

VALORIZACIÓN DE HEMICELULOSAS.

MAESTRÍA EN INGENIERÍA DE CELULOSA Y PAPEL



FACULTAD DE
INGENIERÍA



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Ingeniería de
Procesos Forestales

Componentes estructurales de la biomasa

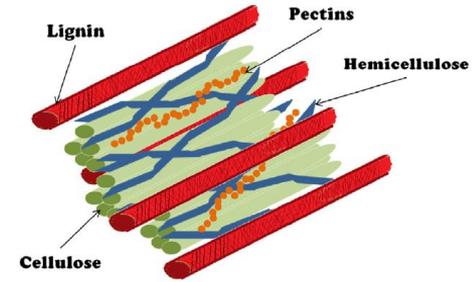
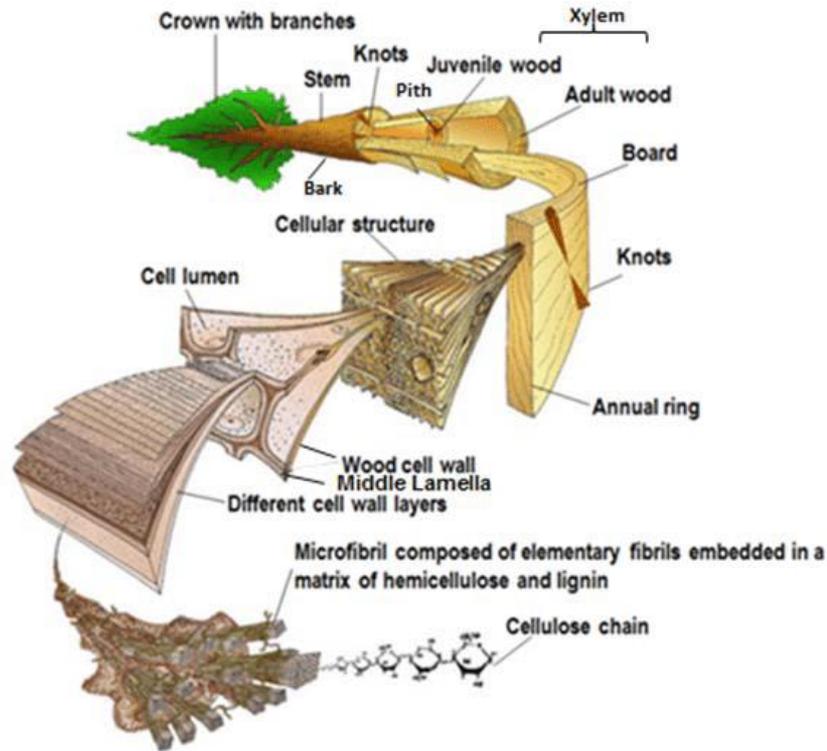


Figure 2.5 Structural polysaccharides of lignocellulosic biomass.

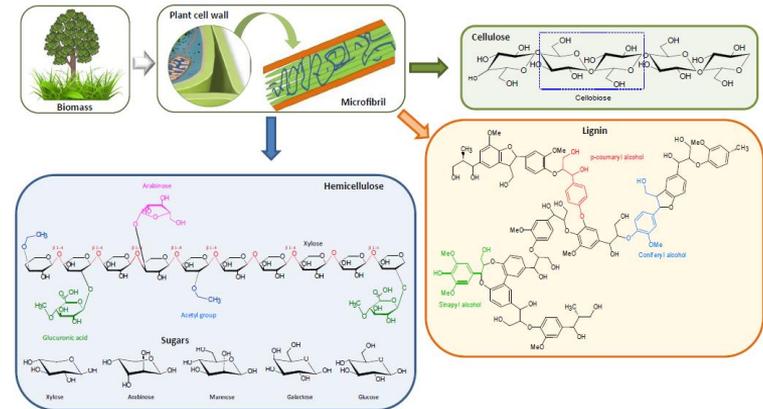


Figure 1.1 Structure and main components of lignocellulosic biomass.

Tab. 2.4 Chemical composition of some typical cellulose-containing materials (adopted from [8]).

Source	Composition [%]			
	Cellulose	Hemicelluloses	Lignin	Extract
Hardwood	43–47	25–35	16–24	2–8
Softwood	40–44	25–29	25–31	1–5
Bagasse	40	30	20	10
Coir	32–43	10–20	43–49	4
Corn cobs	45	35	15	5
Corn stalks	35	25	35	5
Cotton	95	2	1	0.4
Flax (retted)	71	21	2	6
Flax (unretted)	63	12	3	13
Hemp	70	22	6	2
Jute	71	14	13	2
Sisal	73	14	11	2
Wheat straw	30	50	15	5

Sixta H, 2006

Hemicelulosas

Hemicelulosas son **heteropolisacáridos** que pueden contener las unidades:

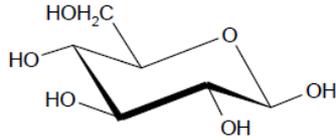
- hexosas (D-glucosa, D-manosa, D-galactosa).
- pentosas (D-xilosa, L-arabinosa, D-arabinosa).
- deoxihexosas (L-ramnosa (6-deoxi-L-manosa),
- L-fucosa (6-deoxi-L-galactosa)).

Pequeñas cantidades de ácidos urónicos

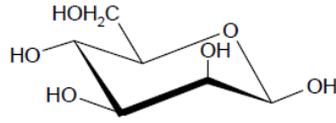
- (ácido 4-O-metil-D-glucurónico, ácido D-galacturónico,
- ácido D-glucurónico)

Monómeros que componen las Hemicelulosas

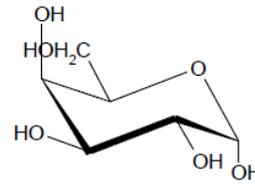
Hexosas



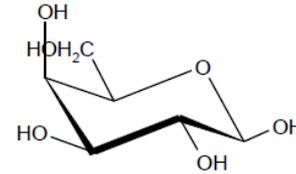
β -D-glucopyranose
(β -D-Glcp)



β -D-mannopyranose
(β -D-Manp)

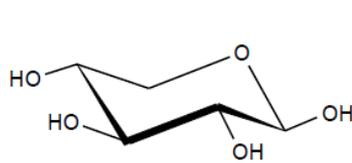


α -D-galactopyranose
(α -D-Galp)

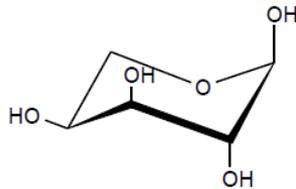


β -D-galactopyranose
(β -D-Galp)

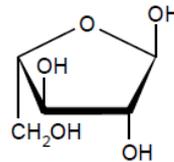
Pentosas



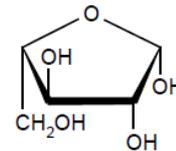
β -D-xylopyranose
(β -D-Xylp)



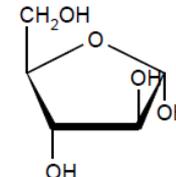
α -L-arabinopyranose
(α -L-Arap)



α -L-arabinofuranose
(α -L-Araf)



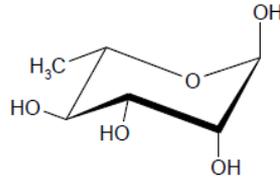
β -L-arabinofuranose
(β -L-Araf)



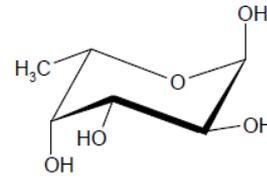
α -D-arabinofuranose
(α -D-Araf)

Monómeros que componen las Hemicelulosas

Deoxihexosas

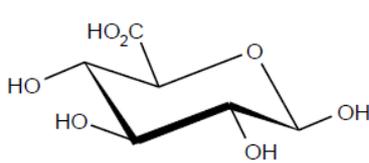


***α*-L-rhamnopyranose
(*α*-L-Rhamp)**

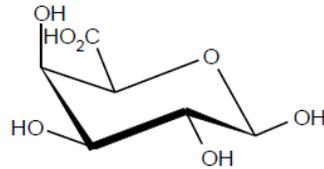


***α*-L-fucopyranose
(*α*-L-Fucp)**

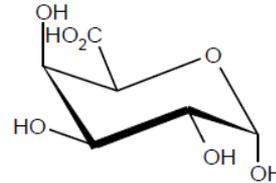
Ácidos Urónicos



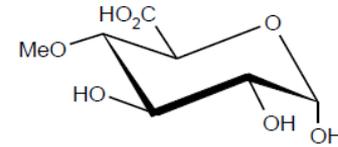
***β*-D-glucuronic acid
(*β*-D-GlcpA)**



***β*-D-galacturonic acid
(*β*-D-GalpA)**



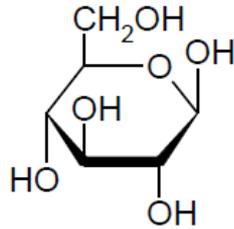
***α*-D-galacturonic acid
(*α*-D-GalpA)**



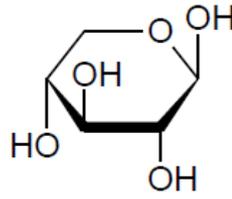
**4-O-methyl-D-glucuronic acid
(4-O-Me-*α*-D-GlcpA)**

Hemicelulosas

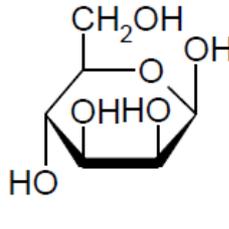
- La madera tiene 2 tipos principales de hemicelulosas:
glucomananos y xilanos
- Sus principales componentes son glucosa, xilosa, manosa y galactosa



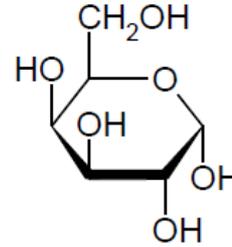
β -D-Glcp



β -D-Xylp

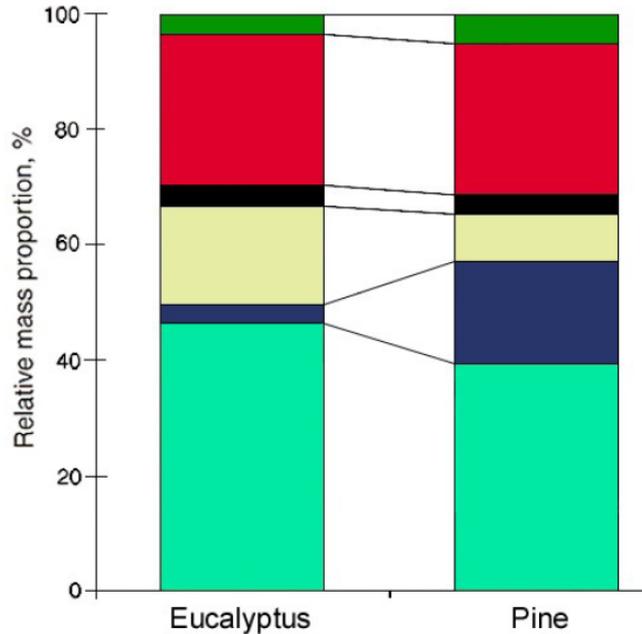


β -D-Manp



α -D-Galp

Hemicelulosas



- La composición de hemicelulosas difiere en angiospermas y gimnospermas:
 - Contenido Hemicelulósico
 - El porcentaje de cada constituyente
 - Generalmente, gimnospermas tienen más manosas y galactosas y menos xilosas y grupos OH acetilados que angiospermas

Hemicelulosas

- Las hemicelulosas más relevantes son xilanos y glucomananos, siendo los xilanos los más abundantes.
- Los xilanos son los componentes principales de las hemicelulosas de las paredes celulares secundarias de las maderas de latifoliadas y de plantas herbáceas.
- En algunos tejidos de gramíneas y cereales los xilanos pueden representar hasta el 50%.
- Las hemicelulosas del tipo mananos como glucomananos y galactoglucomananos son los principales componentes hemicelulósicos de la pared secundaria de maderas de coníferas

Principales hemicelulosas en madera

Hemicellulose type	Occurence	Amount (% of wood)	Units	Molar ratios	Linkage
Galactoglucomannan	Softwood	5-8	β -D-Manp	3	1→4
			β -D-Glcp	1	1→4
			α -D-Galp	1	1→6
			Acetyl	1	
(Galacto)glucomannan	Softwood	10-15	β -D-Manp	4	1→4
			β -D-Glcp	1	1→4
			α -D-Galp	0.1	1→6
			Acetyl	1	
Arabinoglucuronoxylan	Softwood	7-10	β -D-Xylp	10	1→4
			4-O-Me- α -D-GlcpA	2	1→2
			α -L-Araf	1.3	1→3
Arabinogalactan	Larch wood	5-35	β -D-Galp	6	1→3,6
			α -L-Araf	2/3	1→6
			β -L-Arap	1/3	1→3
			β -D-Glcp	Little	1→6
Glucuronoxylan	Hardwood	15-30	β -D-Xylp	10	1→4
			4-O-Me- α -D-GlcpA	1	1→2
			Acetyl	7	
Glucomannan	Hardwood	2-5	β -D-Manp	1-2	1→4
			β -D-Glcp	1	1→4

Xilanos en latifoliadas

- Los xilanos de las plantas terrestres son heteropolímeros que presentan un esqueleto de unidades β -D-xilopiranosas unidas por enlace 1-4.
- El componente principal de las hemicelulosas en las maderas de latifoliadas es el O-acetil-4-O-metilglucorono- β -D-xilano, normalmente denominado glucoronoxilano o xilano.
- Los grupos OH de las unidades de xilosa están mayoritariamente sustituidos por un grupo O-acetilo en el C2 o C3 (aprox. 4 - 7 de cada 10 residuos).
- Adicionalmente las unidades de xilosa de la cadena principal pueden estar sustituidas por enlaces 1-2 a residuos de ácidos 4-O-metil- α -D-glucorónico a razón de un ácido urónico por cada 10 unidades de xilosas.

