Bio-cascading of Heat Treated Wood After Service Life to Obtain Lignocellulosic Derivatives

Eduardo Robles, René Herrera, Oihana Gordobil, Jalel Labidi

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BioRP Bio Refinery Processes
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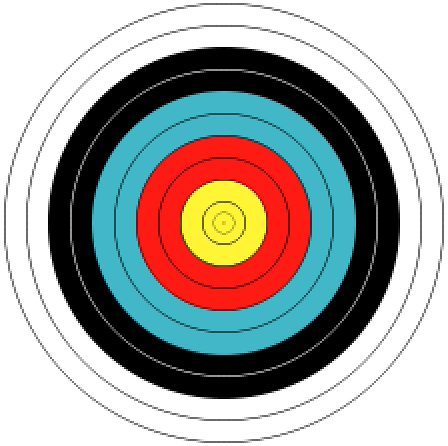

Aims

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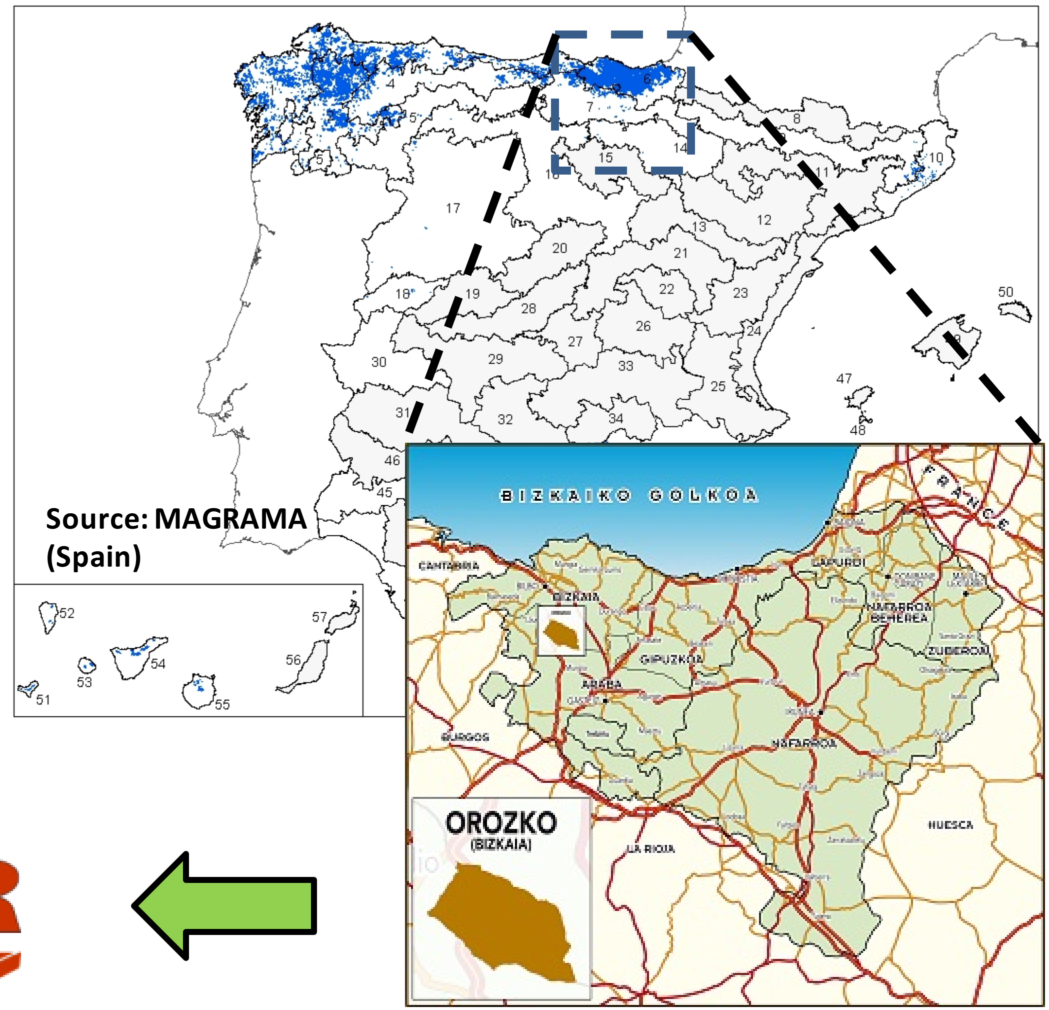
termogenik
MADERA TIMEPROOF



TORREZAR
maderas

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Heat-treatment of wood is an effective method to enhance biological durability and physical stability of wood with a low environmental impact.



The target is promote native and non-durable wood by improving its properties, and therefore adding economic value to Pine wood.

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Wooden deck.

termogenik
MADERA TIMEPROOF


Façade, San Sebastián.


Building façade, Bilbao

TORREZAR
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Hospital façade, Madrid


Park floor, Bilbao.

