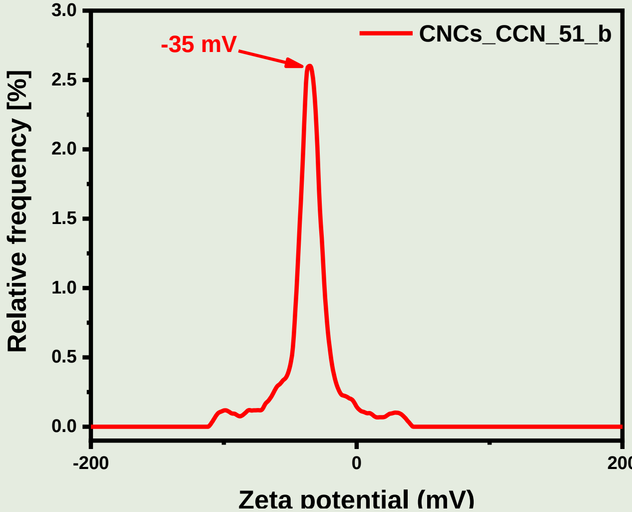




NCS_CCN_51_b

64 wt. % H_2SO_4
45-50ºC
1 h





CNCs_CCN_51_b

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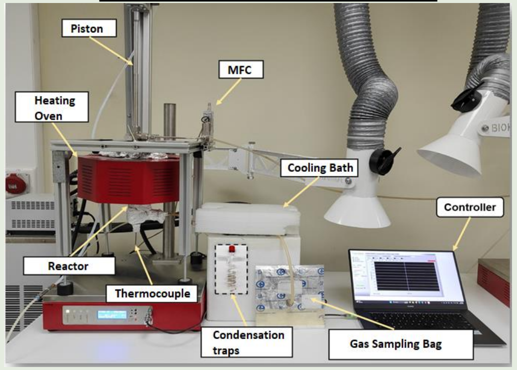
WP1 (D1.3)

- AUTH is involved in the biomass/waste pyrolysis, towards value added products, using a fixed bed lab scale reactor and micro pilot unit

Biomass (e.g., Cocoa bean shell)