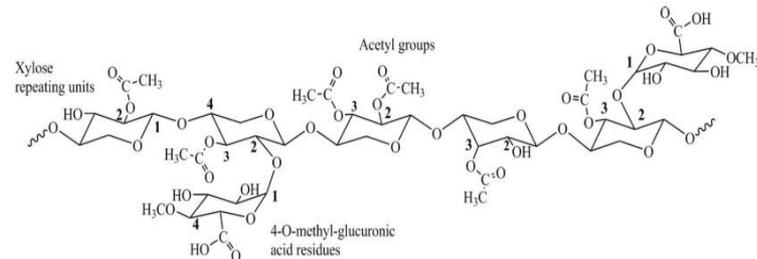


Table 2Hemicelluloses composition of various lignocellulosic materials.^{a,b,c}

Raw material	Xyl	Ara	Man	Gal	Rha	UA	AcG	References ^d
<i>Softwoods</i>								
Douglas fir	6.0	3.0	–	3.7	–	–	–	(1)
Pine	5.3–10.6	2.0–4.2	5.6–13.3	1.9–3.8	–	2.5–6.0	1.2–1.9	(2, 3)
Spruce	5.3–10.2	1.0–1.2	9.4–15.0	1.9–4.3	0.3	1.8–5.8	1.2–2.4	(2, 4–7)
<i>Hardwoods</i>								
Aspen	18–27.3	0.7–4.0	0.9–2.4	0.6–1.5	0.5	4.8–5.9	4.3	(1, 2, 4, 8)
Birch	18.5–24.9	0.3–0.5	1.8–3.2	0.7–1.3	0.6	3.6–6.3	3.7–3.9	(2, 4)
Black locust	16.7–18.4	0.4–0.5	1.1–2.2	0.8	–	4.7	2.7–3.8	(2, 9)
Eucalypt	14–19.1	0.6–1	1–2.0	1–1.9	0.3–1	2	3–3.6	(10–13)
Maple	18.1–19.4	0.8–1	1.3–3.3	1.0	–	4.9	3.6–3.9	(2, 9)
Oak	21.7	1.0	2.3	1.9	–	3	3.5	(14)
Poplar	17.7–21.2	0.9–1.4	3.3–3.5	1.1	–	2.3–3.7	0.5–3.9	(2, 15)
Sweet gum	19.9	0.5	0.4	0.3	–	2.6	2.3	(16)
Sycamore	18.5	0.7	1.0	–	–	–	3.6	(9)
Willow	11.7–17.0	2.1	1.8–3.3	1.6–2.3	–	–	–	(4, 17)
<i>Agricultural and agro-industrial materials</i>								
Almond shells	34.3	2.5	1.9	0.6	–	–	–	(18)
Barley straw	15	4.0	–	–	–	–	–	(19)
Brewery's spent grain	15	8	0	1	0	2	0.8	(12)
Cardoon	26.0	2.5	3.7	1.4	0.9	–	–	(20)
Corn cobs	28–35.3	3.2–5.0	–	1–1.2	1	3	1.9–3.8	(9, 13, 21, 22)
Corn fibre	21.6	11.4	–	4.4	–	–	–	(23)
Corn stalks	25.7	4.1	<3.0	<2.5	–	–	–	(24)
Corn stover	14.8–25.2	2–3.6	0.3–0.4	0.8–2.2	–	–	1.7–1.9	(9, 25, 26)
Olive stones	2.0–3.7	1.1–1.2	0.2–0.3	0.5–0.7	0.3–0.5	1.2–2.2	–	(27)
Rice husks	17.7	1.9	–	–	–	–	1.62	(28)
Rice straw	14.8–23	2.7–4.5	1.8	0.4	–	–	–	(23, 26)
Sugar cane bagasse	20.5–25.6	2.3–6.3	0.5–0.6	1.6	–	–	–	(29–31)
Wheat bran	16	9	0	1	0	2	0.4	(13)
Wheat straw	19.2–21.0	2.4–3.8	0–0.8	1.7–2.4	–	–	–	(8, 26)

^a Non-glycosidic units.^b Expressed as g/100 g of dry material.^c The percentages of oses were, in some cases, calculated from the corresponding “polymers”. Xyl, xylose; Ara, arabinose; Man, mannose; Gal, galactose; Rha, rhamnose; UA, uronic acids; AcG, acetyl groups.

Productos top de valor agregado a partir de biomasa

Precedente: Top Value Added Chemicals from Biomass Volume (NREL 2004)

El Departamento de Energía de EE. UU. produjo un estudio sistemático destinado a seleccionar los componentes básicos más prometedores basándose en 9 criterios seleccionados

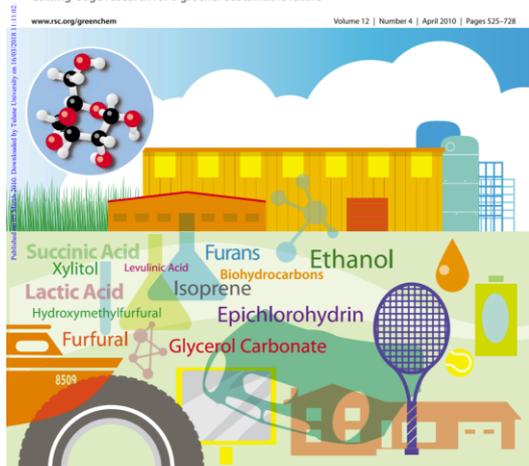
Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy’s “Top 10” revisited (Bozell & Petersen, 2010)

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Bozell and Petersen
Technology development to produce
biobased products

Song and Li et al.
Fe₂O₃ nanoparticle catalyst

Dumic et al.
Catalytic upgrading of levulinic
acid

Ehteshami et al.
Glycerol carbonate synthesis

Productos top de valor agregado a partir de biomasa (Bozell & Petersen, 2010)

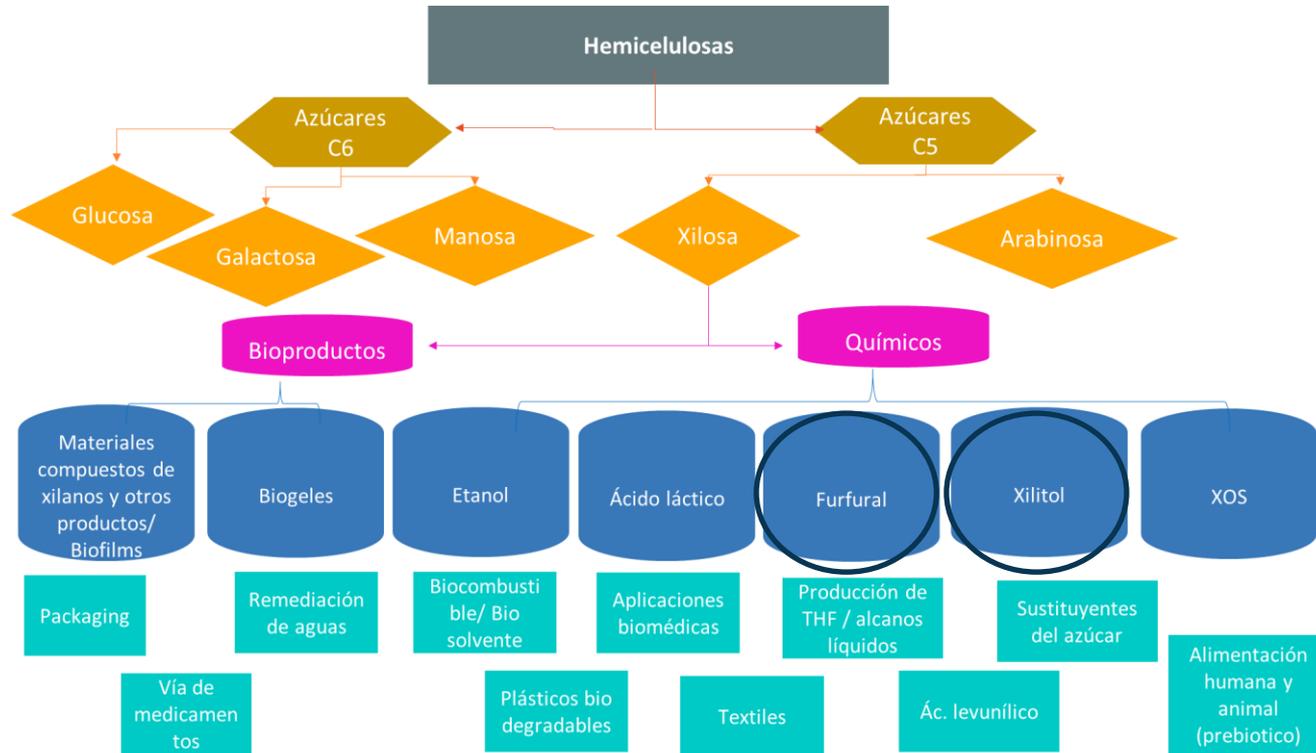
Table 2 Criteria used in evaluating biobased product opportunities from carbohydrates

1. ***The compound or technology has received significant attention in the literature.*** A high level of reported research identifies both broad technology areas and structures of importance to the biorefinery.
2. ***The compound illustrates a broad technology applicable to multiple products.*** As in the petrochemical industry, the most valuable technologies are those that can be adapted to the production of several different structures.
3. ***The technology provides direct substitutes for existing petrochemicals.*** Products recognized by the chemical industry provide a valuable interface with existing infrastructure and utility.
4. ***The technology is applicable to high volume products.*** Conversion processes leading to high volume functional equivalents or utility within key industrial segments will have particular impact.
5. ***A compound exhibits strong potential as a platform.*** Compounds that serve as starting materials for the production of derivatives offer important flexibility and breadth to the biorefinery.
6. ***Scaleup of the product or a technology to pilot, demo, or full scale is underway.*** The impact of a biobased product and the technology for its production is greatly enhanced upon scaleup.
7. ***The biobased compound is an existing commercial product, prepared at intermediate or commodity levels.*** Research leading to production improvements or new uses for existing biobased chemicals improves their utility.
8. ***The compound may serve as a primary building block of the biorefinery.*** The petrochemical refinery is built on a small number of initial building blocks: olefins, BTX, methane, CO. Those compounds that are able to serve an analogous role in the biorefinery will be of high importance.
9. ***Commercial production of the compound from renewable carbon is well established.*** The potential utility of a given compound is improved if its manufacturing process is already recognized within the industry.

Table 3 New top chemical opportunities from biorefinery carbohydrates, criteria for their inclusion and resulting technology needs

Compound	Criteria for inclusion	Illustrative general biorefinery technology needs
Ethanol	1, 2, 3, 4, 5, 6, 7, 8, 9	Selective alcohol dehydrations; improved biochemical production of alcohols from biomass (rate, yield, titer, product, pH, inhibitor tolerance); engineering of optimal fermentation organisms
Furans	<i>Furfural</i> : 1, 2, 7, 8, 9 <i>HMF</i> : 1, 2, 5, 8 <i>FDCA</i> : 1, 4, 5	Selective dehydrations of carbohydrates; new catalysts and reaction media for dehydration; reactive separations; selective oxidations of alcohols; improved oxidation and dehydration catalysts; catalytic systems for reactions in aqueous solution
Glycerol and derivatives	1, 2, 3, 4, 5, 6, 7, 8, 9	Reactions in aqueous solution; selective reductions and oxidations of polyols; improved biological conversions of polyols
Biohydrocarbons	<i>Isoprene</i> : 1, 2, 3, 4, 6, 7 <i>Biohydrocarbons</i> : 1, 2, 6	Improved biohydrocarbon production; engineering of organisms to convert sugars to hydrocarbons; optimizing rate, yield, titer, product tolerance
Lactic acid	1, 2, 4, 7	Optimization of bioconversion of carbohydrates; bioprocesses with high rate, yield, titer, product, pH and inhibitor tolerance; engineering of organisms to produce single materials
Succinic acid	1, 2, 5, 6	Bioconversion of carbohydrates; optimization of yield, rate, titer, separation; engineering of organisms for optimal production of target
Hydroxypropionic acid/aldehyde	1, 3, 4, 5	Optimization of bioconversion of carbohydrates; bioprocesses with high rate, yield, titer, product and inhibitor tolerance; engineering of organisms to produce single materials; selective dehydrations of alcohols; selective reductions of carbonyl groups, new selective hydrogenation catalysts; chemical processes in aqueous solution
Levulinic acid	1, 2, 3, 5, 6, 8	Selective dehydrations of carbohydrates; improved separations of products; utility of co-product schemes by biorefinery; improved catalysts for selective carbohydrate conversion processes
Sorbitol	1, 2, 3, 4, 5, 6, 7, 8, 9	Selective hydrogenolysis of polyols; new catalysts for reduction of carbohydrate derivatives; selective dehydrations of polyols; comparative assessment of chemical and biochemical conversion technology; selective bond breaking/bond making technology for polyols
Xylitol	1, 2, 5, 8, 9	Selective hydrogenolysis of polyols; new catalysts for reduction of carbohydrate derivatives; selective dehydrations of polyols; comparative assessment of chemical and biochemical conversion technology; selective bond breaking/bond making technology for polyols

Principales productos a partir de hemicelulosas



(Adaptado de (Deutschmann and Dekker, 2012))

El pretratamiento es clave y determina los tipos de compuestos que podemos producir con las hemicelulosas.

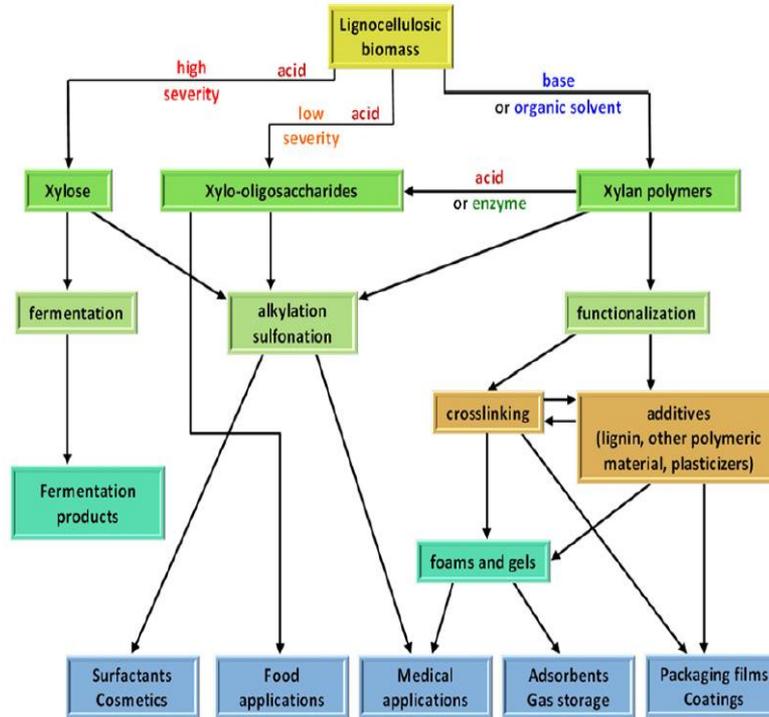


Fig. 2. Pathways towards xylan-based products from lignocellulosic materials.