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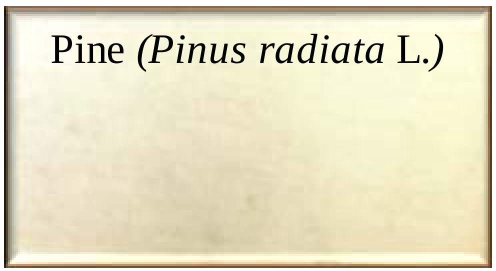
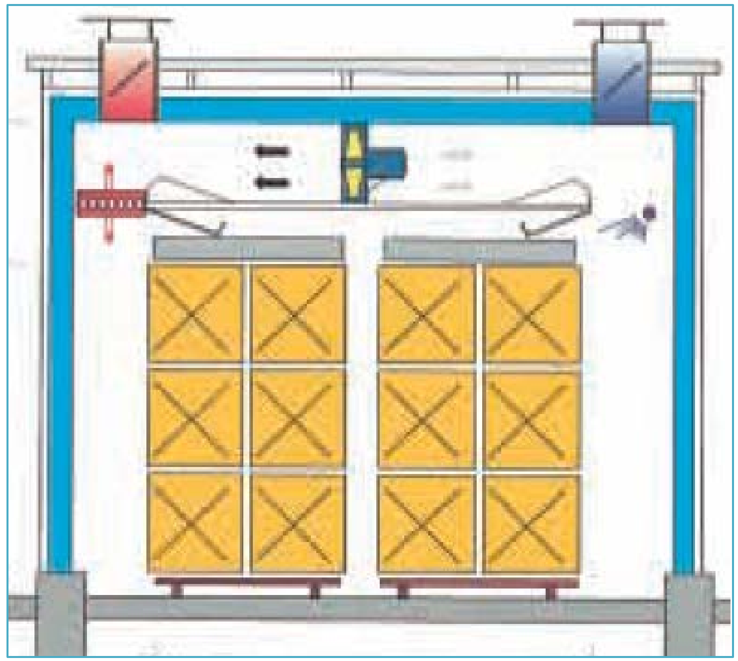
Thermal treatment





MAHILD kiln type

The heat- treatment was performed at 212 ºC in an airtight chamber under reducing atmosphere (N_2) and steam for a period between 60 and 70 h, until all stages of the modification process were achieved according to the industrial standards (Termogenik©, Spain).

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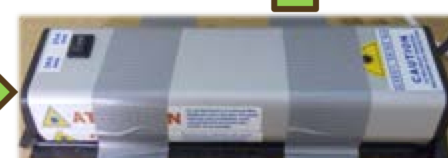
Heat-treated samples

↓

Accelerated aging

Based on a modified EN 927-6:2007

40 cycles
1060 hours



15 hours submerged in distilled water at 20 kPa	9 hours dried in a convection oven at 75 ºC	2.5 hours of UV-A lamp

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Physical Properties

Sample	Initial[1]		Artificial weathering[2]	
	ρ [g cm^{-3}]	MC [%]	ρ [g cm^{-3}]	MC [%]
Pine	0.59 ± 0.02	11.02 ± 0.10	0.54 ± 0.01	9.10 ± 0.08
T-Pine	0.44 ± 0.01	6.07 ± 0.08	0.40 ± 0.01	8.74 ± 0.15

[1]control time 0; [2]Artificial weathering 40 cycles

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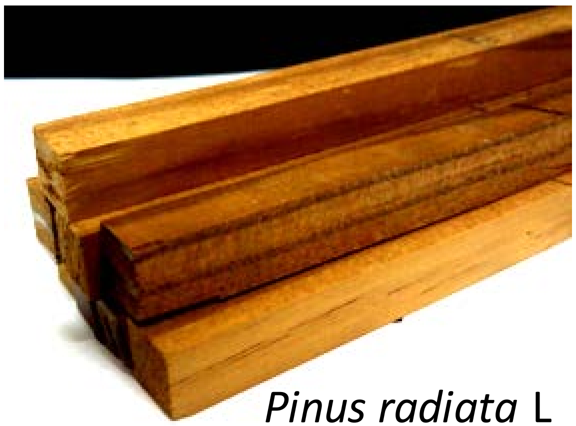
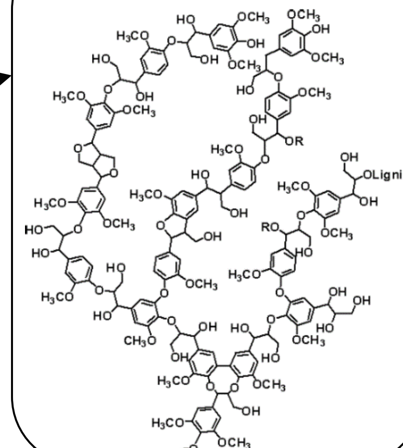


Pinus radiata L
Thermotreated

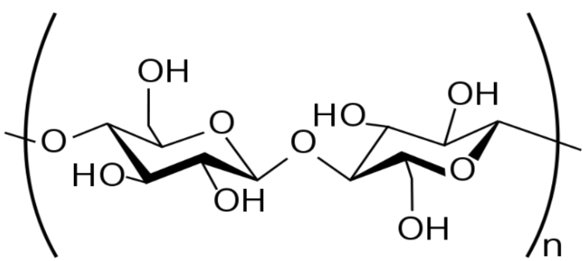
EXTRACTIVES

Waxes, resins, fatty acids, etc...

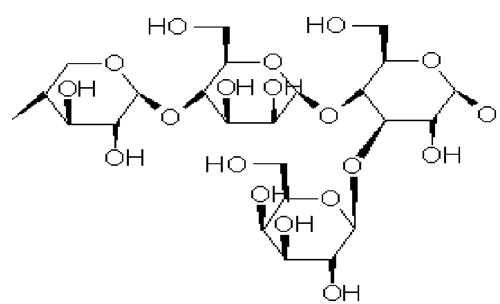
LIGNIN



CELLULOSE



HEMICELLULOSES



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Chemical composition

Sample	Lignin [%]	α-Cellulose [%]	Hemicellulose [%]	Extracts [%]
Pine	27.65 ± 1.24	45.15 ± 1.36	23.61 ± 1.55	2.85 ± 0.24
T-Pine	40.20 ± 2.04	41.48 ± 2.04	12.89 ± 1.06	4.77 ± 0.88

- Lignin content to be valorized over 40 %
- High cellulose content → Cellulose platform valorization
- Lower hemicelluloses → Degradation
- Higher extracts content due to chemical reconfiguration

