Inorganic Salt Hydrates as solvent to selective fragmentation of Lignocellulosic Biomass.

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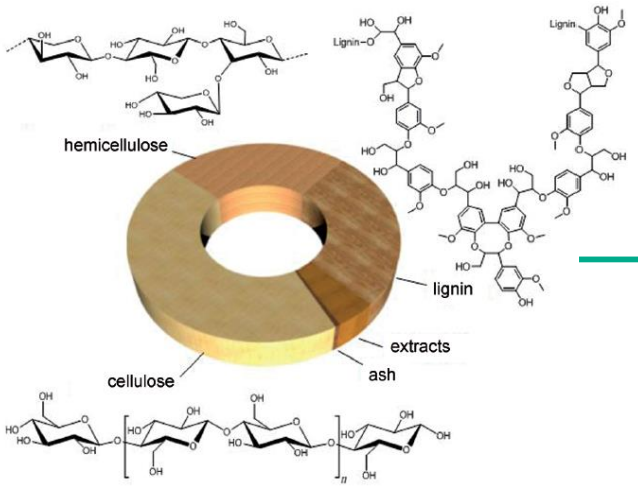
Comisión Europea

Comunidad de Madrid

Proyecto BIOTRES-CM (P2018/EMT-4344), financiado por la Comunidad de Madrid y el Fondo Europeo de Desarrollo Regional.

Use of gardens pruning waste of Madrid city



Pruning waste

NREL

Composition	CIEMAT
Soluble Lignin	7,8%
Insoluble Lignin	29,1%
Cellulose	37,1%
Xylose (Hemicellulose)	14%
Ash	3,7%
Extractives	8,3%

Composition analysis (wt.%) of samples of pruning waste

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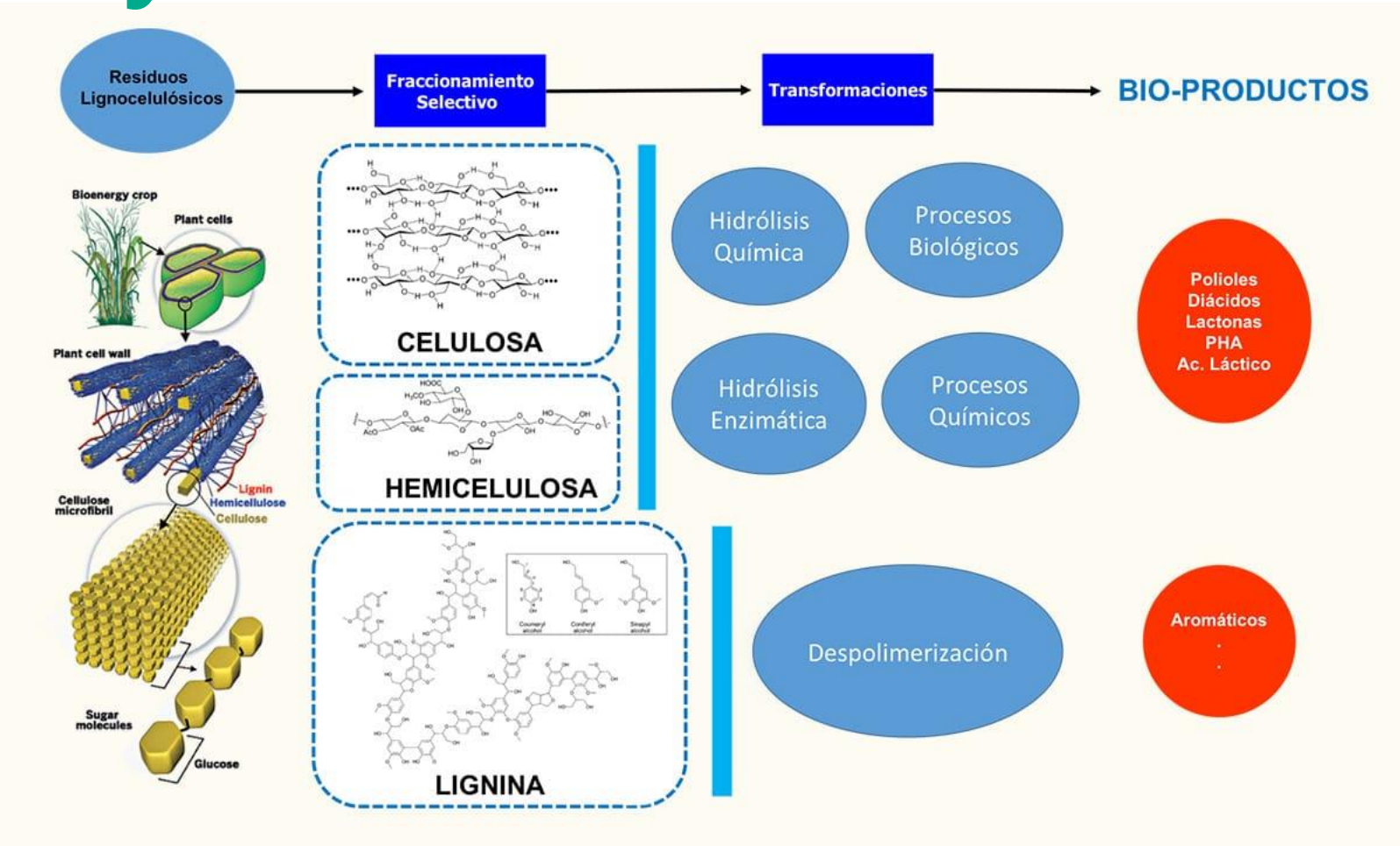