Productos que utilizan los monómeros constituyentes de las hemicelulosas

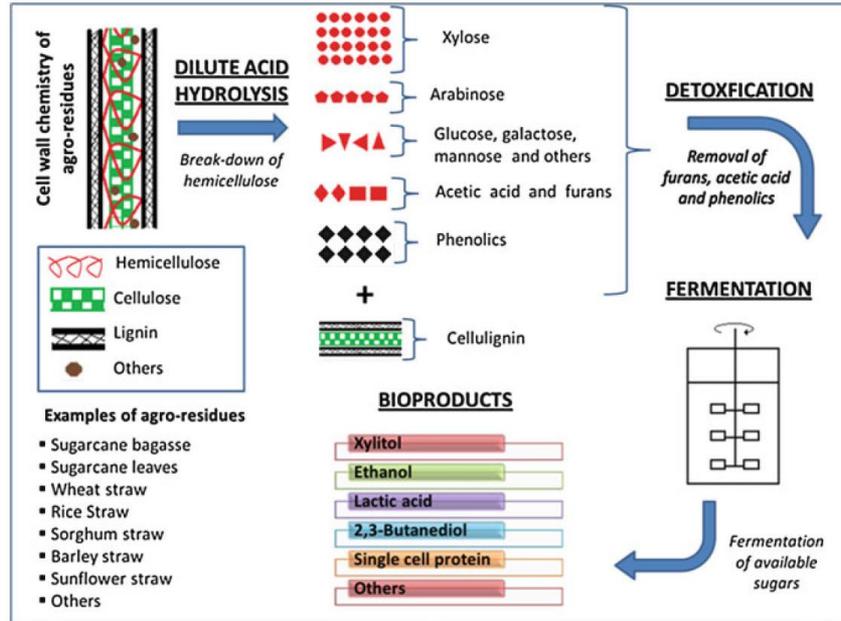
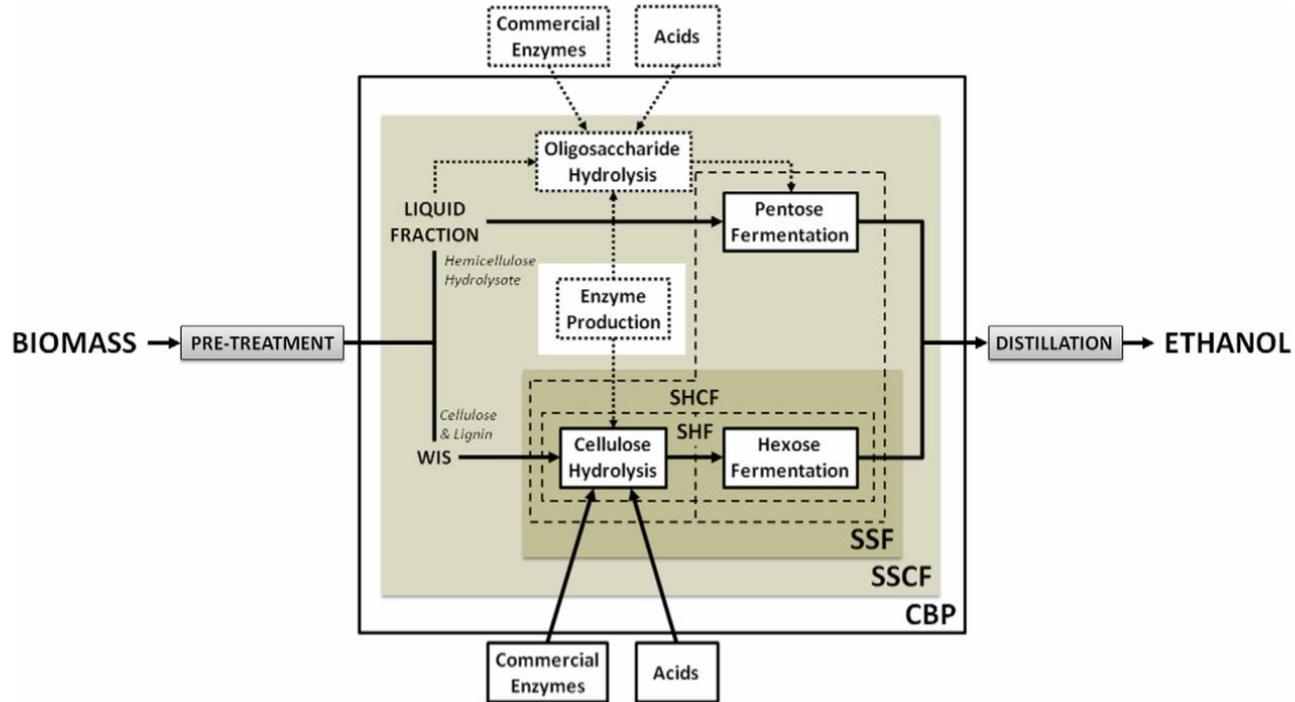


Fig. 2.1 Process configuration summarizing the dilute acid hydrolysis of various agro-residues into monomeric constituents and their conversion into value-added products

Bioetanol



Bioetanol

- Para el balance económico de la producción de etanol a partir de lignocelulósicos, es deseable la fermentación de glucosa (C6) y pentosas (C5)
- La mayoría de las levaduras, incluida *Saccharomyces cerevisiae* no fermentan pentosas.
- Las fermentaciones bacterianas están asociadas con bajos rendimientos de etanol, tasas de fermentación lentas, formación de subproductos (ácidos) que requieren separación adicional del producto, requisitos de pH neutro, etc.
- Las fermentaciones bacterianas son más sensibles a los inhibidores y presentan intolerancia a altas concentraciones de etanol.

Bioetanol

Table 4

Characteristics of most relevant microorganisms considered for ethanol production from hemicelluloses.

Characteristics	Microorganism			
	<i>E. coli</i>	<i>Z. mobilis</i>	<i>S. cerevisiae</i>	<i>P. stipitis</i>
D-glucose fermentation	+	+	+	+
Other hexose utilization (D-galactose and D-mannose)	+	–	+	+
Pentose utilization (D-xylose and L-arabinose)	+	–	–	+
Direct hemicellulose utilization	–	–	–	w
Anaerobic fermentation	+	+	+	–
Mixed-product formation	+	w	w	w
High ethanol productivity (from glucose)	–	+	+	w
Ethanol tolerance	w	w	+	w
Tolerance to lignocellulose- derived inhibitors	w	w	+	w
Osmotolerance	–	–	+	w
Acidic pH range	–	–	+	w
GRAS microorganism	–	+	+	+

+, Positive; –, negative; w, weak.

Table 4

SSCF by xylose-fermenting already engineered strains of *S. cerevisiae*.

Microorganism	Substrate	Temp. (°C)	Titer g/L	Yield g/g	Refs
<i>S. cerevisiae</i> RWB222	Waste paper sludge	37	40	0.39	[104]
<i>S. cerevisiae</i> XR/ARSdR/XK	Glucose (5 g/L) + xylose (15 g/L)	30	8	0.43	[105]
<i>S. cerevisiae</i> ICV D254	Rice hull hydrolysate	28	10.5	0.45	[106]
<i>S. cerevisiae</i> TMB3400	Pretreated corn stover	35	30.03	0.27	[107]
<i>S. cerevisiae</i> 259ST	Spent sulfite liquor	–	22.6	0.42	[108]
<i>S. cerevisiae</i> KE6–12b	Pretreated wheat straw	35	37.5	0.32	[109]

Bioetanol-VPP- “valorization prior pulping”

- Ahorra 1/3 del capital de infraestructura (frente a Greenfield)
- Servicios de vapor y energía, agua y efluentes, almacenes, depósitos de madera, tanques de almacenamiento, etc.
- Planta de pulpa kraft produce aprox. un 30% de exceso de energía.
- Produce químicos in situ

Bioetanol-VPP- “valorization prior pulping”

- Extraer las hemicelulosas antes de pulpear considerando que el HHV de los azúcares es de 18,6 MJ/kg y el HHV de la lignina es de $25 \pm 1,5$ MJ/kg. (Van heiningen 2006)
- Se debe mantener el rendimiento de la pulpa y la calidad de la pulpa kraft \Rightarrow optimizar el pulpeo kraft considerando la extracción de hemicelulosas

VPC: “Valorization prior combustion”

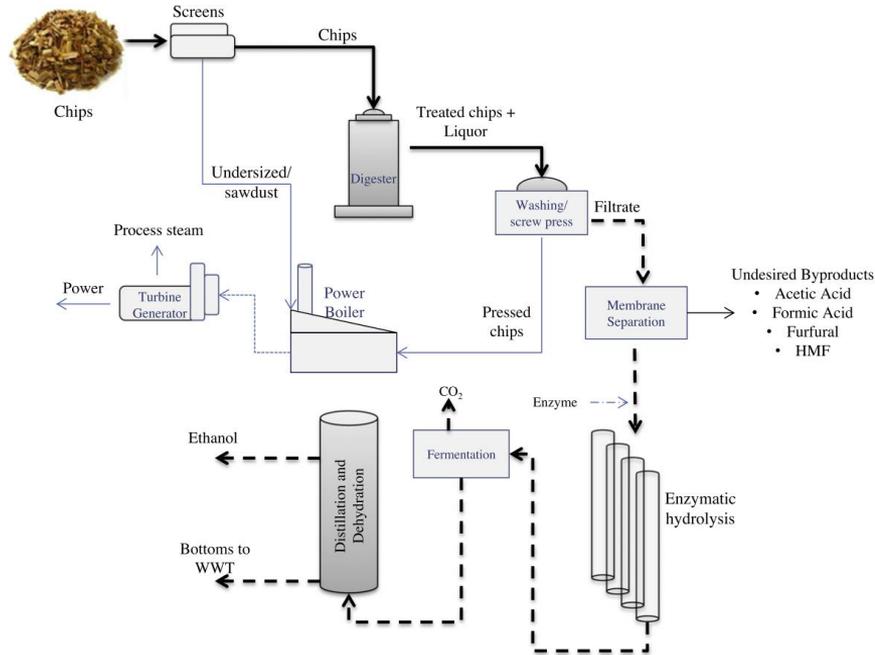


Fig. 1. Proposed integrated system for power and lignocellulosic ethanol production.

Treasure et al, 2012.
USDA, NC University

VPC: “Valorization prior combustion”

Table 1
Chemical composition of softwood and hardwood feedstocks.

Component	Hardwood (%)	Softwood (%)
Lignin	27	29
Glucan	46	46
Hexan	4	14
Xylan	19	7
Extractives	3	3
Ash	1	1

*Treasure et al, 2012.
USDA, NC University*

Table 2
Alternative cases in power and ethanol production.

Case	I	II	III	IV	V	VI
Feedstock	Hardwood	Hardwood	Hardwood	Softwood	Softwood	Softwood
Autohydrolysis temperature (°C)	160	170	180	160	170	180
Reaction time	1 h	1 h	1 h	1 h	1 h	1 h
Product	Power	Power	Power	Power	Power	Power
Co-product	Ethanol	Ethanol	Ethanol	Ethanol	Ethanol	Ethanol

Table 3

Extract and residues mass balance for hardwood after autohydrolysis.

Mass balance hardwood									
Starting material 1000 kg (O.D.)			Temperature 160 °C Solids		Temperature 170 °C Solids		Temperature 180 °C Solids		
Component	%	kg	Component	kg	Component	kg	Component	kg	
Lignin	27	270.0	Lignin	264.6	Lignin	264.6	Lignin	264.6	
Glucan	46	460.0	Glucan	448.9	Glucan	449.0	Glucan	358.4	
Hexan	4	40.0	Hexan	0.0	Hexan	0.0	Hexan	0.0	
Xylan	19	190.0	Xylan	86.8	Xylan	24.2	Xylan	0.0	
Extractives	3	30.0	Extractives	0.0	Extractives	0.0	Extractives	0.0	
Ash	1	10.0	Ash	1.0	Ash	1.0	Ash	1.0	
Total		1000.0	Sub total	801.3	Sub total	738.7	Sub total	624.0	
			Dissolved solids		Dissolved solids		Dissolved solids		
			Lignin	5.4	Lignin	5.4	Lignin	5.4	
			Glucan	1.9	Glucan	4.3	Glucan	6.8	
			Hexan	6.1	Hexan	10.0	Hexan	9.0	
			Xylan	3.7	Xylan	19.0	Xylan	29.2	
			Extractives	3.0	Extractives	3.0	Extractives	3.0	
			Ash	9.0	Ash	9.0	Ash	9.0	
			Oligomers	82.6	Oligomers	90.5	Oligomers	65.6	
			Acetic acid	11.0	Acetic acid	24.0	Acetic acid	40.0	
			Furfural	1.0	Furfural	5.0	Furfural	13.0	
			HMF	1.0	HMF	1.0	HMF	2.0	
			Formic acid	11.0	Formic acid	16.0	Formic acid	18.0	
			Volatiles	63.0	Volatiles	74.0	Volatiles	175.0	
			Sub total	198.7	Sub total	261.3	Sub total	376.0	
			Total material	1000.0	Total material	1000.0	Total material	1000.0	

Treasure et al, 2012.
 USDA, NC University

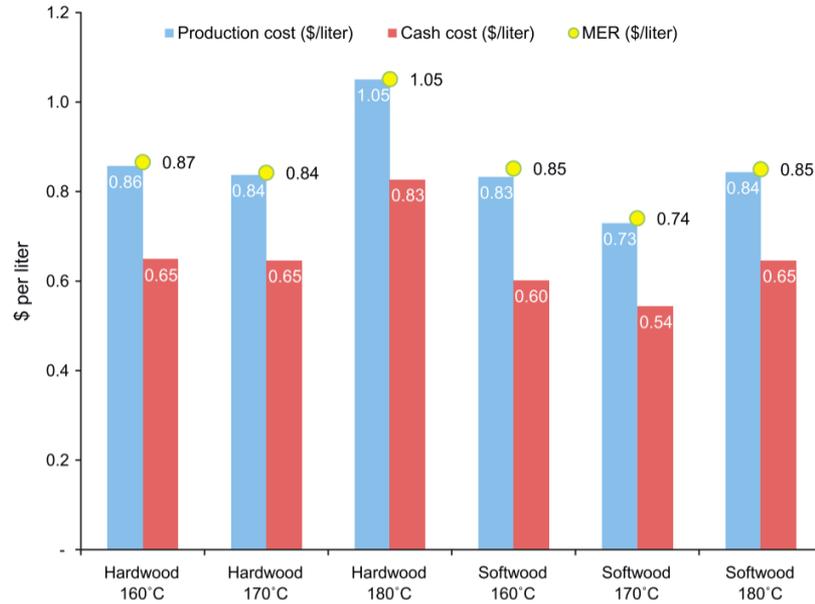


Fig. 8. Minimum ethanol revenue required (12% IRR), cash cost and production cost for each autohydrolysis condition.

*Treasure et al, 2012.
USDA, NC University*

Extracción de hemicelulosas en condiciones “Near-neutral”

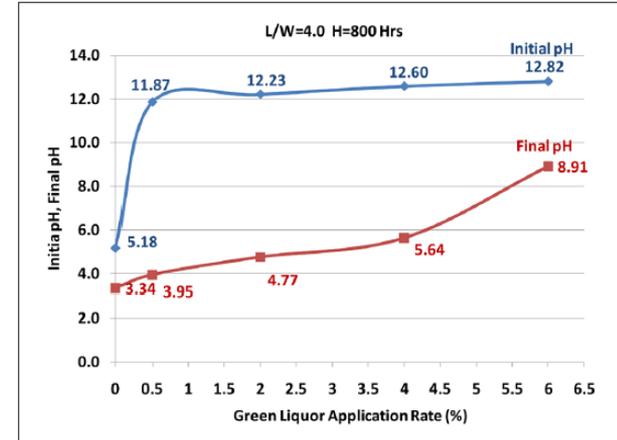
Chemical Component	Amount (% by wt.)	Chemical Component	Amount (% by wt.)
Arabinan	0.56±0.01	Lignin	26.5±0.2
Galactan	1.22±0.02	Extractives ^a	0.61±0.05
Glucan	42.7±0.6	Ash	0.51±0.05
Xylan	22.8±0.4	AcG ^b	3.65±0.08
Mannan	2.23±0.05	UAG ^c	2.80±0.10

^a Dichloromethane (DCM) as solvent.
^b AcG : Acetyl groups.
^c UAG : Uronic acid groups.