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Considerations

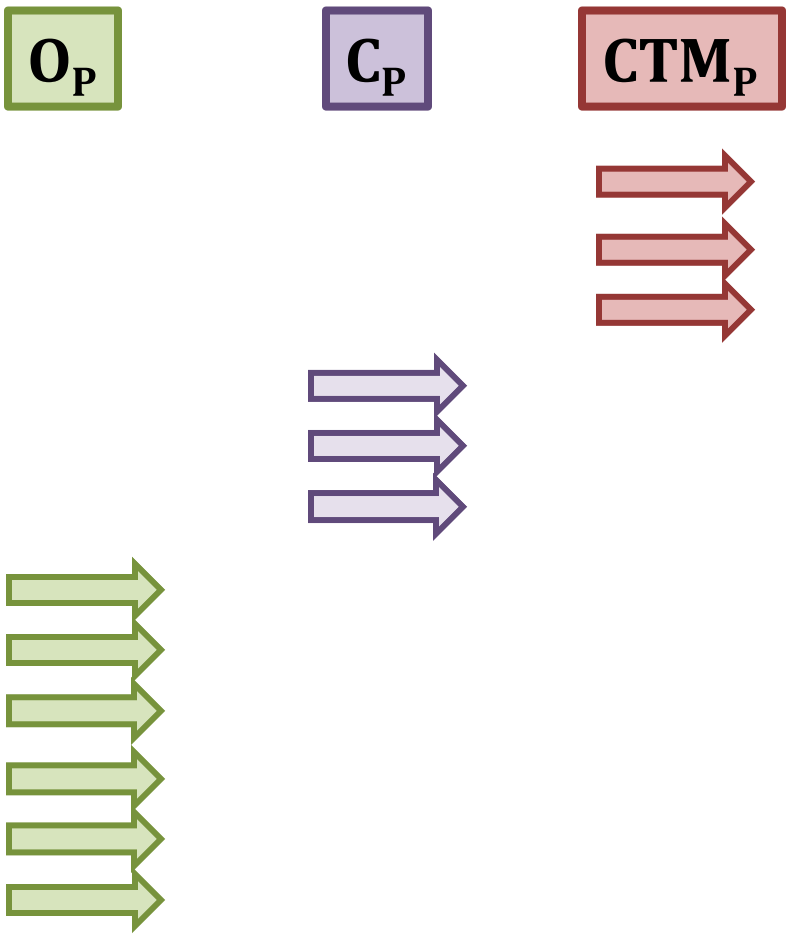
Hydrothermal treatments of wood can be considered an autohydrolysis process, since different cycles varying temperature and humidity inside an inert (N_2) atmosphere induce the degradation of arabinose and the cleavage of acetyl groups of hemicelluloses (Rangel et al., 2016).

The degradation of wood by fungi has been studied intensely for many years due to its importance in preservation of in-service wood and nutrient cycles of forest ecosystems. Nowadays, the reasons for the improvements in the resistance of hydrothermal wood against fungal decay are discussed and are focused on the fact that pyrolytic degradation of material involves a decrease of thermally unstable components of the wood such as the polyoses present in the hemicellulosic fraction, in addition to the volatilization of some extractive compounds (Herrera et al., 2015)

Since the solid phase from autohydrolysis can be subjected to further processing (for example, delignification to separate cellulose and lignin), mild autohydrolysis can be conceived as the first step of a possible multi-stage process for LCM utilization (Garrote et al., 2002).