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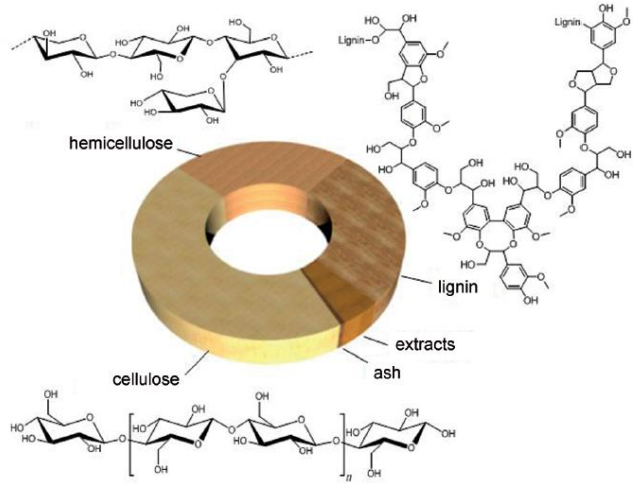

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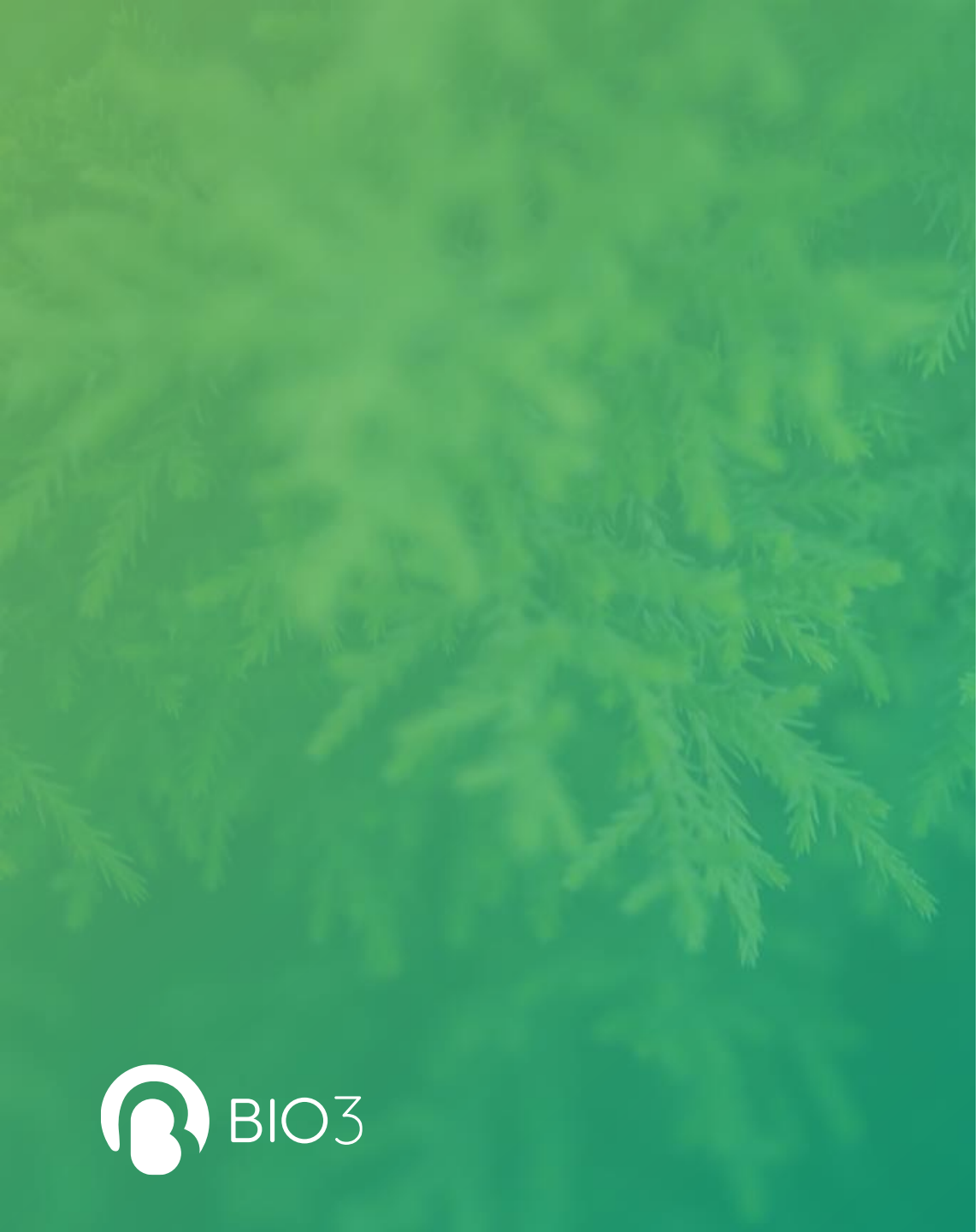

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Inorganic Salt Hydrates

Study of dissolution/precipitation pretreatment of cellulose

Inorganic Salt Hydrates

Salt hydrates are the result of an anhydrous salt forming a solid crystalline structure in the presence of water in specific molar ratios.

Some of them are liquids at RT and can be used in the dissolution of lignocellulosic biomass.

- ✓ **Low price** and high availability.
- ✓ **Thermally stable**, easy to recycle
- ✓ Works at **low temperature** ≈70 ^{0}C and no long times

-$ZnCl_2 \cdot 4H_2O$
-$ZnBr_2 \cdot 4H_2O$
-$LiCl \cdot 8H_2O$
-$LiBr \cdot 4H_2O$

Inorganic Salt Hydrates as solvent

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Inorganic Salt Hydrates

Dissolution Conditions:

28,5g of Inorganic Salt Hydrates

1,5g of Cellulose

Temperature: 70 ºC

Avicel PH-101

Dissolution

Water

Precipitation

Treated cellulose

High reactive

Catalyst

Hydrolysis

Inorganic Salt Hydrate

Solvent + Excess of water

Evaporation

Study of dissolution/precipitation pretreatment of cellulose

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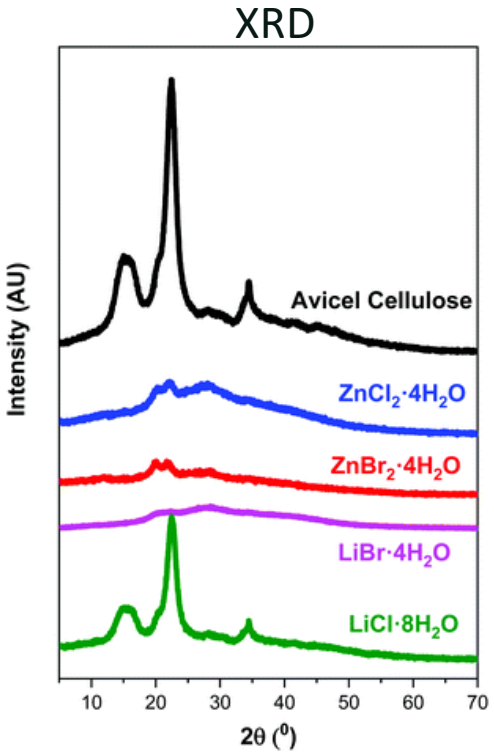
Inorganic Salt Hydrates

Cellulose Dissolution Study

Sample	Dissolution time (min)	Cellulose recovered (%)	CI (%)
Avicel Cellulose PH-101	-	-	82
$ZnCl_2 \cdot 4H_2O$	30	~100	45
$ZnBr_2 \cdot 4H_2O$	15	97	21
$LiCl \cdot 8H_2O$	>60	~100	79
$LiBr \cdot 4H_2O$	25	99	36



XRD of untreated cellulose and solids obtained after dissolution/precipitation with inorganic salt hidrates.

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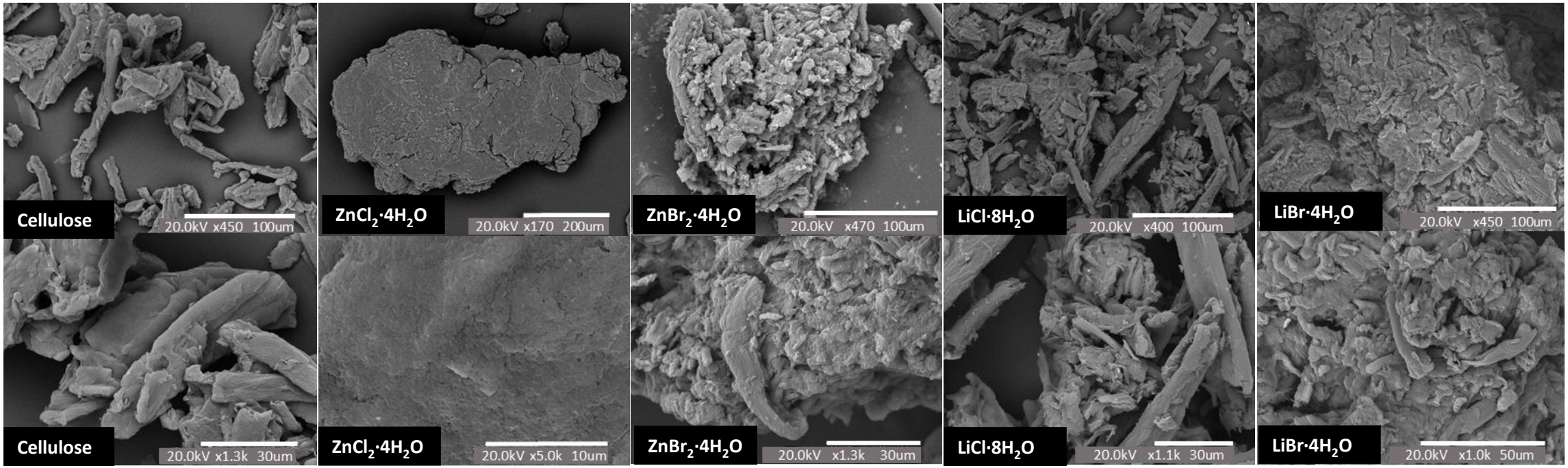
Inorganic Salt Hydrates

Cellulose Dissolution Study

SEM



SEM micrographs of the original cellulose (Avicel PH-101) without pretratment and the solids obtained after pretreatment with different inorganic salt hydrates. The bottom panel depicts the same samples with higher magnification.