II. Composition of northeastern hardwood mixture (% on wood).

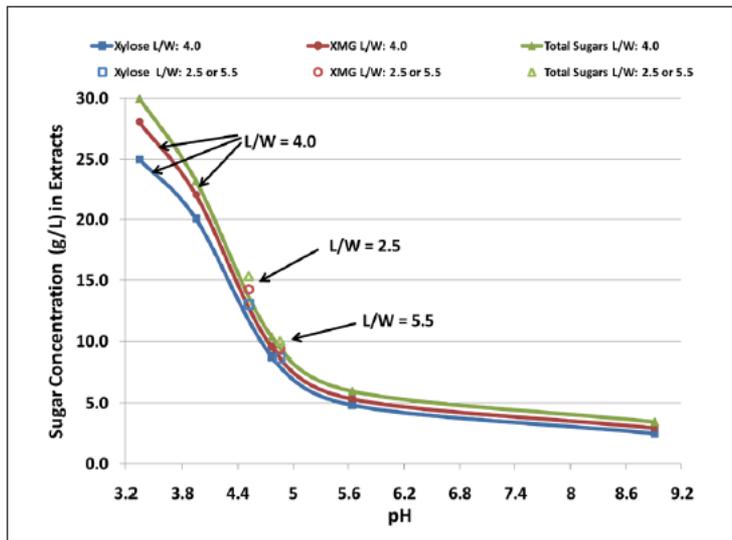
Experiment No.	Green Liquor Application (%) ^a	Liquor-to-Wood Ratio	H-Factor (hours)
1	0 (Water)	4	778
2	2	4	771
3	4	4	802
4	6	4	807
5	2	2.5	410
6	2	5.5	804
7	2	4	1254
8	2	4	433
9	0.5	4	790
10	2	2.5	819

^a 0.05% AQ was added based on wood.

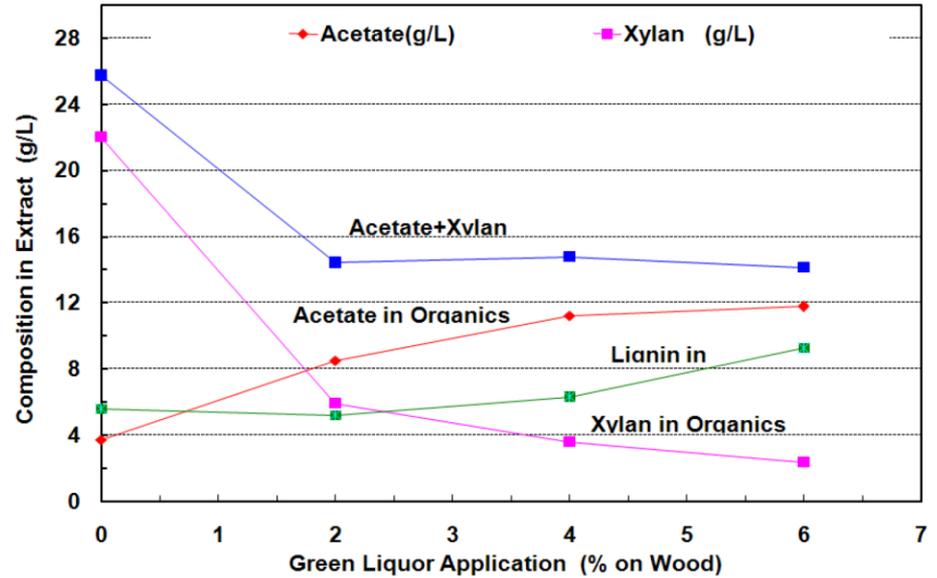


2. Initial and final pH of the extract following green liquor extraction.

Luo, Genco, & Zou 2011
 U. Maine



5. Total sugar concentration after hydrolysis versus pH at different green liquor charge and liquor-to-wood ratios.



Luo, Genco, & Zou 2011
U. Maine

Effect GL charge on total pulp yield

(van Heiningen et al. 2011)

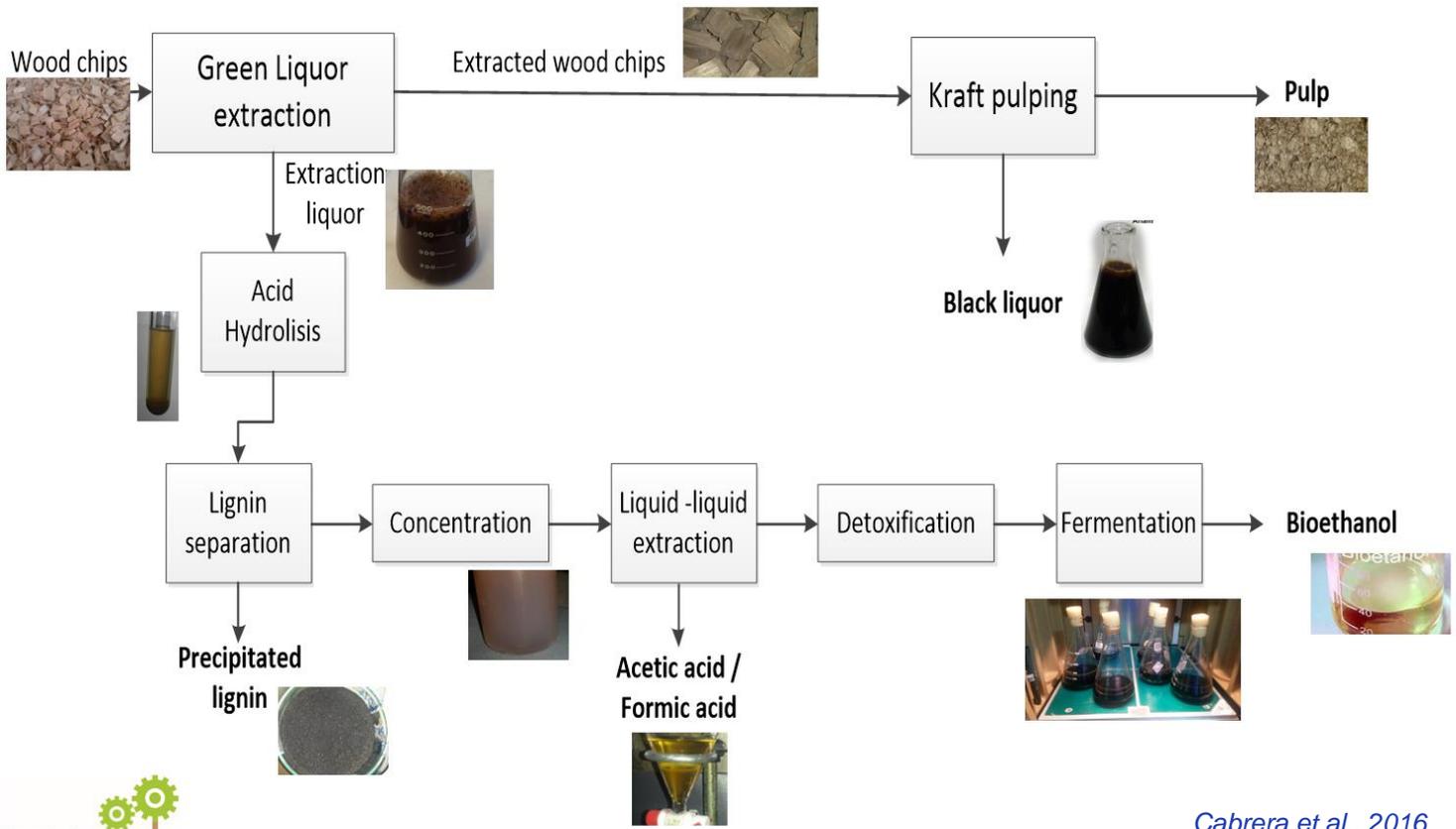
Green Liquor (%)	Effective Alkali (%) during Pulping	H-Factor (Hrs)	Total Pulp Yield (%)	Kappa No.	Calculated Yield @ 18 Kappa (%)*
0	12	1363	38.0	15.2	38.8
2	12	1362	46.9	18.9	46.6
4	12	1368	48.6	17.0	48.5
6	10	1365	49.7	18.4	49.7
Kraft Control 1	14	1313	50.8	18.4	50.7
Kraft Control 2	16	1368	48.6	15.7	49.3

Van Heiningen 2012
U. Maine

Old Town Fuel and Fiber (OTFF) - 2012



VPP: valorization prior pulping



Cabrera et al., 2016

VPP: valorization prior pulping

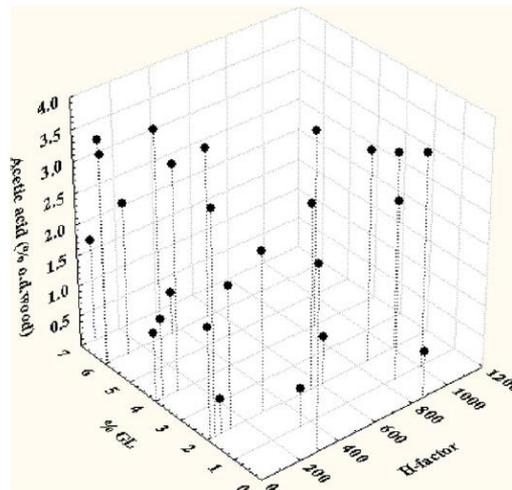
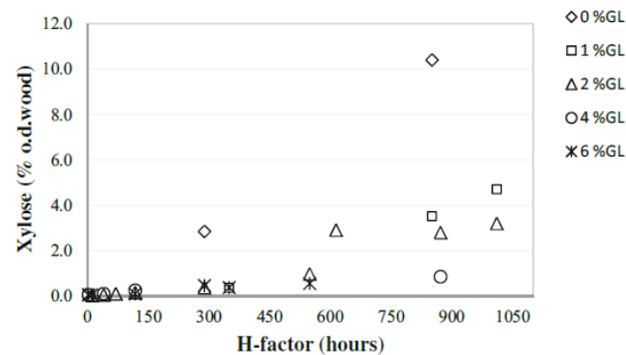
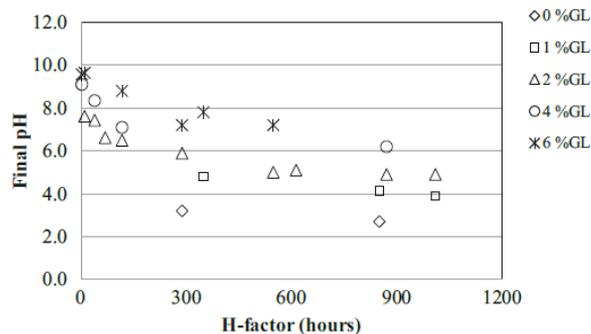
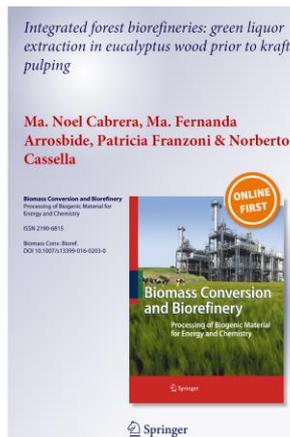


Table 1 Chemical composition of the *Eucalyptus grandis* wood (expressed in g/100 g wood in oven-dry basis \pm relative standard deviation based on four determinations)

Chemical component	Weight percent (o.d. basis)
Ash	0.37 \pm 0.01
Extractives ^a	2.36 \pm 0.07
Glucose	49.0 \pm 4.9
Xylose	15.0 \pm 0.1
Arabinose	<1 %
Klason lignin	24.9 \pm 0.1
Acid soluble lignin	3.1 \pm 0.2
Acetyl groups	3.8 \pm 0.1

^a Acetone and water as solvent



VPP: valorization prior pulping



Mairan D. Guigou, Florencia Cebreiros, Maria N. Cabrera, Mario D. Ferrari & Claudia Lareo



Fig. 1 Strategy of ethanol production from *Eucalyptus grandis* in an integrated biorefinery concept

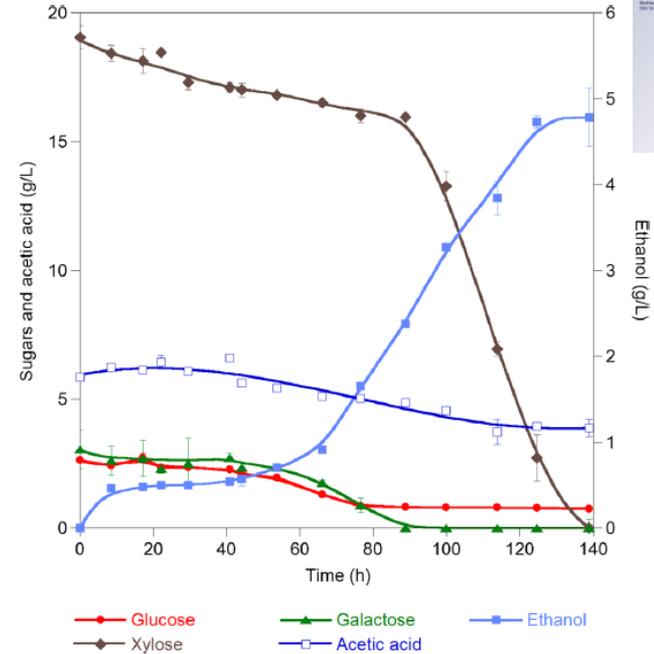
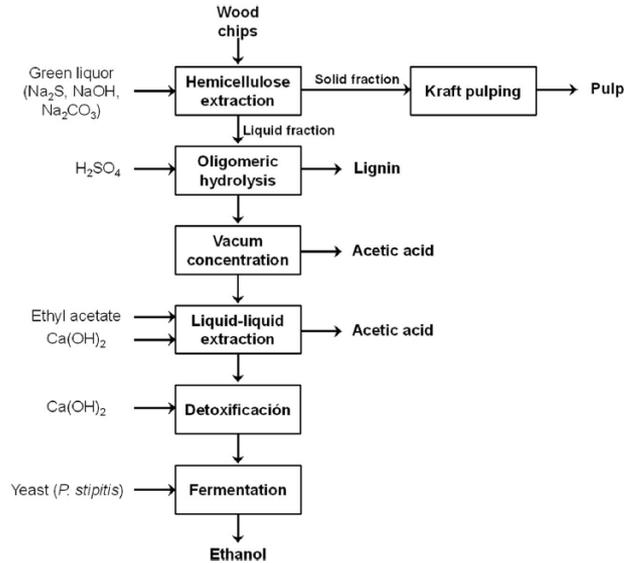


Fig. 3 Fermentation profiles of hydrolyzate of eucalyptus (referred as medium D in Table 3)

VPP: valorization prior pulping

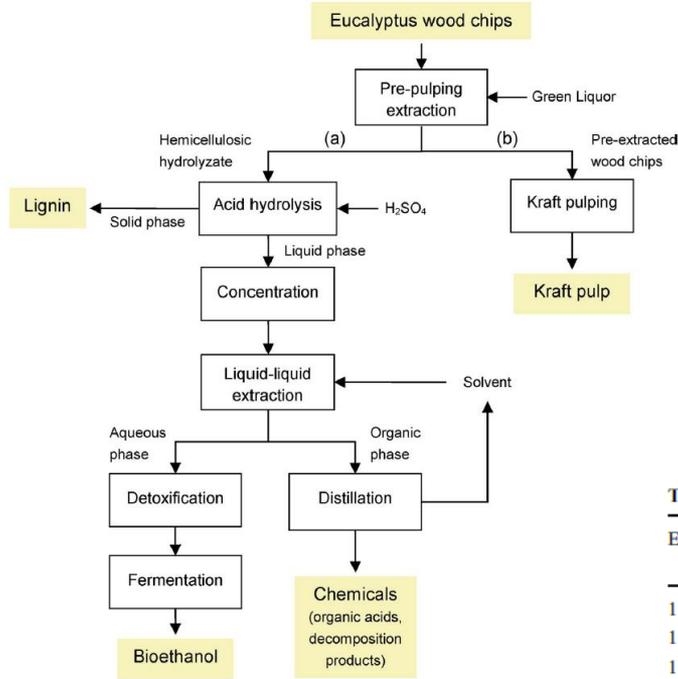


Table 6
Acetic acid recovery from pre-pulping hemicellulosic extracts of *E. grandis* wood.