Pyrolysis



Bio-oil GC-MS, NMR, Karl-Fisher

Gases GC-FID

Char

Activation

Characterization

Elemental, ATR, XRD, BET, SEM, TGA

Adsorption/purification applications

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Biochar via pyrolysis

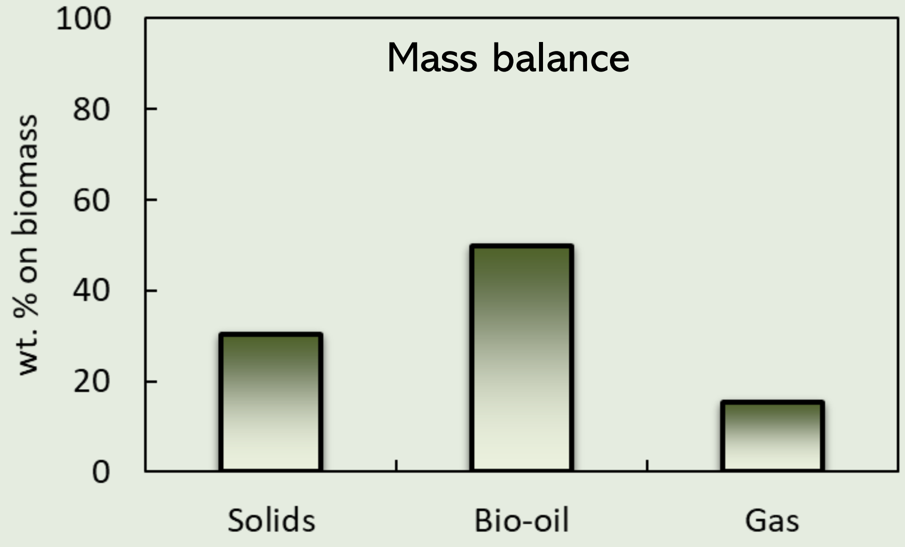
Thermal pyrolysis

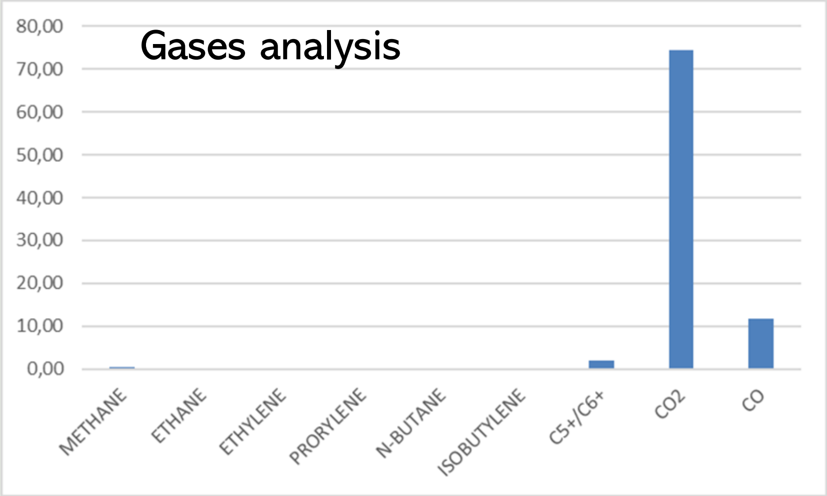
500ºC

CCN-51

Bio-oil

Bio-char





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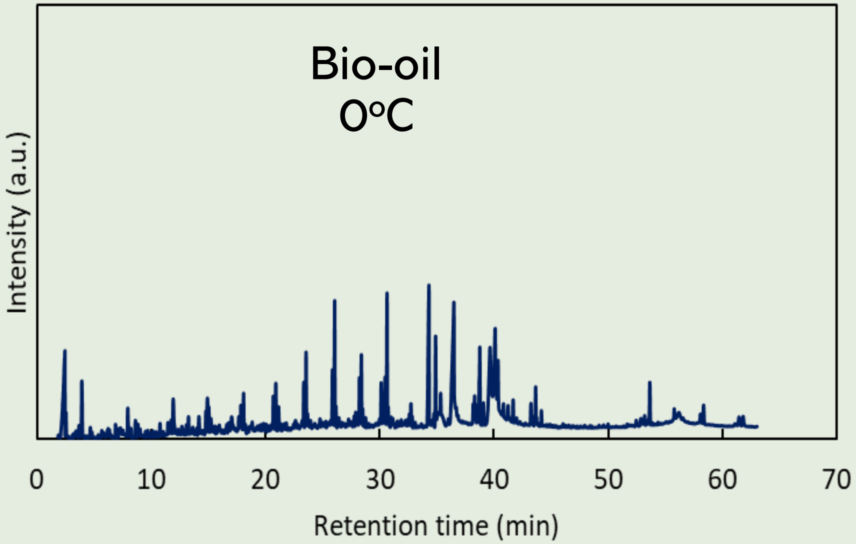
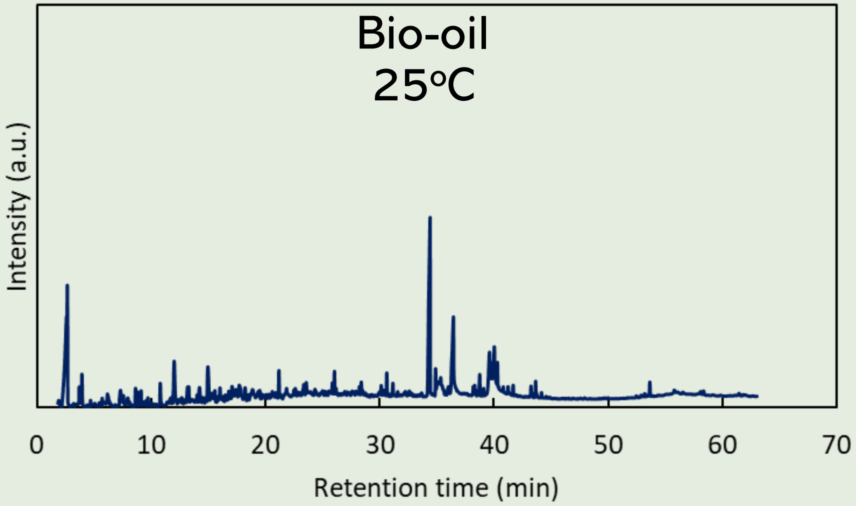
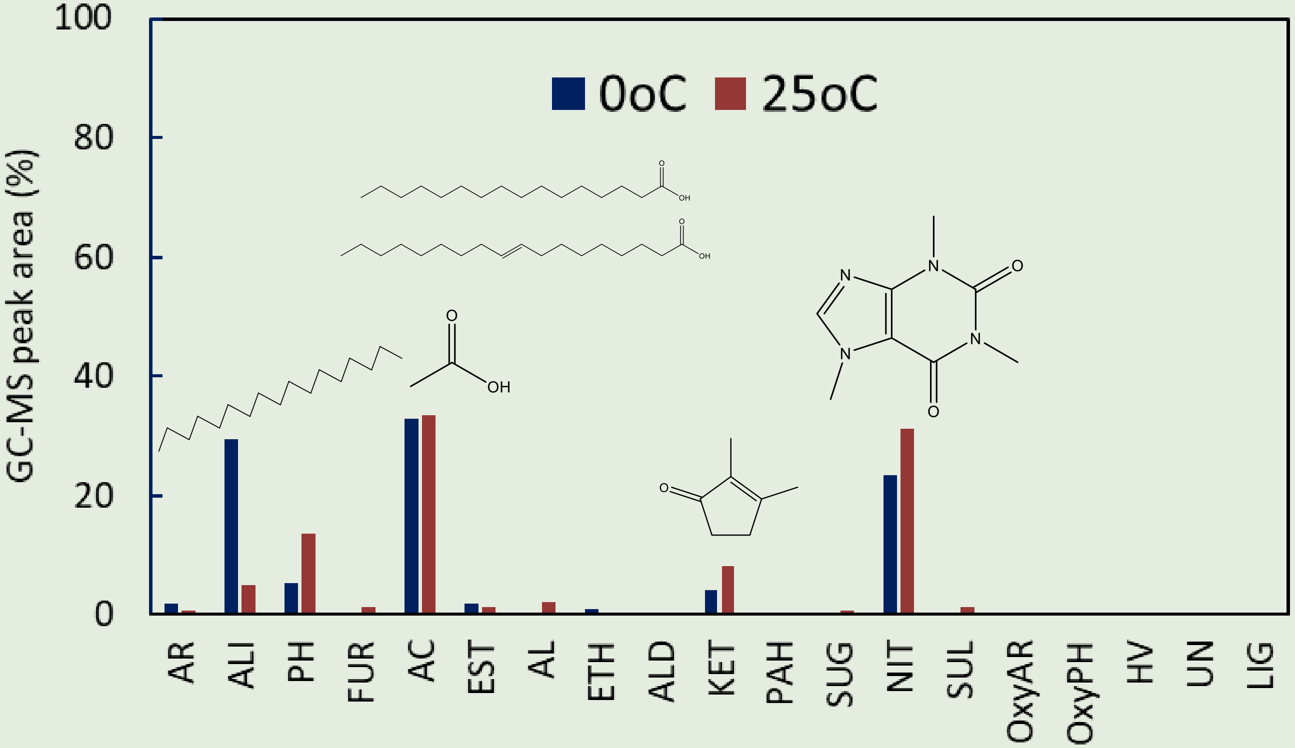
Bio-oil composition