Pathway

Pulping



Process

Sodium carbonate

Sodium hydroxide

Sodium sulfite

Kraft

Sulphite

Soda

Ethanol

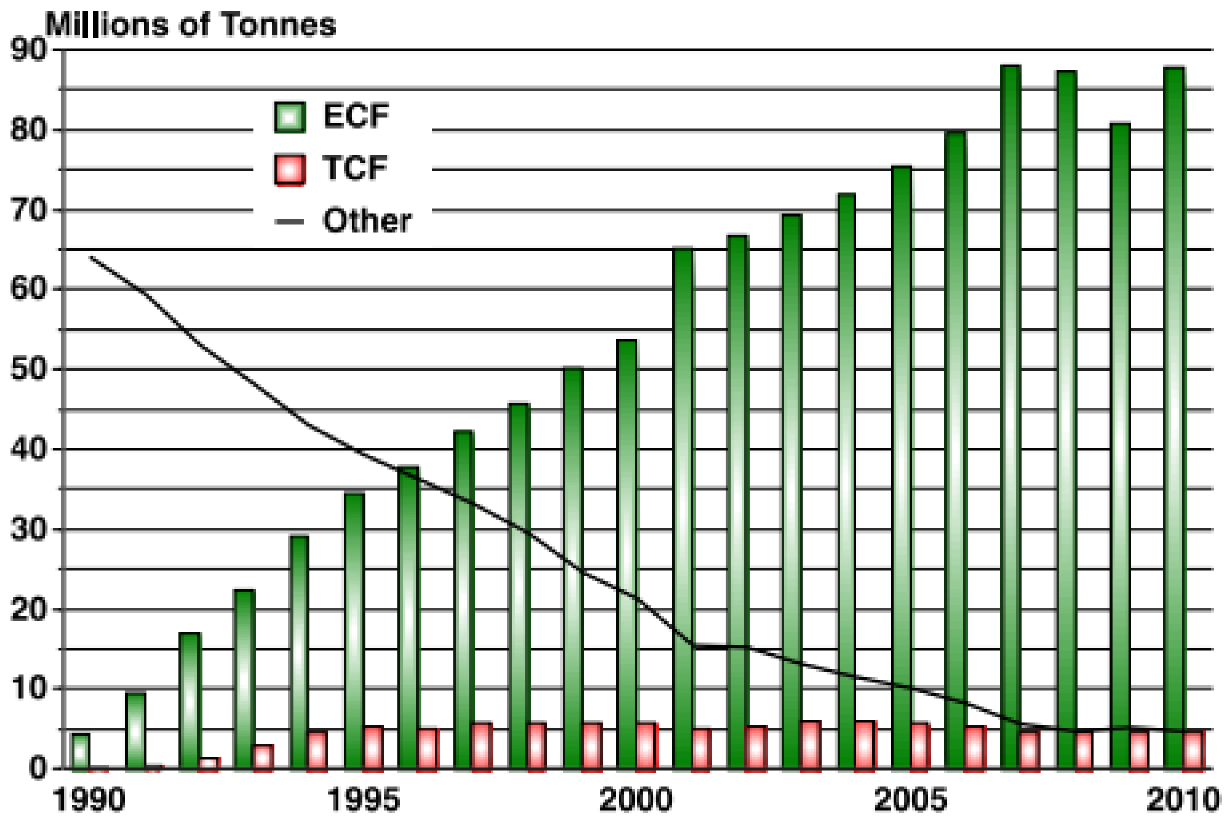
Methanol

Acetone

Butanol

Formic acid

World Bleached Chemical Pulp Production



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Bleaching Stages

TCF	ECF	Process	Letter designation
		Chlorine	C
	→	Sodium hypochlorite	H
→	→	Chlorine dioxide	D
→	→	Extraction with sodium hydroxide	E
→	→	Oxygen	O
→		Alkaline hydrogen peroxide	P
		Ozone	Z
		Chelation (metal removing)	Q
		Enzymes (xylanase)	X
→		Peracids (peroxy acids)	Paa
		Sodium dithionite (sodium hydrosulfite)	Y

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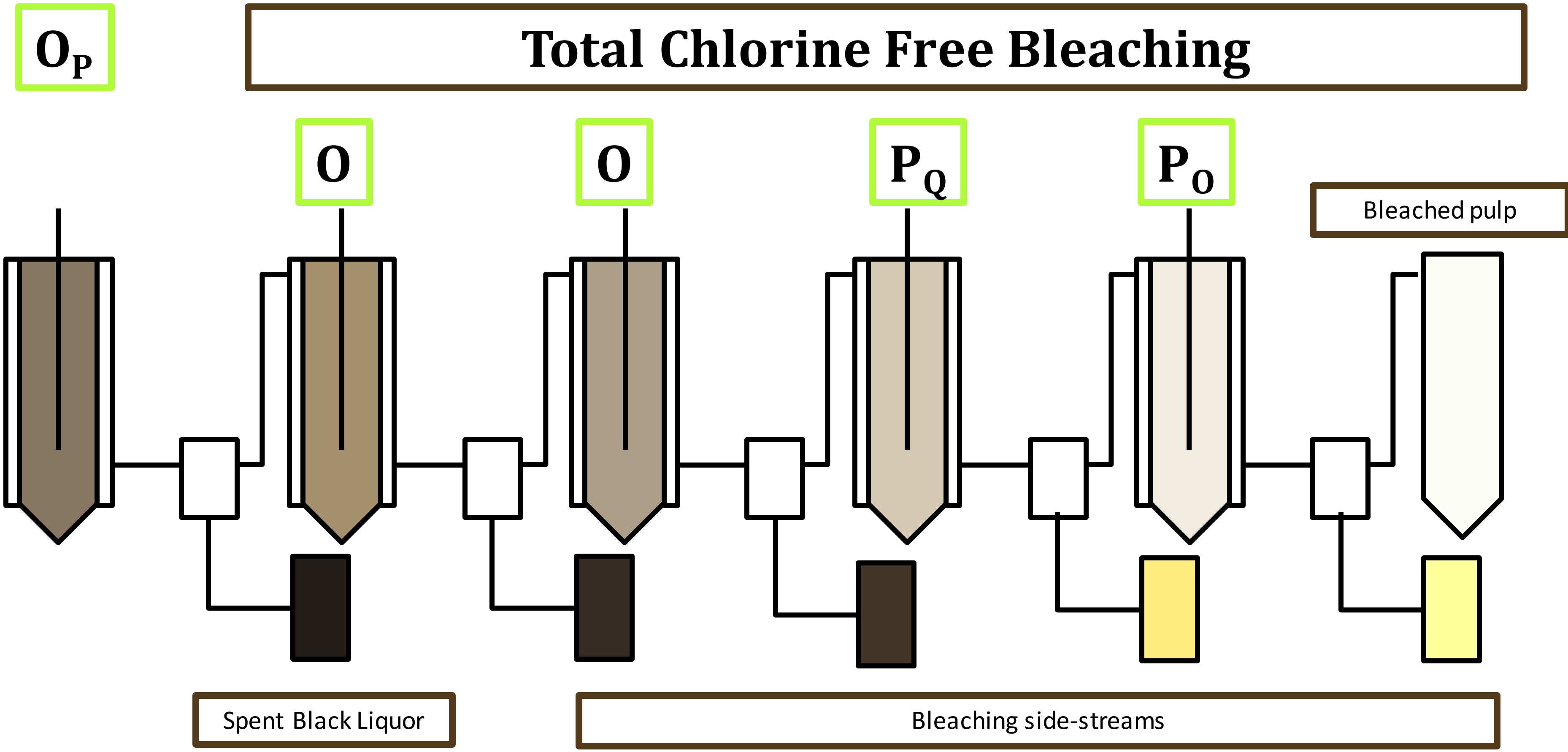
Process Design