Pre-pulping extraction conditions	Acetic acid yield ^a (%)	Acetic acid extraction ^b (%)	Recovery efficiency ^c (%)	Overall yield ^d (L _{acetic acid} /t _{dry wood})
2% GL, 155 °C, 613 ^b	1.6 ± 0.5	84.9 ± 0.8	41 ± 0.3	15 ± 2
2% GL, 160 °C, 1010 ^b	2.8 ± 0.1	94.7 ± 0.7	72 ± 0.1	26 ± 1

^a Expressed as g of acetic acid recovered per 100 g of dry wood.

^b Extraction conditions: pH 2.47, H/S of 1:1, three extraction stages, room temperature, and reaction time of 36 min.

^c Calculation based on the original wood composition.

^d Calculated as L of acetic acid recovered per 100 g of dry wood. Acetic acid density at 20 °C: 1.05 L/kg.

Table 4 Three pre-extraction conditions are selected and the chips are pulped to obtained pulps with a kappa number of 18.5 ± 1

Extraction condition	Xylose extraction yield (% o.d. wood)	Active alkali (as %Na ₂ O)	Pulping yield (% o.d. wood)	Kappa number	Viscosity (mL/g)
155 °C, 150 min, 2 %	2.9 ± 0.6	11.9 ± 0.2	47.0 ± 0.6	18.1 ± 0.3	1427 ± 28
160 °C, 120 min, 1 %	3.5 ± 0.4	12.0 ± 0.2	43.2 ± 0.7	19.5 ± 0.3	1306 ± 11
160 °C, 150 min, 2 %	3.2 ± 0.5	11.2 ± 0.2	48.3 ± 0.5	18.2 ± 0.4	1363 ± 12
Control pulp	–	16.5 ± 0.2	52.3 ± 0.7	18.1 ± 0.3	1218 ± 11

Pulping conditions: $T_{max} = 155$ °C, time at $T_{max} = 120$ min, and active alkali = variable. The table shows the main characteristics for the selected pulps obtained after the partial hemicellulose pre-extractions (value ± RSD for five replicates)

Industrial Crops & Products 109 (2017) 101–108

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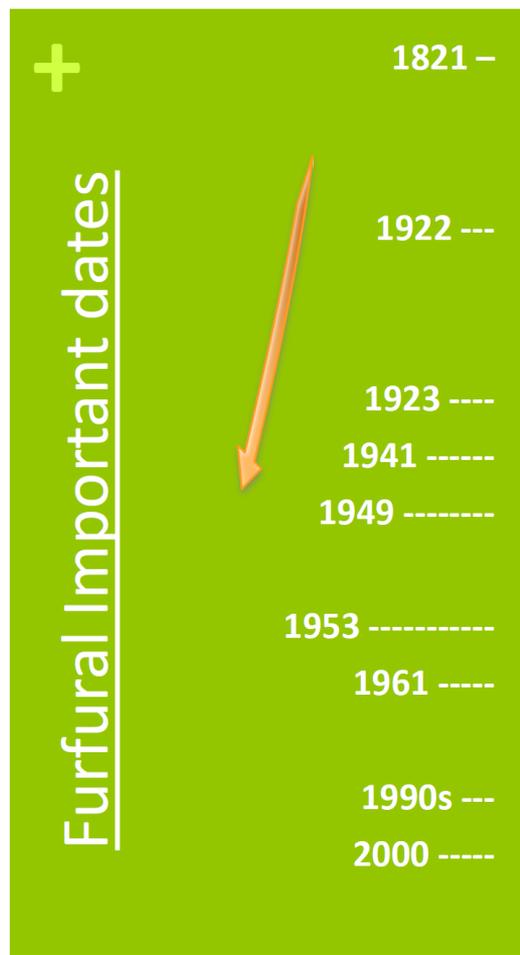
Research Paper

Integrated forest biorefineries: Recovery of acetic acid as a by-product from eucalyptus wood hemicellulosic hydrolysates by solvent extraction

Florencia Cebreiros^{a,*}, Mairan D. Guigou^a, María N. Cabrera^b



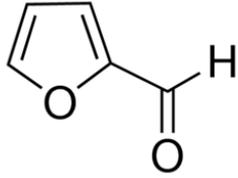
Furfural



- Döbereiner first isolated a milky distillate during the preparation of formic acid from sugars. The molecule was given the name furfural (C₅H₄O₂), and in 1840 Emmet observed that it can be produced from most vegetable substances.
- The Quacker Oats company start the industrial production of furfural from oats hulls in Iowa, USA, *rapidly distilling the aldehyde from the reaction chamber during the period of its formation.*
- Durite Plastics Inc. is the first manufacturer of phenol-furfural resins.
- Furfural derivatives are tested as automotive fuel in blends with gasoline.
- Du Pont starts the production of adiponitrile for the manufacture of nylon 6.6 from furfural and THF.
- A.P.Dunlop, F.N.Peters, The Furans, ACS Mon. series published. Commercial availability of furfuryl alcohol.
- Du Pont abandons the furfural-THF-adiponitrile process opting for oil derivatives as starting materials.
- Furfural market around 270 kton/year, mainly to furfuryl alcohol and furan resins.
- Karl J. Zeitsch writes a very successful book: *The chemistry and technology of furfural and its many by-products*

Marcotullio, G, 2013
“Furfural the sleeping beauty”

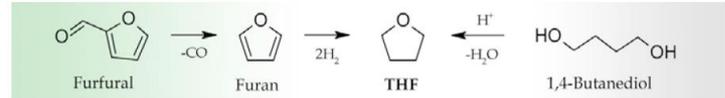
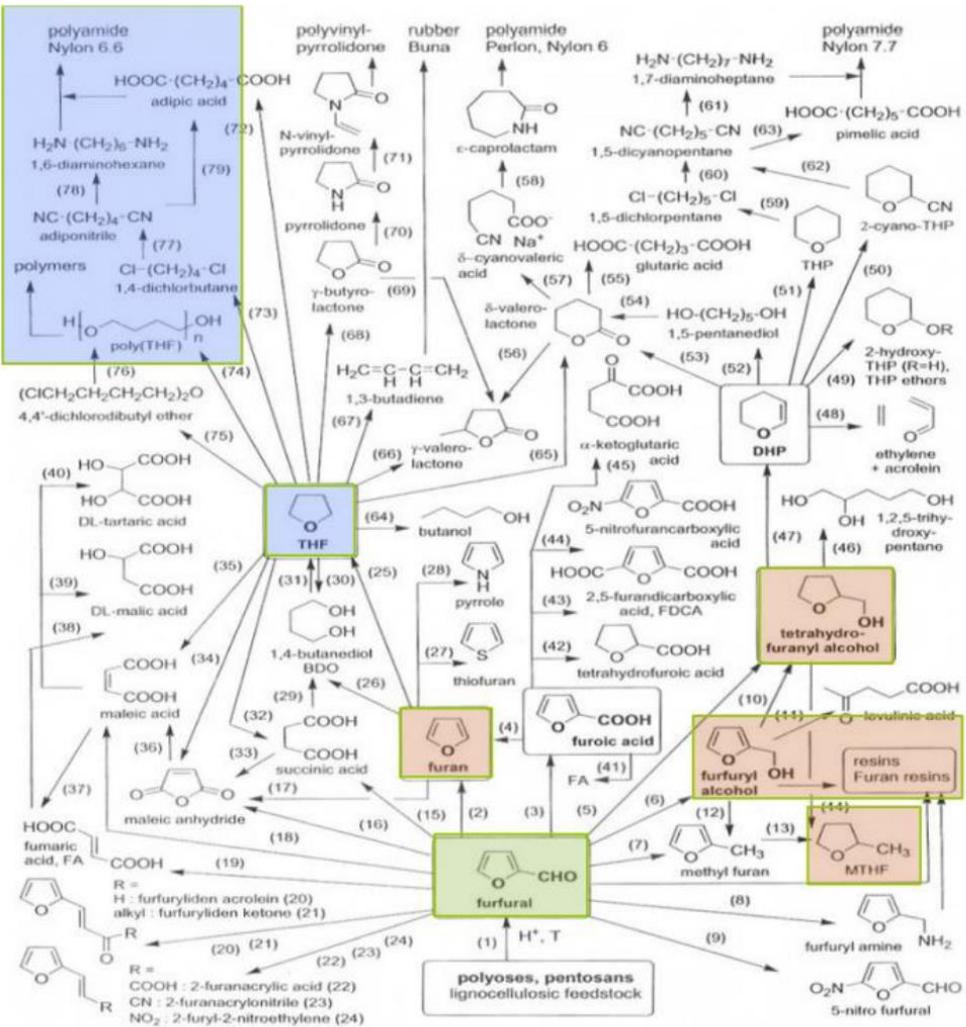
Furfural



Furfuraldehído o furan-2-metanal



- “commodity” intermedio, precursor muy versátil para la producción de amplia variedad de productos químicos.
- Principal destino: producción de alcohol furfurílico (60 – 70 %), con importante crecimiento de la demanda.
- Utilizado para la producción de THFA, THF, PTMEG y nylon, refinación de aceites lubricantes y de butadieno,
- agente decolorante para resinas de madera
- fungicida, resinas de fundición y en la industria farmacológica, entre otros



Furfural

Global furfural market volume by application, 2012-2020 (Kilo Tons)

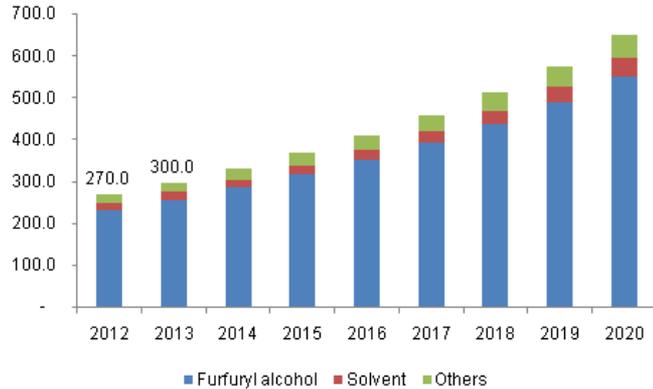


Tabla 1: Industrias productoras de furfural. (Watson, 2008)

País	Compañía	Producción (kton/año)	Materia prima	Proceso
China	(Varias)	>200 (total)	Mazorcas de maíz	Chino
República Dominicana	Central Romana	40,5	Bagazo	Quaker
Sudáfrica	Illovo	20,5	Bagazo	Rosenlew
Tailandia	Aurus Speciality Company Limited	8,4	Mazorcas de maíz	Chino
Austria	Lenzing	5,4	Efluente de pulpa de papel	s/d
Argentina	Indunor	6,0	Madera del quebracho	s/d
Eslovenia	Tanin Sevnica	1,5	Castaño	s/d
España	NUTRAFUR S.A.	5,0	Cáscara de almendras	s/d

Furfural

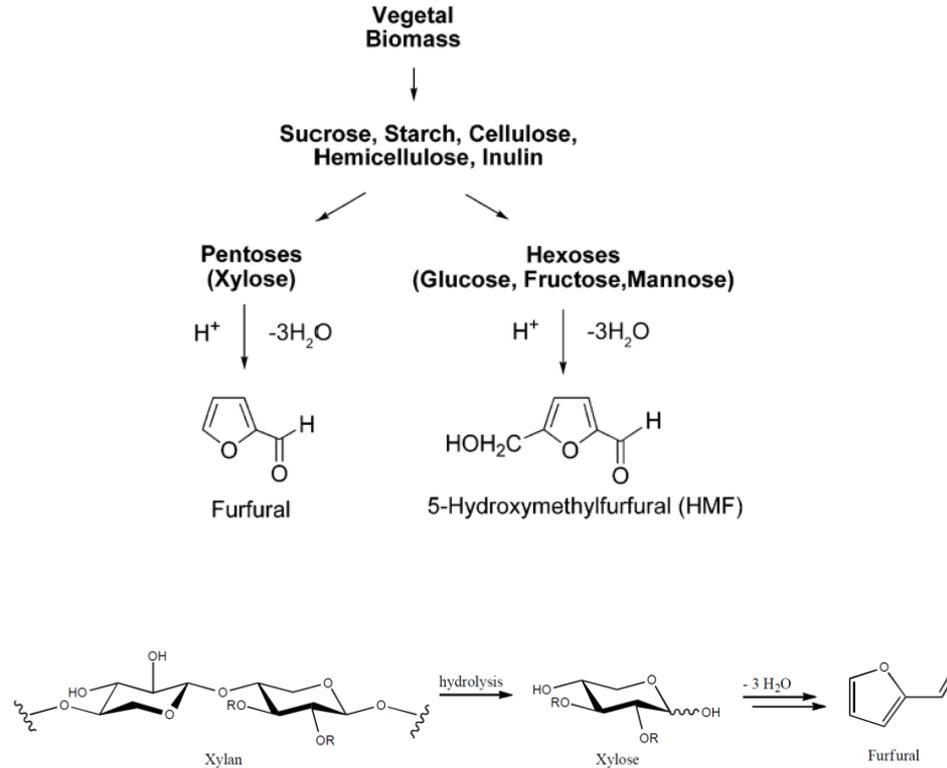
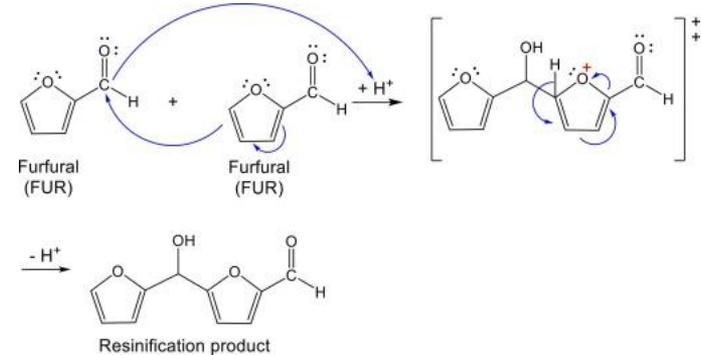
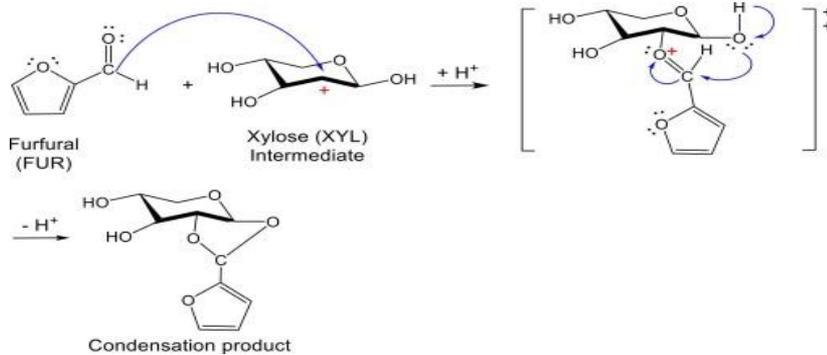


Figura 4. Hidrólisis de xilanos en xilosa y deshidratación de esta en furfural. Tomado de (Bariani et al., 2020).