Hydrodeoxygenation of lignin pyrolysis oil towards (alkyl)cyclohexanes

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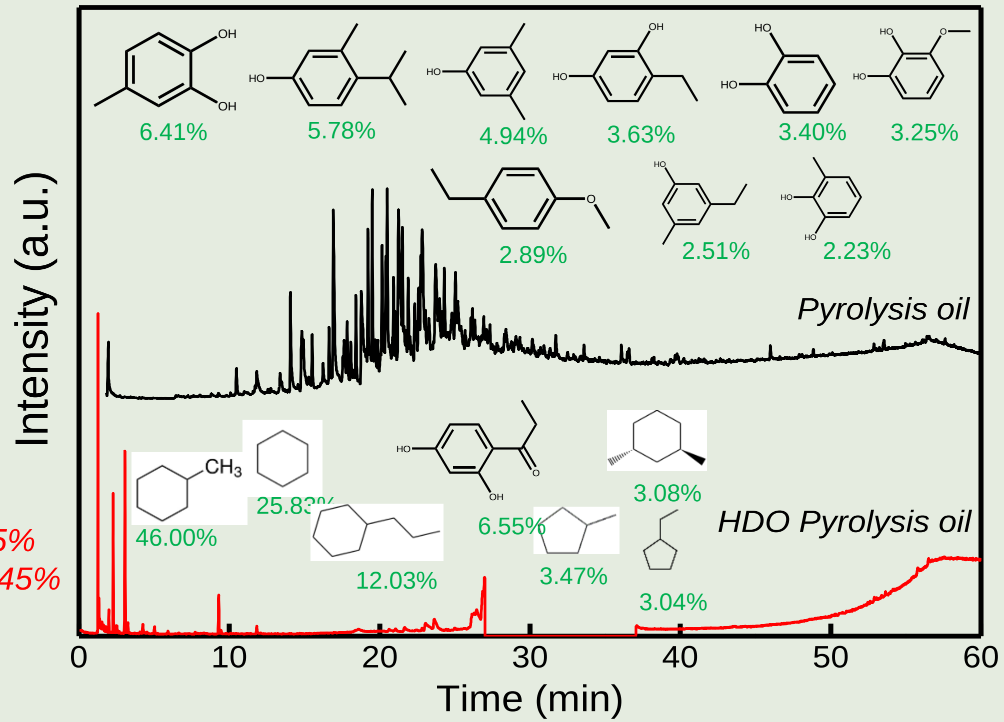
Thermal (600ºC) pyrolysis bio-oil of beechwood Organosolv lignin