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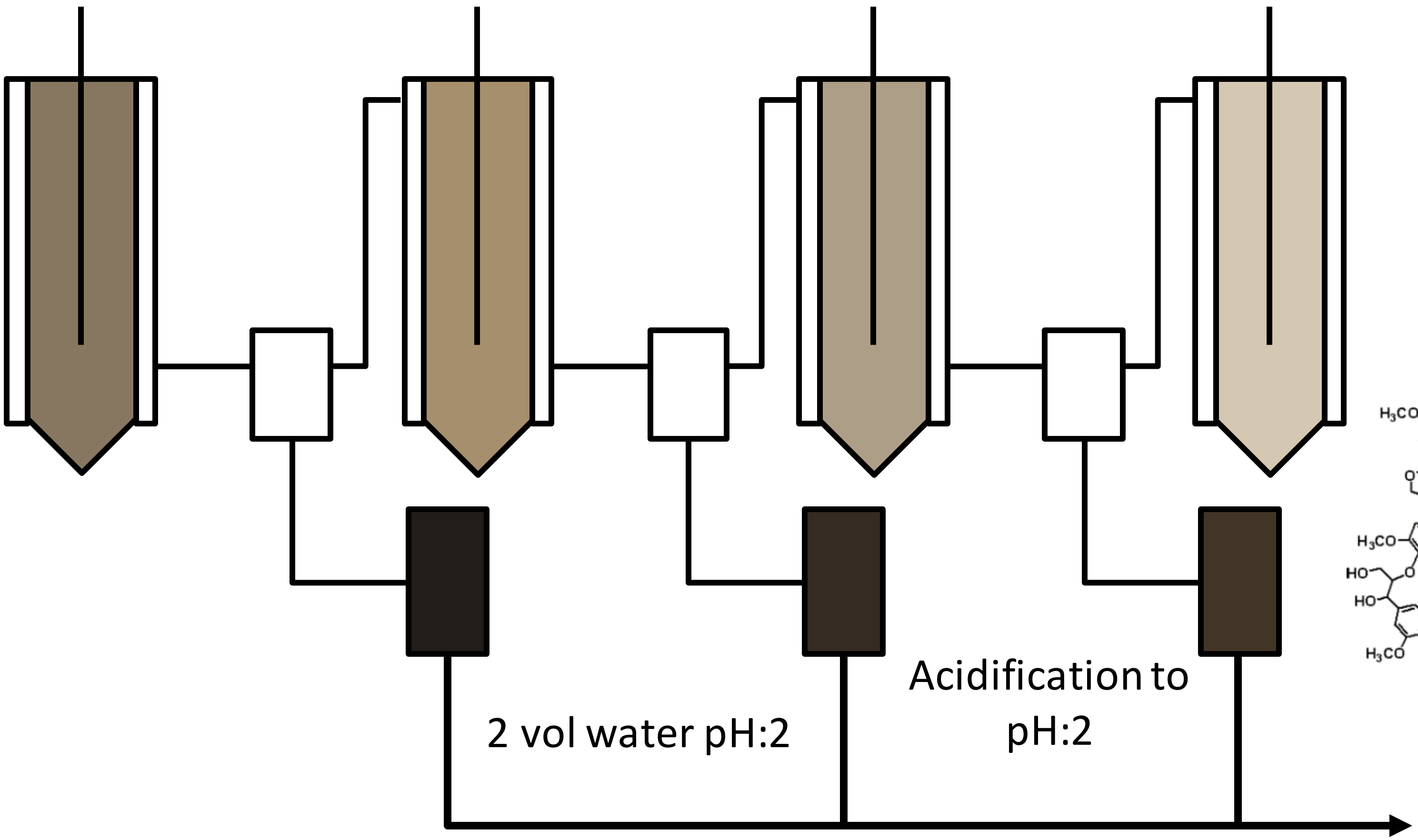
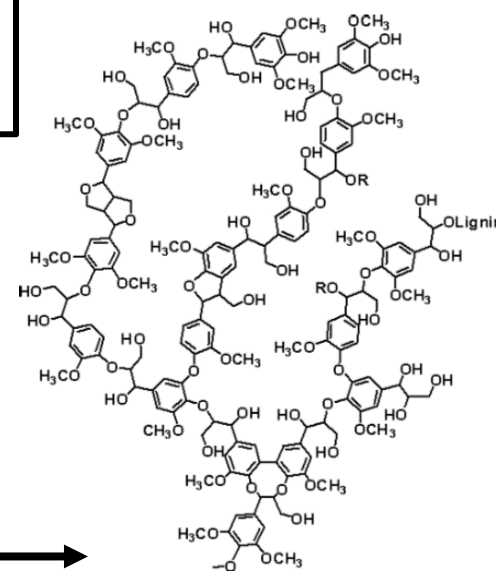
Potential valorization



Lignin



Precipitation

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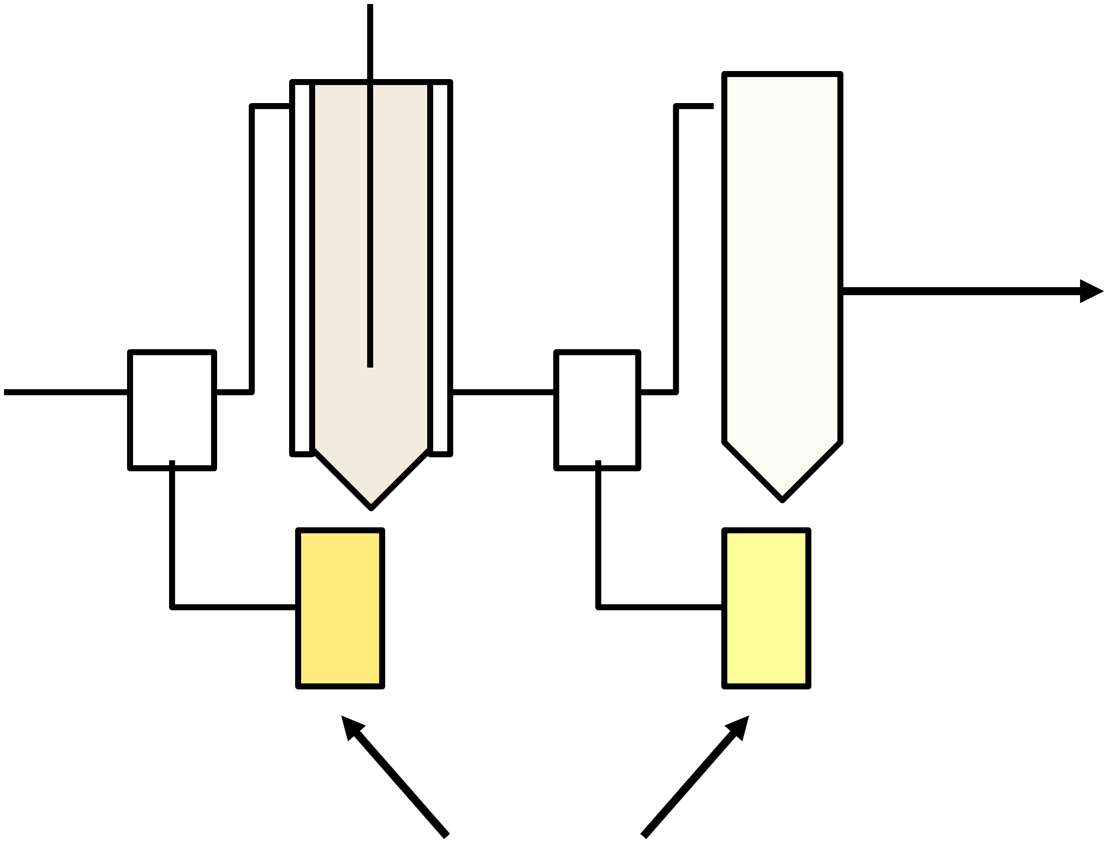
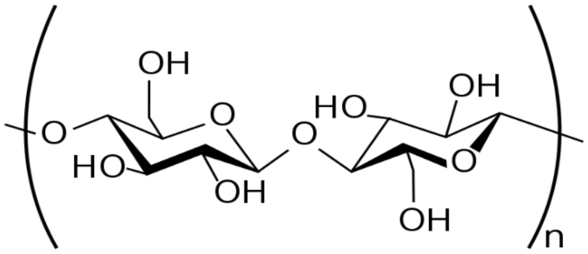
Potential valorization