Furfural

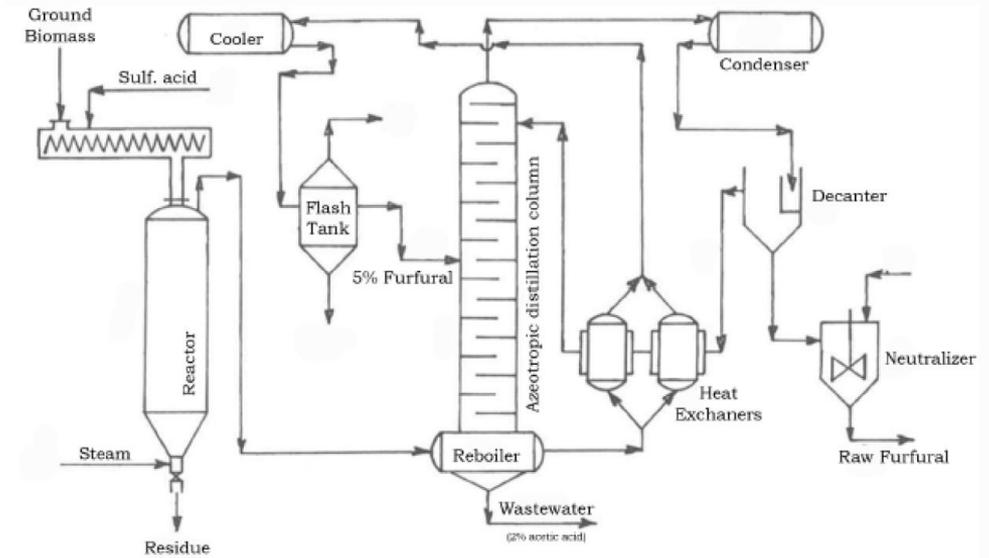
- El furfural también puede sufrir fragmentación para formar varias moléculas más pequeñas, como ácido fórmico, formaldehído, acetaldehído, piruvaldehído, gluceraldehído, glicollaldehído y ácido láctico.
- Al igual que con la formación de furfural, estas reacciones secundarias y de pérdida son catalizadas por los ácidos de Brønsted.
- Los mecanismos precisos para la formación, reacciones secundarias y de pérdida no se han aclarado por completo



Sanches Jorquera et al, 2023

Furfural – proceso productivo actual (mayoritario)

- Rendimientos bajos, aprox. 50% del teórico.
- Alto uso de energía. 20-50 toneladas de vapor por tonelada de furfural.
- Alto consumo de ácido (sulfúrico), aprox. 20% en peso de la producción de furfural.
- No hay integración excepto la incineración de residuos.
- Efluentes extremadamente ácidos



Furfural – Procesos integrados– 2 etapas

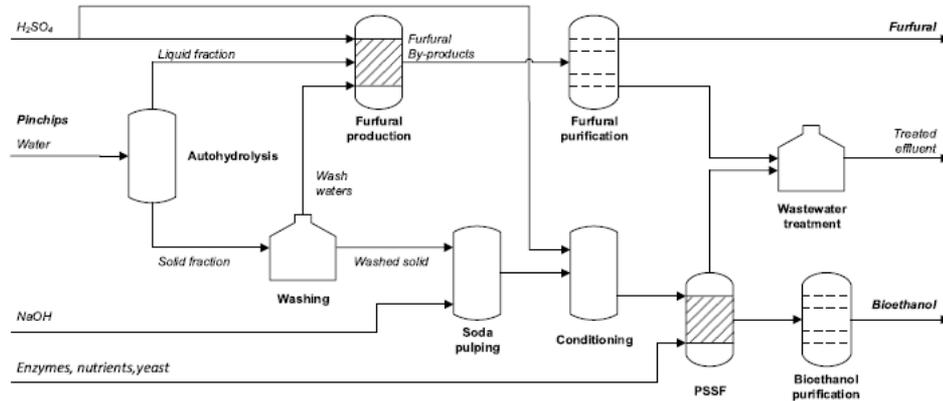


Fig. 1 Schematic diagram of the proposed process for furfural and bioethanol co-production illustrating the four main areas: biomass pretreatment area including autohydrolysis, washing, soda-pulping and conditioning stages to produce autohydrolysis liquor and eucalyptus pulp; furfural production and purification area including acid hydrolysis of autohydrolysis liquor for furfural production followed by furfural purification to obtain furfural with commercial characteristics; pre-hydrolysis and simultaneous saccharification and fermentation (PSSF) area to produce bioethanol from Eucalyptus pulp; bioethanol recovery area to produce marketable bioethanol

Wood Science and Technology (2022) 56:1149–1173
<https://doi.org/10.1007/s00226-022-01396-9>

ORIGINAL



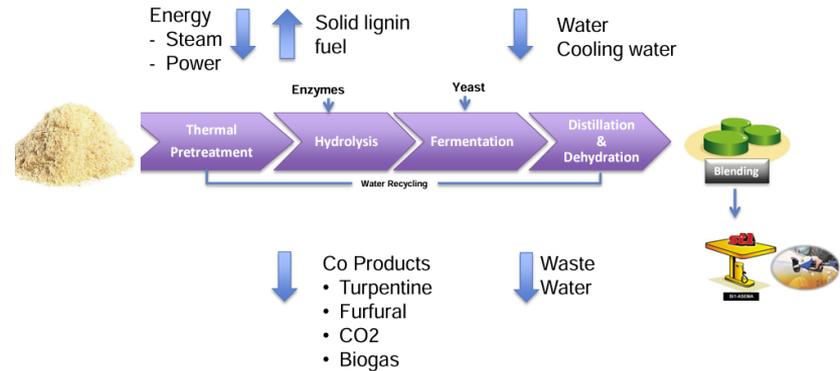
Integrated production of furfural and second-generation bioethanol from Eucalyptus wood residues: experimental results and process simulation

Melissa Bariani¹ · Florencia Cebreiros² · Mairan Guigou² · María Noel Cabrera¹

Furfural – Procesos integrados- 2 etapas



St1 Cellunolix® - Ethanol from sawdust



Tomado de <https://content.st1.fi/sites/default/files/2018-05/10184f10-dfc5-4d34-b296-f718a1f291b4.pdf>

Furfural – Procesos integrados– 2 etapas

Project Cellulonix Kajaani



Project Owner...	St1
Project name	Cellulonix Kajaani
Status	idle
Startup	2017

Geodata

Country	Finland
City	Kajaani

Production

Type	TRL 6-7 Demonstration
Technology	PVC5: Alcohol fuels from cellulosic sugars
Technology additional information	St1 Biofuels
Raw Material	forest residues
Input 1	sawdust (80,000 t/y)
Output 1	ethanol (8,000 t/y)
Output additional information	By-products are terpentine, wood vinasse, lignin, furfural, biogas and CO2

Additional Information

Total Investment	EUR 40,000,000
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<https://demoplants21.best-research.eu/projects/info/3301/8JBaZy>

Furfural – Procesos en investigación (escala lab)

- Catálisis heterogénea

D.S.S. Jorquera et al.

Applied Catalysis A, General 665 (2023) 119360

Table 2
Selected results for XYL dehydration separated by solvents.

Catalyst	Solvent	Co-solvent	T (°C)	Time (h)	FUR yield (%)	Reference
Nb ₂ O ₅	H ₂ O	-	120	3.0	45	[52]
Sulfonated foam	H ₂ O	-	190	0.073 *	42	[103]
Nb ₂ O ₅	H ₂ O	TOL	120	3.0	71	[52]
Sulfonated carbon	H ₂ O	TOL	170	0.5	65	[102]
Ion exchange resin	H ₂ O	TOL	120	2.0	83	[65]
WO ₃ /SiO ₂	H ₂ O	TOL	170	8.0 * *	87	[66]
SO ₃ H-MCM-41	H ₂ O	TOL	155	2.0	88	[68]
SiO ₂ -PSSA	H ₂ O	CPME	180	0.5	60	[74]
Nb ₂ O ₅	H ₂ O	CPME	130	6.0	55	[53]
Terephthalic acid	H ₂ O	CPME	180	3.0	54	[67]
H ₂ SO ₄ solution	H ₂ O	Ethanol	200	0.25	84	[56]
H ₂ SO ₄ solution	H ₂ O	Ethanol	220	0.083	90	[56]
Terephthalic acid	H ₂ O	MIBK	180	3.0	44	[67]
Terephthalic acid	H ₂ O	Butylacetate	180	3.0	43	[67]
Nb ₂ O ₅	H ₂ O	GVL	130	6.0	46	[53]
SBA-15-Ar-SO ₃ H	Isopropanol	-	150	4.5	60	[55]
ZrO ₂ -SO ₄ ²⁻	Isopropanol	-	150	8.0	50	[55]
Heteropolyacids	DMSO	-	140	4.0	72	[59]
Heteropolyacids	DMSO	MIBK	140	4.0	73	[59]
OMC-SO ₃ H	GVL	H ₂ O	200	0.75	80	[108]
Amberlyst-70	Methyl formate	-	150	0.67	72	[48]

* : continuous operation, * *: crop waste as starting material

Sanches Jorquera et al, 2023

Furfural – Procesos en investigación (escala lab)

- Procesos con solventes orgánicos monofásicos

Table 4

Organic system furfural production.

Biomass	Solvent	Catalyst	Temperature (°C)	Duration (min)	Furfural Yield	Ref.
Corn cob	GVL	FeCl ₃	185	100	79.6%	[36]
Wheat Straw	Methanol	H ₂ SO ₄	175	120	40.6%	[52]
Oil Palm Fronds	Ethanol	Formic Acid	280	20	35.8%	[53]
Corn Stover	GVL	H ₂ SO ₄	170	180	63%	[56]
Corn cob	GVL	Sulfonated Polytriphenylamine	175	65	66%	[58]
Corn cob	γ -Butyrolactone	Sulfonated Polytriphenylamine	175	45	59.9%	[58]
Corn cob	γ -Undecalactone	Sulfonated Polytriphenylamine	175	45	53%	[58]
Corn Fiber	GVL	H-Beta Zeolite	160	120	62%	[59]
Poplar Wood Chips	GVL	H-mordenite Zeolite	175	90	75%	[60]
Corn cob	GVL	Al-Beta Zeolite	185	85	51.1%	[61]
Corn cob	GVL	Fe-Beta Zeolite	185	85	44.5%	[61]
Sugar Cane Bagasse	GVL	Al-Beta Zeolite	185	85	40.9%	[61]
Corn Stover	GVL	SC-CaC ₁ -700	200	100	93%	[62]
Corn Stover	γ -Butyrolactone	SC-CaC ₁ -700	200	100	89%	[62]
Xylan	GVL	PTSA-POM	170	10	69.2%	[63]
Corn Stalk	GVL	PTSA-POM	190	100	83.5%	[63]

Lee, C. B. T. L., & Wu, T. Y. (2021)

Furfural – Procesos en investigación (escala lab)

- Procesos con solventes orgánicos- bifásicos

Table 5

Biphasic system furfural production.

Biomass	Solvent	Catalyst	Temperature (°C)	Duration (min)	Furfural Yield	Ref.
Corn Stover	H ₂ O-MIBK	H ₂ SO ₄	170	20	80.1%	[64]
Corn Stover	H ₂ O-Toluene	H ₂ SO ₄	170	20	76.3%	[64]
Corn Stover	H ₂ O-MIBK	Purolite CT275	170	20	71.5%	[64]
Maple Wood	H ₂ O-MIBK	H ₂ SO ₄	170	50	85.3%	[65]
Maple Wood	H ₂ O-MIBK	HCl	170	30	56.2%	[65]
Sugarcane Bagasse	H ₂ O-Acetone	30.5 wt% H ₃ PO ₄	150	5	45.8%	[66]
Corn cob	H ₂ O-Toluene	H ₂ SO ₄ , ZnSO ₄	150	360	60%	[67]
Pine	H ₂ O-Toluene	H ₂ SO ₄ , ZnSO ₄	160	360	64.4%	[67]
Birch	H ₂ O-Toluene	H ₂ SO ₄ , ZnSO ₄	160	360	59.4%	[67]
Corn cob	H ₂ O-Toluene	CrCl ₃ ·6H ₂ O-NaCl	140	60	23.88%	[68]
Corn Stover	H ₂ O-THF	AlCl ₃ ·6H ₂ O-NaCl	160	60	55%	[69]
Pinewood	H ₂ O-THF	AlCl ₃ ·6H ₂ O-NaCl	160	60	38%	[69]
Switchgrass	H ₂ O-THF	AlCl ₃ ·6H ₂ O-NaCl	160	60	56%	[69]
Poplar	H ₂ O-THF	AlCl ₃ ·6H ₂ O-NaCl	160	60	64%	[69]
Pubescens	H ₂ O-THF	NaCl	200	120	76.9%	[70]
Cardoon	H ₂ O-CPME	1 wt% H ₂ SO ₄	170	125	>80%	[71]
Cardoon	H ₂ O-CPME	1 wt% H ₂ SO ₄ , NaCl	170	50	>80%	[71]
Corn Stover	H ₂ O-THF	γ-Al ₂ O ₃ /SO ₄ ²⁻	160	120	35.88 wt%	[72]
Corn cob	H ₂ O-Toluene	SO ₄ ²⁻ /SnO ₂ MMT	190	20	66.13%	[73]
Switchgrass	H ₂ O-GVL	SAPO-34	190	480	<30%	[74]
Bagasse	H ₂ O-Toluene	SAPA-44	170	480	92%	[75]

Lee, C. B. T. L., & Wu, T. Y. (2021)

Furfural – Procesos en investigación (escala lab)

- Procesos que utilizan líquidos iónicos

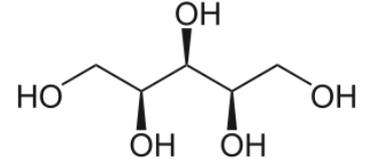
Table 6

Ionic liquid system furfural production.