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Inorganic Salt Hydrates

Cellulose Reactivity

Stirred tank reactor BERGHOF:

Reaction conditions:

- Reaction Time: 5 h
- Temperature: 140 ºC
- Cellulose 0.5 g
- 50 mL Final volume
- Homogeneous acid catalyst (0.2 mol/L) → H_2SO_4

Study of dissolution/precipitation pretreatment of cellulose

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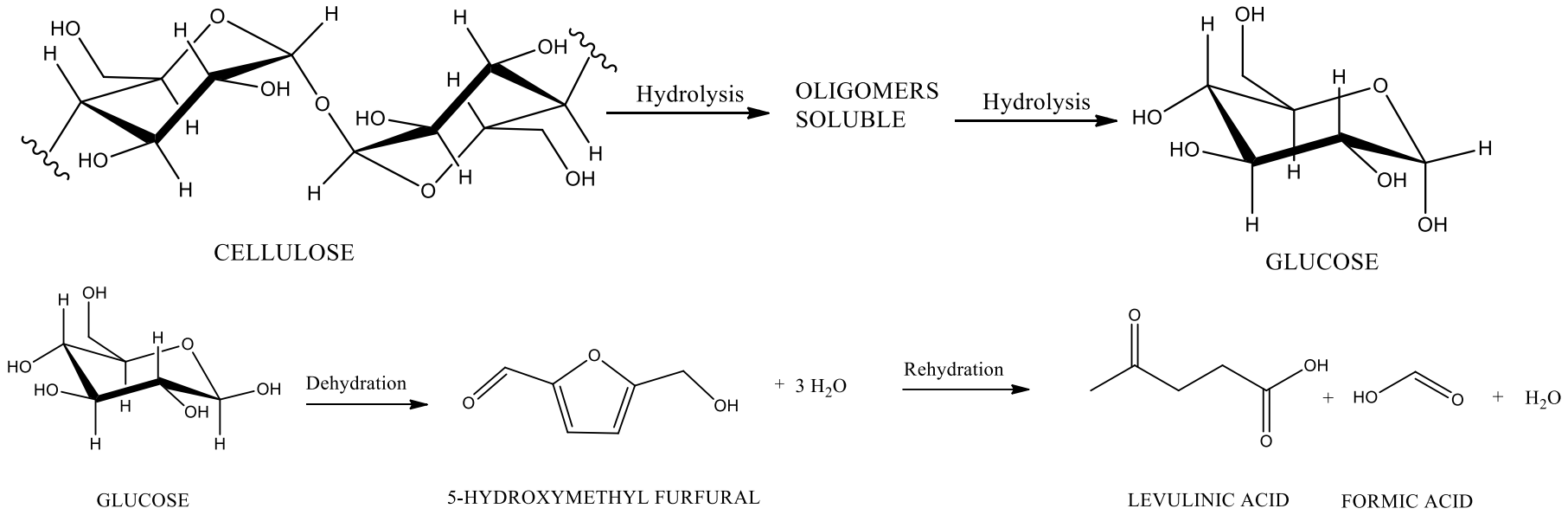

Study of dissolution/precipitation pretreatment of cellulose

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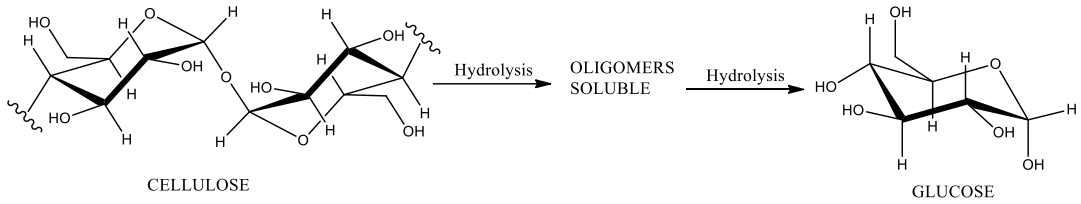