Cellulose

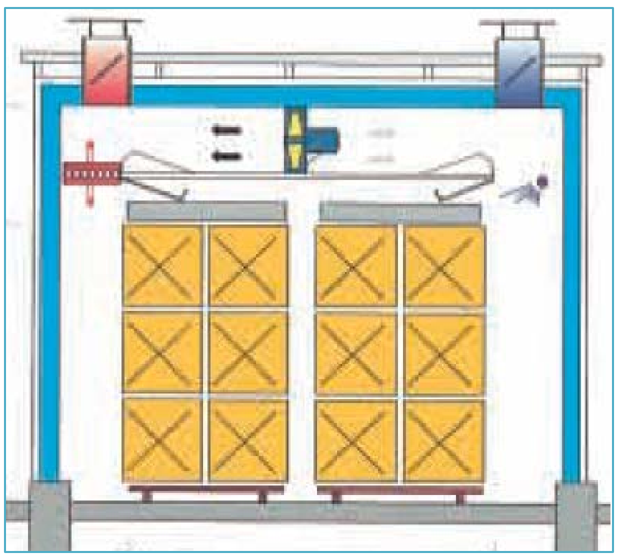


Low valuable chemicals

Results

Untreated pine sample

Treated pine sample



Treated pine sample (weathered)