Biomass	Solvent	Catalyst	Temperature (°C)	Duration (min)	Furfural Yield	Ref.
Corn cob	[BMIM]Cl	HCl	160	3	14.9%	[76]
Corn cob	[BMIM]Cl	H ₂ SO ₄	160	3	14.4%	[76]
Corn cob	[BMIM]Cl	AlCl ₃	160	3	19.1%	[76]
Pine Wood	[BMIM]Cl	AlCl ₃	160	3	33.6%	[76]
Grass	[BMIM]Cl	AlCl ₃	160	3	31.4%	[76]
Corn Stalk	[BMIM]Cl	CrCl ₃ ·6H ₂ O	200	3	23%	[77]
Rice Straw	[BMIM]Cl	CrCl ₃ ·6H ₂ O	200	3	25%	[77]
Pine Wood	[BMIM]Cl	CrCl ₃ ·6H ₂ O	200	3	31%	[77]
Pine Wood	[BMIM]Br	CrCl ₃ ·6H ₂ O	200	3	28%	[77]
Corn cob	[BMIM]Cl	H ₃ PW ₁₂ O ₄₀	160	10	15.3%	[78]
Pine Wood	[BMIM]Cl	H ₃ PW ₁₂ O ₄₀	160	10	22.3%	[78]
Grass	[BMIM]Cl	H ₃ PW ₁₂ O ₄₀	160	10	26.8%	[78]
Corn Stover	[BMIM]PF ₆	PEG–OSO ₃ H–MnCl ₂	120	18	36%	[79]
Poplar	[BMIM]PF ₆	PEG–OSO ₃ H–MnCl ₂	120	18	24%	[79]
Straw	[BMIM]PF ₆	PEG–OSO ₃ H–MnCl ₂	120	18	25%	[79]
Beechwood	H ₂ O	[C ₃ SO ₃ HMIM][HSO ₄]	170	240	21%	[80]
Beechwood	H ₂ O-Toluene	[C ₃ SO ₃ HMIM][HSO ₄]	170	240	85%	[80]
Eucalyptus Wood	[BMIM]HSO ₄	[BMIM]HSO ₄	160	240	59.1 wt%	[81]
Wheat Straw	[BMIM]HSO ₄	[BMIM]HSO ₄	161	104.5	32.2 wt%	[82]
Miscanthus Giganteus	[BMIM]HSO ₄	[BMIM]HSO ₄	120	1320	33 wt%	[83]
Miscanthus Giganteus	[BMIM]MeSO ₃	[BMIM]MeSO ₃	120	1320	13 wt%	[83]
Eucalyptus Saligna	H ₂ O-GVL	[BMIM]Cl–AlCl ₃	140	240	34.82%	[84]
Tsuga chinensis	H ₂ O-GVL	[BMIM]Cl–AlCl ₃	140	240	23.68%	[84]
Corn Stalk	H ₂ O-GVL	[BMIM]Cl–AlCl ₃	140	240	47.96%	[84]

Lee, C. B. T. L., & Wu, T. Y. (2021)

Xilitol

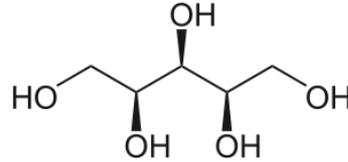


- En 1891, un químico alemán y francés descubrieron simultáneamente el xilitol
- Varios años más tarde, los cristales de xilitol se purificaron con éxito y se utilizó ampliamente como alternativa al azúcar durante la Segunda Guerra Mundial.
- Actualmente se utiliza como edulcorante bajo en calorías y agente preventivo contra las caries dentales (popular en chicles, pastas dentales y productos para diabéticos)

Attributes	Details
Market Size Value in 2023	US\$ 713.4 Million
Market Forecast Value in 2033	US\$ 1,086.8 Million
Global Growth Rate (2023 to 2033)	4.3%
Forecast Period	2023 to 2033
Global Market Share of USA, Germany, Japan and Australia	70.1%

<https://www.futuremarketinsights.com/reports/xylitol-market>

Xilitol



(2R, 3R, 4S)-Pentano-1,2,3,4,5-pentol o alcohol de madera (pentitol)

- La producción de xilitol es mayoritariamente a partir de mazorcas de maíz (China), con una producción de 110.000 toneladas por año y maderas de latifoliadas como el abedul en los Estados Unidos y Finlandia.
- Danisco el mayor productor, utilizando hidrolizado proveniente de la industria de celulosa

(Rao Ravella et al., 2012; Hernández-Pérez et al., 2019).

Xilitol

Hou-Rui 2012 en
 S. S. da Silva and A. K. Chandel (eds.), D-
 Xylitol,
 DOI: 10.1007/978-3-642-31887-0_12, Springer-
 Verlag Berlin Heidelberg 2012

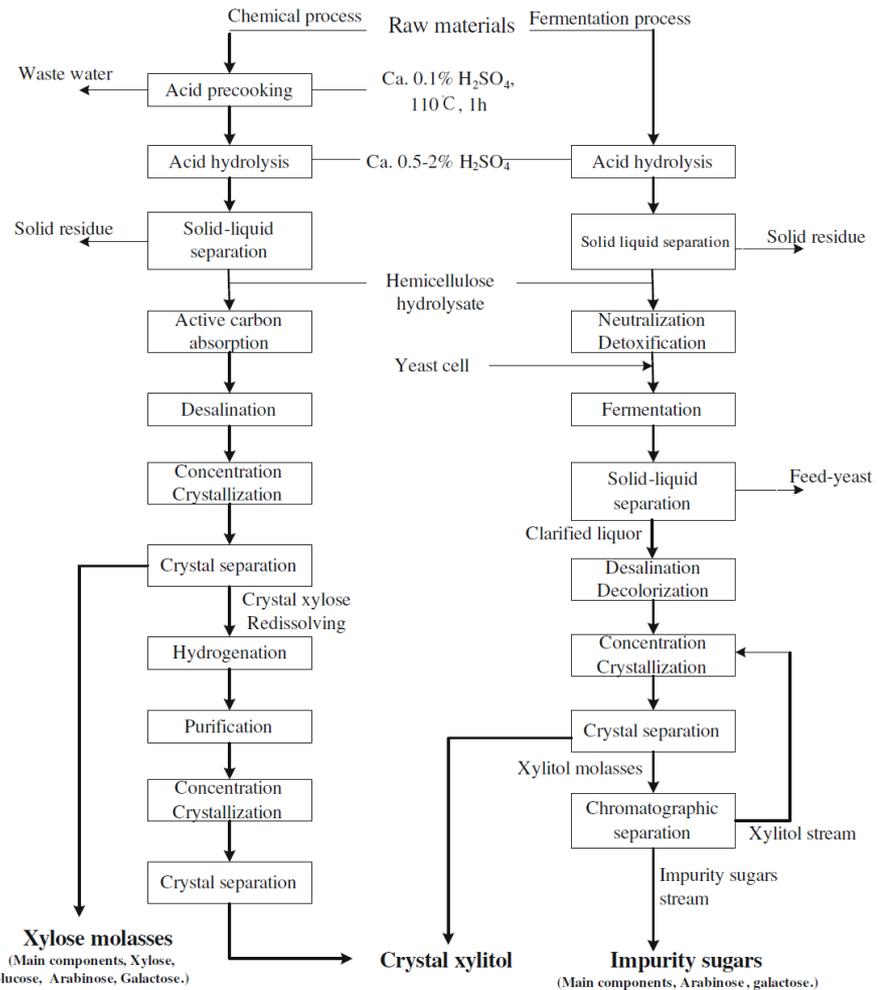


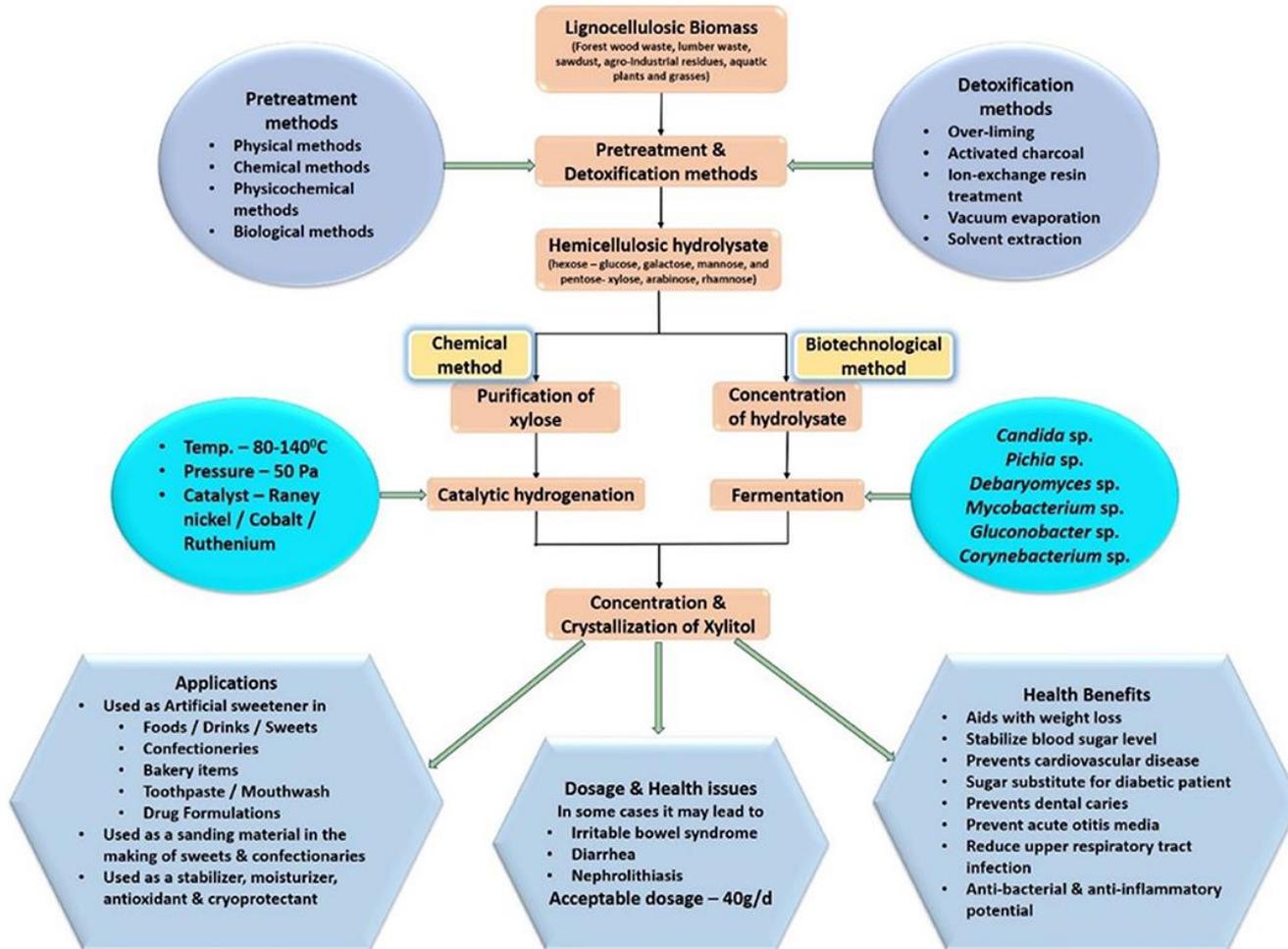
Fig. 12.1 Comparison between chemical and fermentation route for xylitol production

- Actualmente se produce industrialmente por vía química (hidrogenación catalítica de D-xilosa con catalizador de níquel Raney a (80-130 °C) y alta presión (40 bares o más).
- El costo de la hidrogenación de xilosa a xilitol es de unos 350USD/ton y el costo de producción de xilosa (a la pureza requerida) es de aprox. 2.300 - 2.500 USD/t.



Hay un fuerte impulso en la investigación para producir xilitol de una manera más económica y ambientalmente amigable.

Hay dos enfoques biotecnológicos que parecen prometedores: el proceso microbiano (actualmente mejor performance) y el proceso enzimático



Umai et al 2022

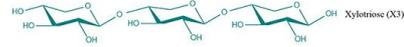
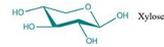
Producción de xilitol por vía biotecnológica

Lignocelulosic biomass	Pretreatment method	Microorganism	Concentration of xylitol produced	Xyliitol productivity	Xyliitol yield	References
Corn cob	Hydrothermal treatment— T_{\max} of 250°C (Autohydrolysis)	Engineered <i>Saccharomyces cerevisiae</i> PE-2	29.6 gL ⁻¹	0.54 gL ⁻¹ h ⁻¹	0.93 gg ⁻¹	Baptista et al., 2018
Corn cob	Dilute acid treatment—with 0.5% HNO ₃ in autoclave for 30 minutes	<i>Candida tropicalis</i> MTCC6192	33.4 gL ⁻¹	1.2 gL ⁻¹ h ⁻¹	0.66 gg ⁻¹	Kumar et al., 2018
Poplar wood	Acid treatment—with 2–2.5% H ₂ SO ₄ at 120°C	<i>Candida guilliermondii</i>	28.78 gL ⁻¹	0.81 gL ⁻¹ h ⁻¹	0.59 gg ⁻¹	Dalli et al., 2017b
Wheat straw	Dilute H ₂ SO ₄ treatment followed by Conc. H ₂ SO ₄ at 70°C under vacuum	<i>Candida guilliermondii</i> FT120037	24.2 gL ⁻¹	0.34 gL ⁻¹ h ⁻¹	0.48 gg ⁻¹	Canilha et al., 2008b
Corn cobs	Dilute acid treatment—with 1% H ₂ SO ₄ at 121°C for 60 minutes	<i>Candida magnoliae</i>	18.7 g xylitol/25g xylose within 36 h of fermentation	0.525 gL ⁻¹ h ⁻¹	0.75 gg ⁻¹	Tada et al., 2004
Corn cobs	Dilute acid treatment—with 1% H ₂ SO ₄ at 125°C for 1 hr	<i>Candida tropicalis</i> CCTCC M2012462	38.8 gL ⁻¹ after 84 h of fermentation	0.46 gL ⁻¹ h ⁻¹	0.7 gg ⁻¹	Ping et al., 2013
Corn stover	Vapor-phase diethyl oxalate	<i>Pichia stipitis</i> YS-30	–	0.18 gg ⁻¹ L ⁻¹	0.61 gg ⁻¹	Rodrigues et al., 2011
Corn straw	Steam explosion	<i>Candida tropicalis</i>	35.6 gL ⁻¹ after 38 h of fermentation	0.94 gg ⁻¹ L ⁻¹	0.71 gg ⁻¹	Wang et al., 2015

Umai et al 2022

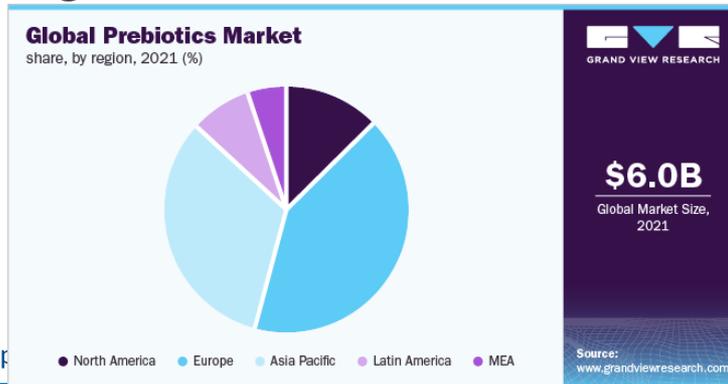
Oligosacáridos:

- Xilooligosacáridos (XOS), arabinoxilooligosacárido (AXOS), galactooligosacárido (GOS) y mananooligosacárido (MOS): son estructuras poliméricas de bajo grado de polimerización (de 2 a 10-12)
- Se utilizan como prebiótico dado que puede estimular selectivamente el crecimiento y la actividad de una o varias bacterias para producir efectos beneficiosos en el huésped, mejorando así su salud.