Sample	Conversion of Cellulose (%)	Yield of Glucose(%)	Selectivity of Glucose (%)
Avicel Cellulose PH-101	25	12	48
$ZnCl_2 \cdot 4H_2O$	60	54	90
$ZnBr_2 \cdot 4H_2O$	88	80	91
$LiCl \cdot 8H_2O$	26	12	46
$LiBr \cdot 4H_2O$	74	63	85

Hydrolysis of cellulose in samples treated with different inorganic salt hydrate at 140°C for 300min

$ZnBr_2 \cdot 4H_2O$ > $LiBr \cdot 4H_2O$ > $ZnCl_2 \cdot 4H_2O$ > $LiCl \cdot 8H_2O$ ~Avicel Cellulose

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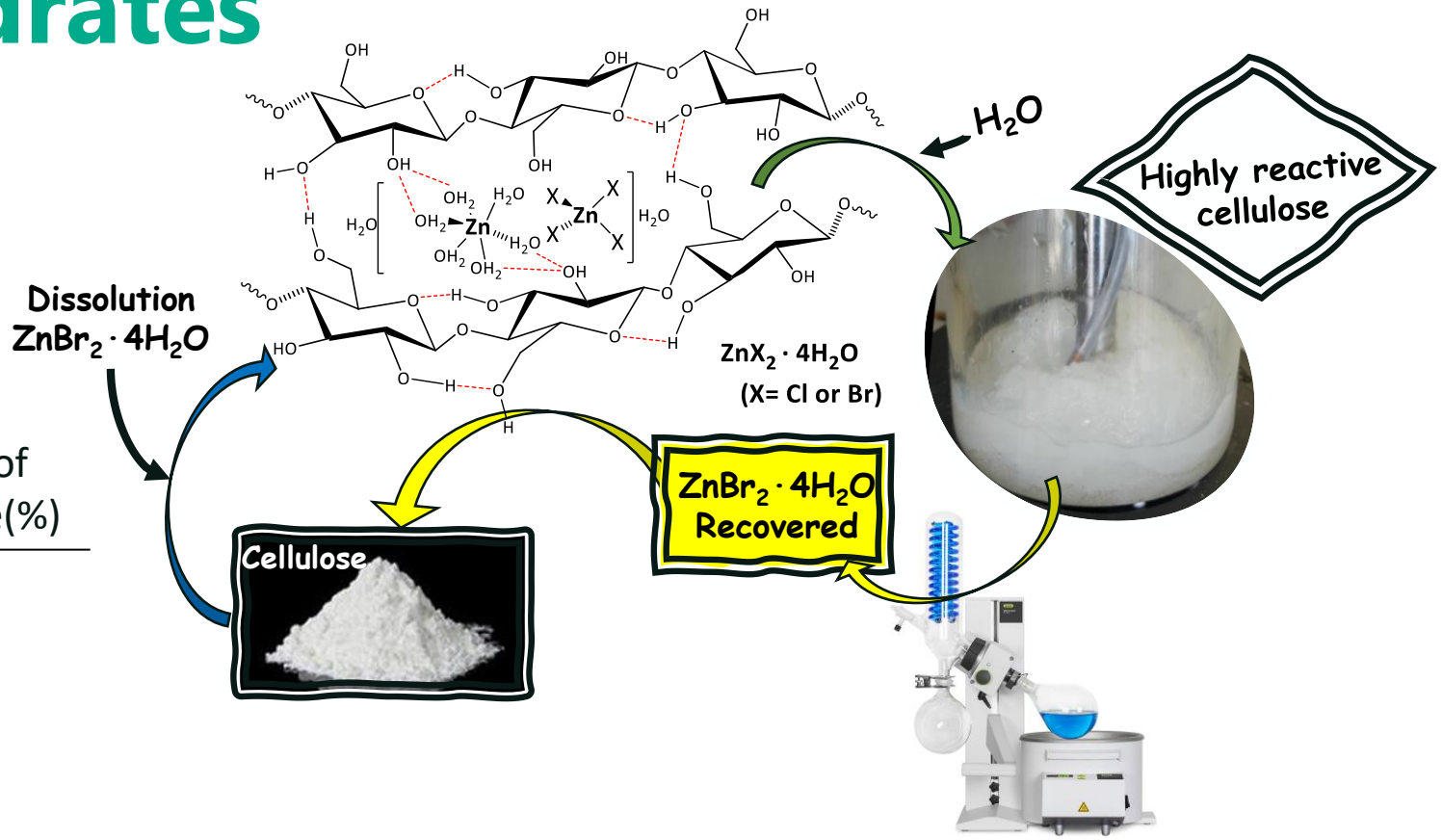
Inorganic Salt Hydrates