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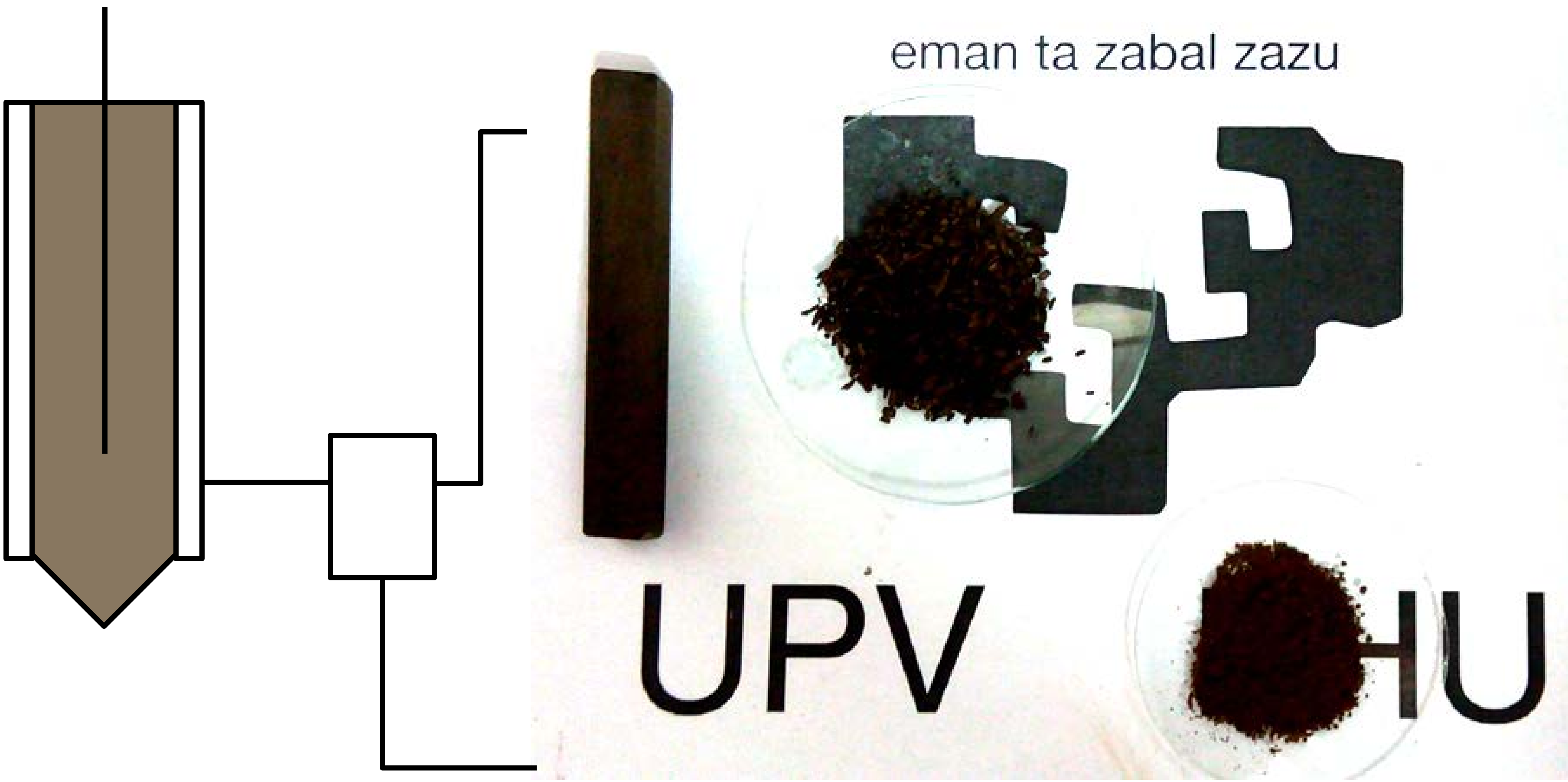
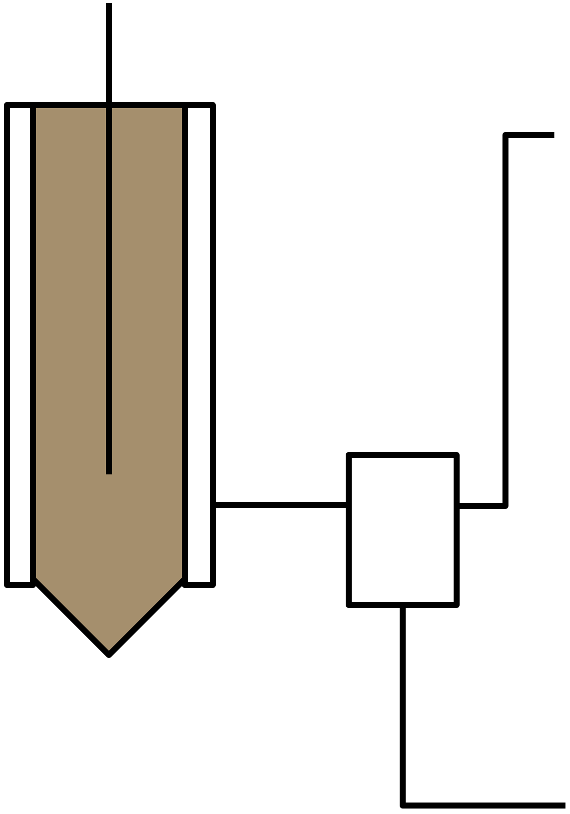
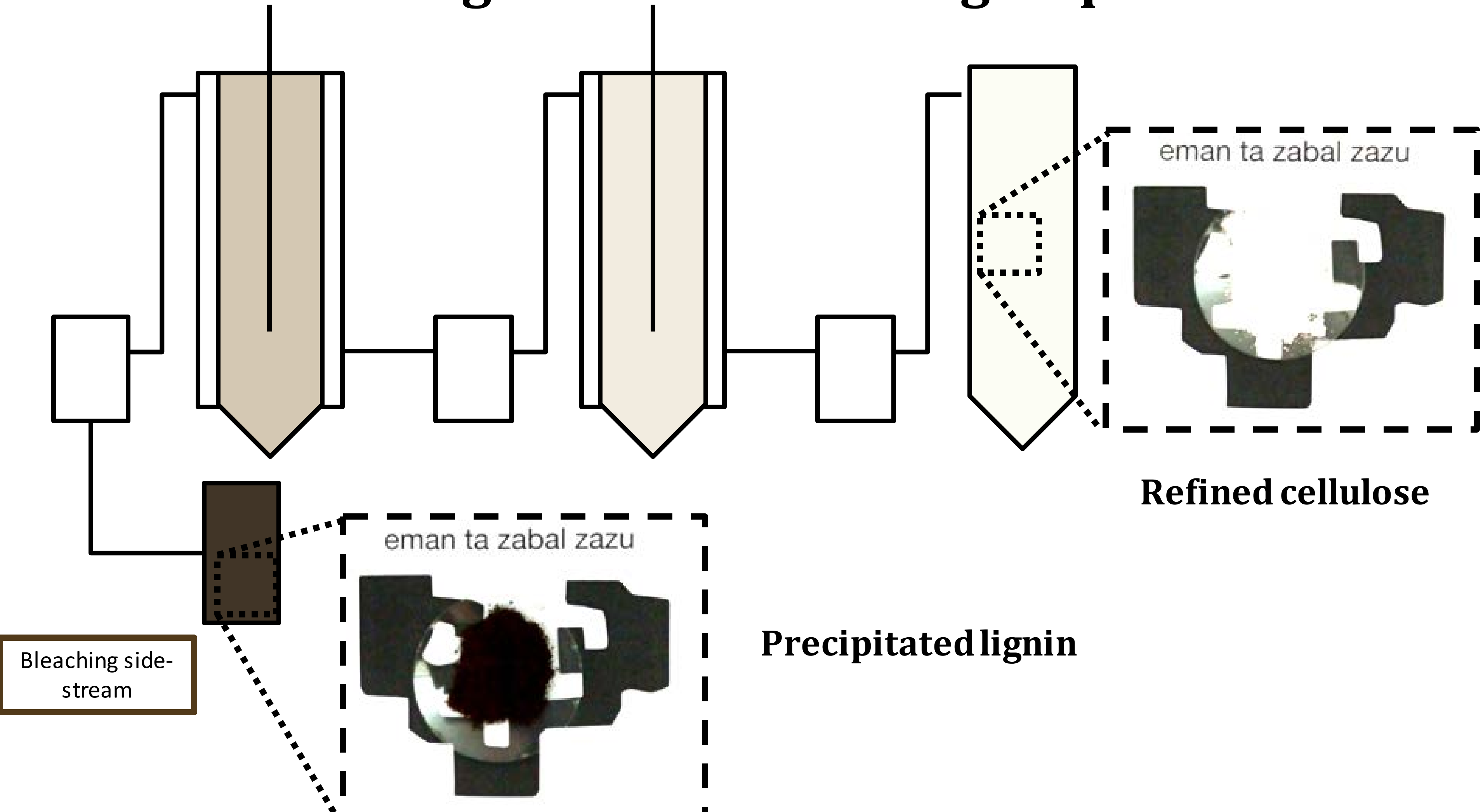
Treated pine sample (weathered)+Organosolv