GC-MS

Reaction conditions:
- 220 ºC
- 50 bar H_2
- 1 hour
- 400 rpm

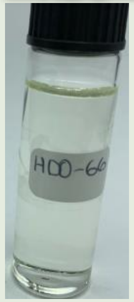
10%Ni/Beta(12.5)

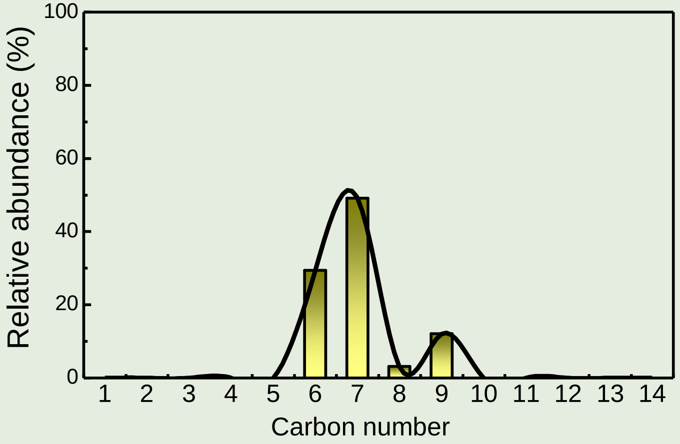
Oxygenated products: 6.55%
Deoxygenated products: 93.45%



Before HDO

After HDO





FLEXI-GREEN FUELS

This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No. 101007130.

AUTH main objective:

Development of non-sulfided catalyst for HDO of lignin bio-oils towards aviation and shipping hydrocarbon fuels

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Conclusions

- Cocoa bean shell wastes can support an integrated biorefinery towards a wide range of value-added products (rest of cocoa production wastes, i.e. branches, can also be co-utilized)
- Sequential fractionation enhances the isolation of hemicellulose in the liquid stream which can be utilized towards the production of furans.
- Lignins isolated via organosolv pretreatment can be used as polymers reactive additive or can be converted to phenolic/aromatic bio-oils.
- Biochar is produced with various down-stream valorization possibilities (sorbent, catalyst, soil improver)
- Highly crystalline cellulose can be isolated via the sequential fractionation and be converted to nanocellulose via mechanical/chemical treatment or to value added chemical via bio/chemocatalytic processes
- More to follow on cocoa and coffee waste biorefining !

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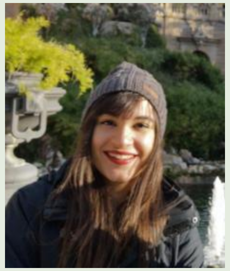

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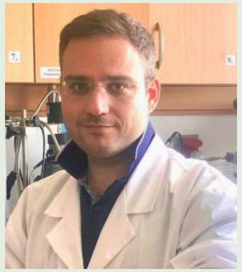

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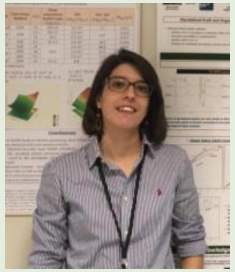

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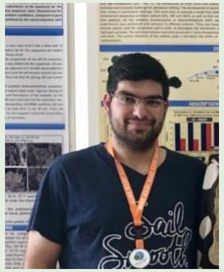

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