Inorganic Salt hydrate reuse

	REUSE		
Samples treated with	$ZnBr_2 \cdot 4H_2O$ recovered (%)	Conversion of Cellulose(%)	Yield of Glucose(%)
$ZnBr_2 \cdot 4H_2O$ fresh		88	80
reuse 1	97	87	81
reuse 2	96	89	80

Reuse of $ZnBr_2 \cdot 4H_2O$. Recovery of salt hydrate and hydrolysis of cellulose in samples treated at 140°C for 300 min using H_2SO_4 (0,2M)



Study of dissolution/precipitation pretreatment of cellulose

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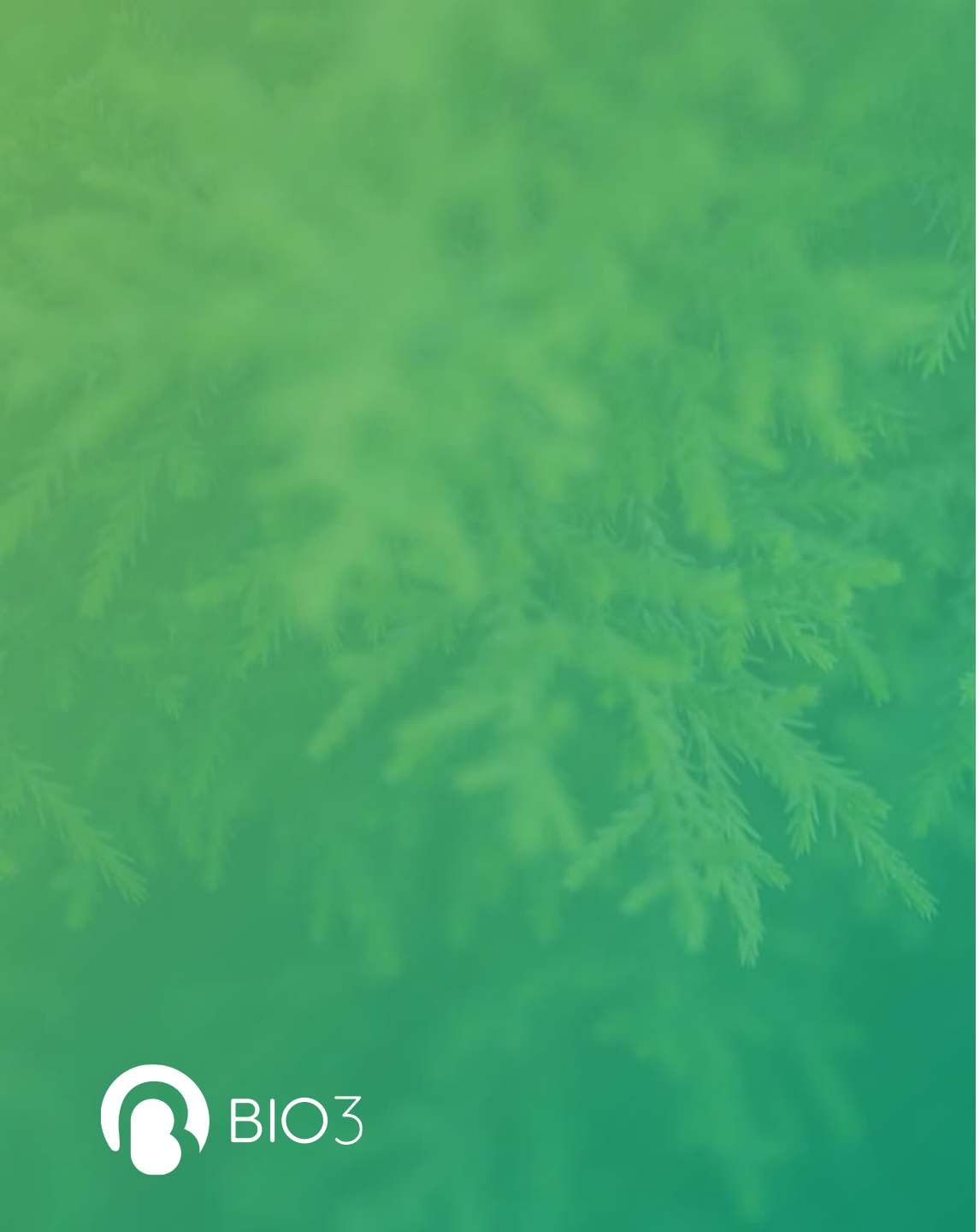