Organosolv + Bleaching sequence



Cellulose and lignin after bleaching sequence



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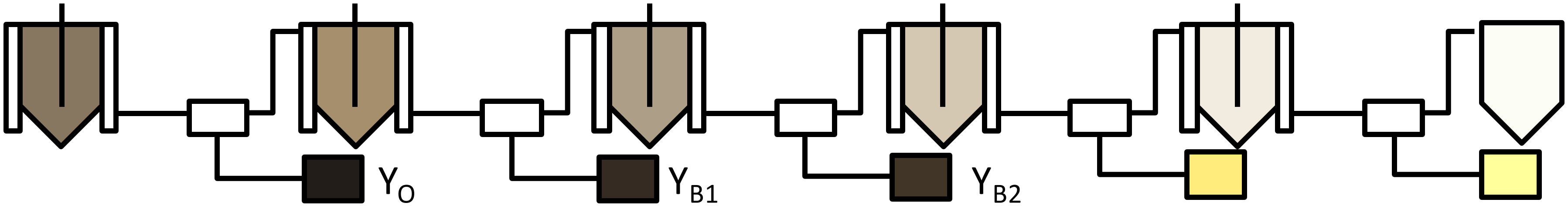

Raw material	Y_O (%)	Y_{B1} (%)	Y_{B2} (%)	Oy[1] (%)	Ry[2] (%)
Pine	13.30	5.57	1.95	20.82	75.32
Pine Th-202	22.54	9.22	4.94	36.71	91.32

[1] Oy corresponds to overall yield, the amount of lignin obtained related to the biomass used.
[2] Ry corresponds to relative yield, the obtained lignin compared to the lignin content as obtained from TAPPI methods.

- High recovery yield for Th-202 Pine: ~90%
- In the 2nd bleaching step, lignin recovery was considerably low
- Cascade process: The lower amount is available, the more difficult is extracted, as it can be seen for both pine samples

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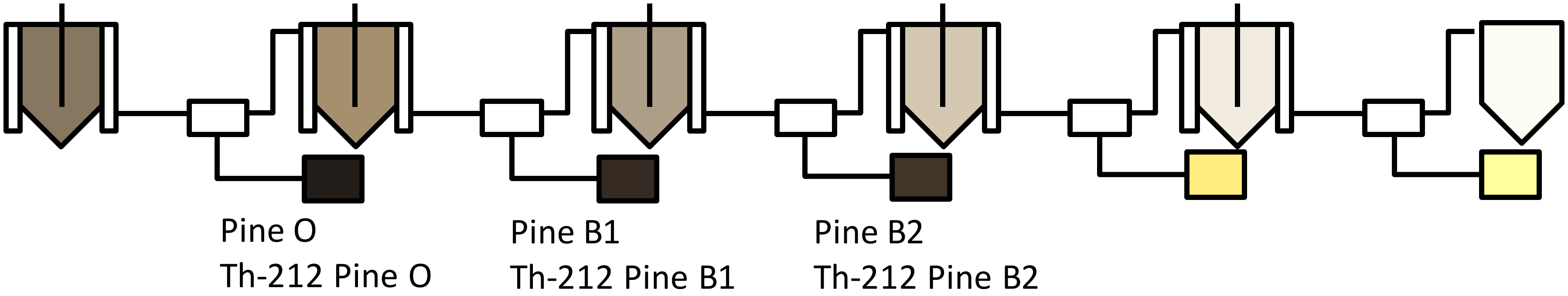

Sample	AIL (%)	ASL (%)	Sugars (%)
Pine O	85.19 ± 0.88	2.51 ±0.51	6.03 ± 0.32
Pine B1	81.49 ± 2.74	1. 46 ± 0. 19	10.47 ± 1. 24
Pine B2	76. 19 ± 1.87	2.83 ± 0.74	11.67 ± 2.11
Th-212 Pine O	89.63 ± 2.73	2.85 ± 0.92	2.67 ± 1.32
Th-212 Pine B1	84.79 ± 2.68	2.87 ± 0.07	8.97 ± 2.75
Th-212 Pine B2	79.99 ± 1.87	2.16 ± 0.29	12.32 ± 2.34

AIL: Acid Insoluble Lignin *ASL: Acid Soluble Lignin*

Conclusions

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- The initial chemical composition of Monterey pine (*Pinus radiata* L) as well as its availability makes this biomass waste capable to be valorized into high value-added product by biorefinery processes, not only based on its high cellulose content, but also the lignin, which is neglected through the cellulose purification process .
- High recovery yields for lignin can be achieved. The extraction in the 1st bleaching stage supposed 36% and 20% of the total lignin extraction for Th-212 pine and untreated pine respectively, justifying the lignin extraction even in the bleaching stages.
- Higher purity lignin was obtained for Th-212 pine than untreated pine, which presented greater sugar impurities
- As summary, Th-212 pine presented higher lignin content, that is easier to extract, with higher purity and better properties for its further valorization.

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Summary

Current Status

- ✓ Chemical characterization of wood samples.
- ✓ Procedure design for wood revalorization after accelerated weathering.
- ✓ Lignin and cellulose valorization after pulping-bleaching train sequence.

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Upcoming analysis

- Polysaccaride quantification (HPLC)
- Inorganic content quantification (TGA)
- Molecular size comparission (GPC)
- Lignin monomer quantitation (Py–GC–MS)
- Cellulose crystallinity (XRD/CP-MAS ^{13}C NMR)

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Thank you!

Eskerrik asko

Děkuji

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Questions?
Comments?
Complains?
Challenges?

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