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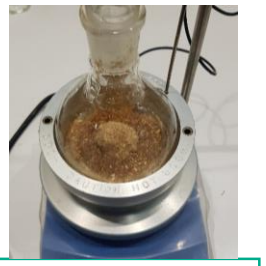
Inorganic Salt Hydrates

Study of Pruning Dissolution

Inorganic Salt Hydrates



Biomass

Dissolution

Inorganic Salt Hydrate
$ZnCl_2 \cdot 4H_2O$

Equivalent
Cheaper

Filtration 1

Solid 1
Lignin + Unreacted biomass

Filter 20um

Liquid 1
Solvent + Cellulose + dissolved Hemicellulose

Water

Filtration 2

Filter 0,20um

Solid 2
Cellulose + Hemicellulose

Liquid 2
Water + Solvent + **Xylanes**

HPLC

<u>????</u>
<u>Time</u>
<u>Temperature</u>

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Inorganic Salt Hydrates

Reaction conditions:

t= 5h y T[a]: 140ºC

Catalyst: H_2SO_4 (0.2 mol/L)

Sample	Solid 1	Solid 2	%Total Recovery	%Biomass Conversion S1	%Biomass Conversion S2	g/L Glucose S1	g/L Glucose S2	g/L Xylose S1	g/L Xylose S2
Original Pruning	-	-	-	83%		1,04		0,44	
24h (60°C)	5,46g (68,0%)	0,513g (6,4%)	74,4%	72,2%	-	1,54	-	0,41	-
24h (70°C)	2,89g (35,9%)	1,74g (21,6%)	57,5%	72,5%	90,4%	2,17	**5,17**	0,22	0,18
24h (80°C)	3,72g (46,2%)	0,71g (8,8%)	55%	65,2%	-	2,37	-	-	-
24h (90°C)	3,97g (49,6%)	0,516 (6,5%)	56,1%	64,6%	-	1,91	-	1,46	-

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Study of Pruning Dissolution

Outlook and Future Perspectives

- The results obtained show that a long reaction time (24h) is required.
- At 70 ºC and 24h of reaction, the best separation of the fractions is obtained. Solid 1 and Solid 2 have been interesting data in the hydrolysis.
- By means of HPLC it can be verified that most of the Hemicellulose fraction remains in the form of xylan when the first Filtrate collected precipitates.

- Check if removing the extractives, the results could be improved.
- Do the pretreatment with $ZnBr_2 \cdot 4H_2O$

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