Mercado de prebióticos

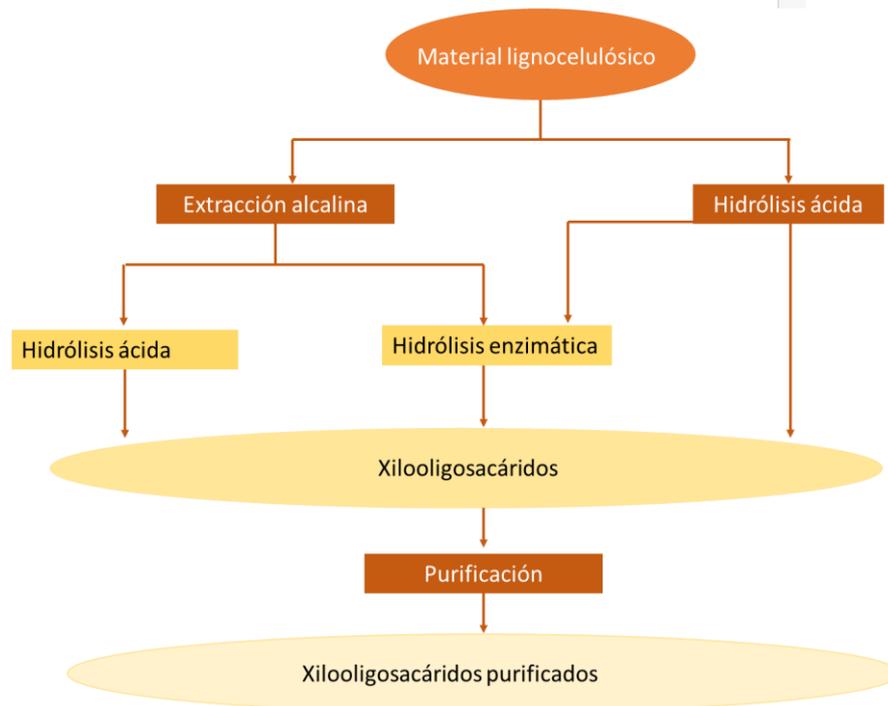
- El tamaño del mercado mundial de prebióticos se valoró en 6.050 millones de dólares en 2021 y se espera que crezca a una tasa de crecimiento anual compuesta (CAGR) del 14,9% entre 2022 y 2030.
- El creciente uso de prebióticos en la industria láctea debido a sus beneficios para la salud
- La creciente aparición de enfermedades del tracto gastrointestinal, como el estreñimiento, el síndrome del intestino irritable (SII), reflujo gastroesofágico (ERG) etc. Ha incentivado el consumo de prebióticos
- Además, es probable que los crecientes avances tecnológicos en el desarrollo de inulina y oligosacáridos reemplacen el azúcar.
- Prebióticos comunes: Inulina, Fructooligosacáridos



Diferentes métodos de producción de OS a partir de biomasa lignocelulósica

Table 1

Materials and methods	Advantages	Disadvantages
Acid hydrolysis	<ol style="list-style-type: none"> 1. Reduce the production of inhibitors 2. Simple process 	<ol style="list-style-type: none"> 1. Difficult to control the speed 2. High-cost input 3. High equipment requirements
Enzyme hydrolysis	<ol style="list-style-type: none"> 1. Low production cost 2. Fewer byproducts 	<ol style="list-style-type: none"> 1. Substrate specificity 2. High price
Hydrothermal pretreatment	<ol style="list-style-type: none"> 1. Simple process 2. Reduce equipment corrosion 	<ol style="list-style-type: none"> 1. Difficult to separate and purify 2. Low conversion of raw materials
Alkali treatment	<ol style="list-style-type: none"> 1. Significantly improve yield 2. Good separation effect 3. Adapt to the lower temperature 	<ol style="list-style-type: none"> 1. Seriously polluted 2. High toxicity



Producción de XOS por vía química

Table 1
Production of XOS from various substrates by different methods.

Substrates	Methods	Yield (%)	Reference
Physicochemical			
Corn cob	Acid hydrolysis, 10 mL of 0.25 M H ₂ SO ₄ , 90 °C, 15–30 min	86.60	Samanta et al. (2012)
Sugarcane bagasse hemicelluloses	Microwave-assisted acid hydrolysis, dilute H ₂ SO ₄ (0.1–0.3M), at 90 °C, 20–40 min	29.02	Bian et al. (2014)
Beechwood xylan	Acid hydrolysis, 0.7 M H ₂ SO ₄ , 90 °C, 45 min	22.10	Chemin et al. (2015)
Hazelnut Shells	Autohydrolysis, Isothermal 190 °C, 5 min (heating), 5 min (holding) up to 45 min at 300 rpm Liquid to Solid Ratio (LSR) = 10, Logarithmic values of severity factor (Log R ₀) = 3.92	10.00	Surek and Buyukkileci (2017)
Chestnut Shells	Autohydrolysis, non-isothermal 180 °C LSR = 8, Severity factor (S ₀) = 3.08	5.70	Gullon et al. (2018)
Corn cobs	Steam explosion using acidic electrolyzed water, <i>Paenibacillus barengoltzii</i> (PbXyn10A) xylanase, 12 h	75.00	Liu et al. (2018)
Almond Shells	Autohydrolysis, Isothermal 200 °C, 20 min (heating), 5 min (holding), LSR = 10, S ₀ = 3.94	High DP (>4) XOS 7.70 Low DP XOS (<4) 3.30	Singh, Talekar, Muir, and Arora (2019)
(Populus) poplar	Acetic acid treatment, pre-treatment at 170 °C, 5% Acetic acid, and 30 min	55.80	Wen, Zhang, Wang, Lian, and Zhang (2019)
-			

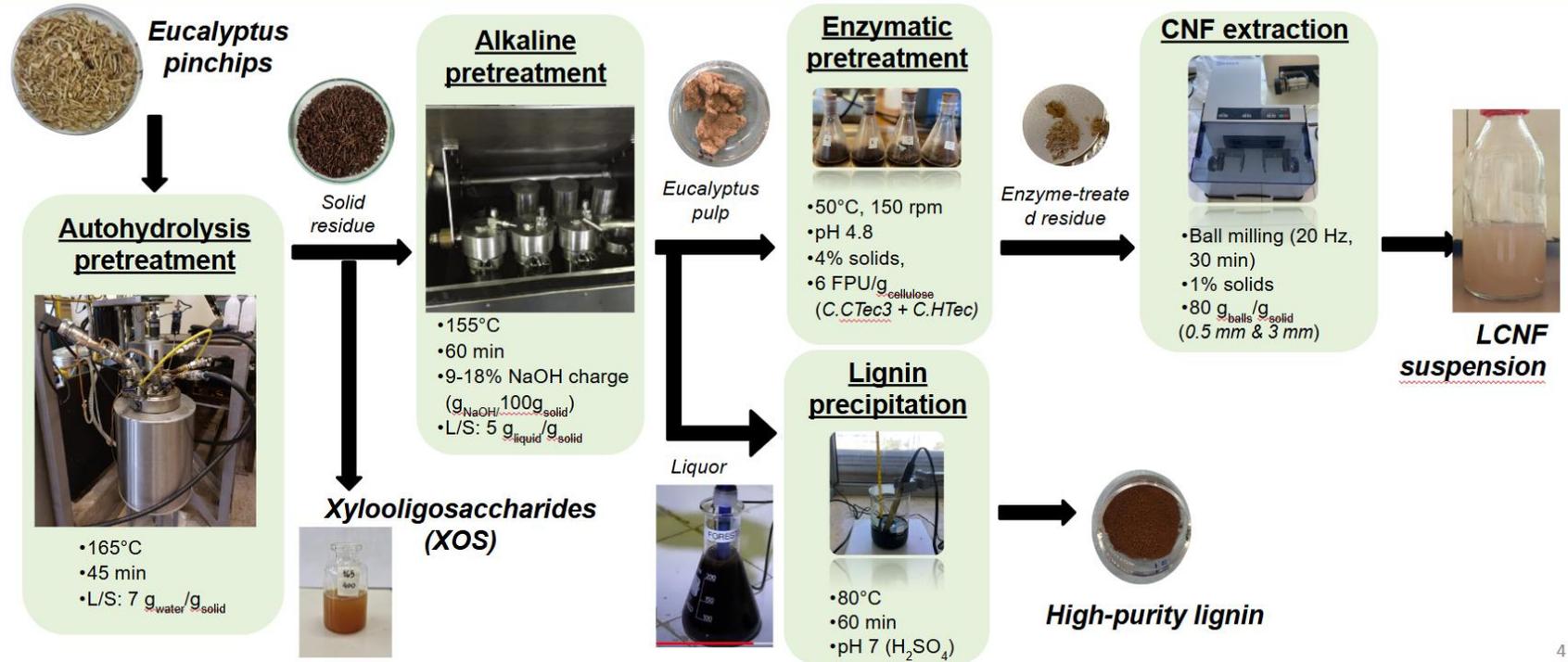
Palaniappan et al. 2021

Producción de XOS por vía enzimática

Enzymatic hydrolysis

Wheat bran	0.28 U Endoxylanase, Finger millet (<i>ragi</i> malt), 50 °C, 2 h	14.40	Manisseri and Gudipati (2010)
Bengal gram husk and wheat bran	0.28 U Driselase (endoxylanase), <i>Basidiomyces</i> sp, 50 °C, 2 h	5.80 & 14.40	Madhukumar and Muralikrishna (2012)
Corn cob	pH - 4.0, 5.0 and 6.0, Temperature - 30, 40 and 50 °C, Endoxylanase, <i>Trichoderma viridae</i> - 2.65, 6.625 and 13.25 U, Incubation time - 8, 16 and 24 h	50.00	Samanta et al. (2012)
Sugar Cane bagasse	2.65 U Endoxylanase, <i>Trichoderma viridae</i> , pH 4, 40 °C, 8 h	0.17	Jayapal et al. (2013)
Wheat straw	0.48 U Endoxylanase A (mutated at K80R), <i>Bacillus halodurans</i> S7, 50, 55, 60 and 65 °C, 7 h	39.77	Faryar et al. (2015)
Sugarcane bagasse	Aqueous ammonia PTT, β -xylosidase-free xylanase of <i>B. subtilis</i> (KCX006), 40 U of endoxylanase and 4.3U of α -L-arabinofuranosidase, 50 °C, 30h	67.00	Reddy and Krishnan (2016)
Pretreated corn cob	Ultra-high-pressure PTT, 100 U Endoxylanase, <i>Streptomyces thermovulgaris</i> (TISTR1984), 55 °C, 24h	10.66	Seesuriyachan, Kawee-ai, and Chaiyaso (2017)
Wheat bran	Washing with sodium acetate buffer followed by alkali extraction. Recombinant <i>Bacillus amyloliquefaciens</i> xylanase A, 0.4 U, 40 °C, 24 h	16.14	Liu, Huo, Xu, and Weng (2017)
Finger millet Seed coat (CO9 v)	Sodium acetate buffer (0.1 M, pH 4.8) 50 °C, 125 U commercial endoxylanase from <i>Trichoderma longibrachiatum</i> , 7 h	72.00	Palaniappan, Balasubramaniam, and Antony (2017)
Rice bran	Sodium acetate buffer (0.1 M, pH 4.8) 50 °C, 125 U commercial endoxylanase from <i>Trichoderma longibrachiatum</i> , 7 h	68.00	Ayyappan and Antony (2017)
Coconut husk	Crude xylanase concentration -1–5%, pH - 4–6, temperature - 45–65 °C, incubation time - 6–18 h	82.50	Jnawali, Kumar, Tanwar, Hirdayani, and Gupta (2018)
Hemicellulose dissolving pulp	Incubation time - 1, 2, 6, 8, 10, 12, 20, and 24 h, endoxylanase dosage - 50, 80, 120, and 150 IU g ⁻¹ substrate, pH 5, 50 °C in a 50 mM sodium acetate buffer solution in the incubator (150 rpm)	45.18	Wang et al. (2018)
Brewers' spent grain	Commercial endo xylanase from <i>Trichoderma longibrachiatum</i> , 20 g/L, 12 h	44.43	Amorim et al. (2018)
Beechwood xylan	Reaction mixture consisted of 3.0% (w/v) xylan in 0.05 M sodium citrate buffer at pH 5.3, endoxylanase concentration 200 U/g of substrate, at 50 °C and 180 rpm for 36 h	0.92	Guido, Silveira, and Kalil (2019)

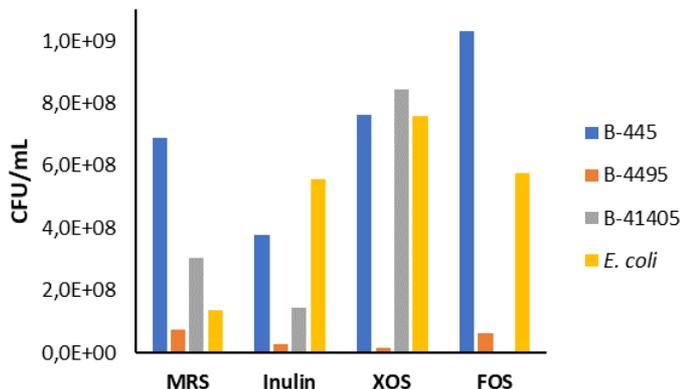
Palaniappan et al. 2021





Prebiotic activity of xylooligosaccharides (XOS) from eucalyptus sawdust hydrolyzate

Alberto Liguori^a, Eugenia Vila^a, Mairan Guigou^a, Santiago Moure^b, Laura Camesasca^a, Florencia Cebreiros^a, Florencia Risso^a, Claudia Lareo^a, Juan Martín Rodao^b, Leonardo Clavijo^b, María Noel Cabrera^b



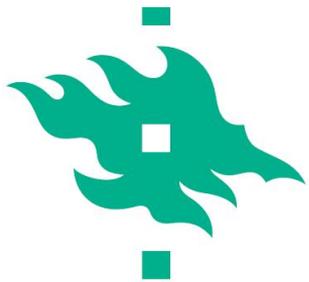
Lactobacillus rhamnosus (B-445),
Lactobacillus acidophilus (B-4495),
Bifidobacterium animalis sub lactis (B-41405)
E. coli (ATCC 25922)

Xilanos de alto peso molecular

Se pueden utilizar como:

- Biofilms
- Biogeles
- Surfactantes

- La obtención de xilanos de alto peso molecular se debe hacer por tratamientos alcalinos o que no degraden las cadenas de hemicelulosas



Bio-based packaging films

- Hemicelluloses are a biobased and biodegradable alternative to plastic packaging.
- Functionality depends of the hemicellulose structure.



- The research focuses on
 - mechanical
 - thermal
 - optical and morphological
 - and barrier properties, as well as
 - the effect of moisture on the film properties.



Dissolution



Air removal



Casting

Tenkanen M. I&S Workshop, 22-25 November 2016, Montevideo Uruguay

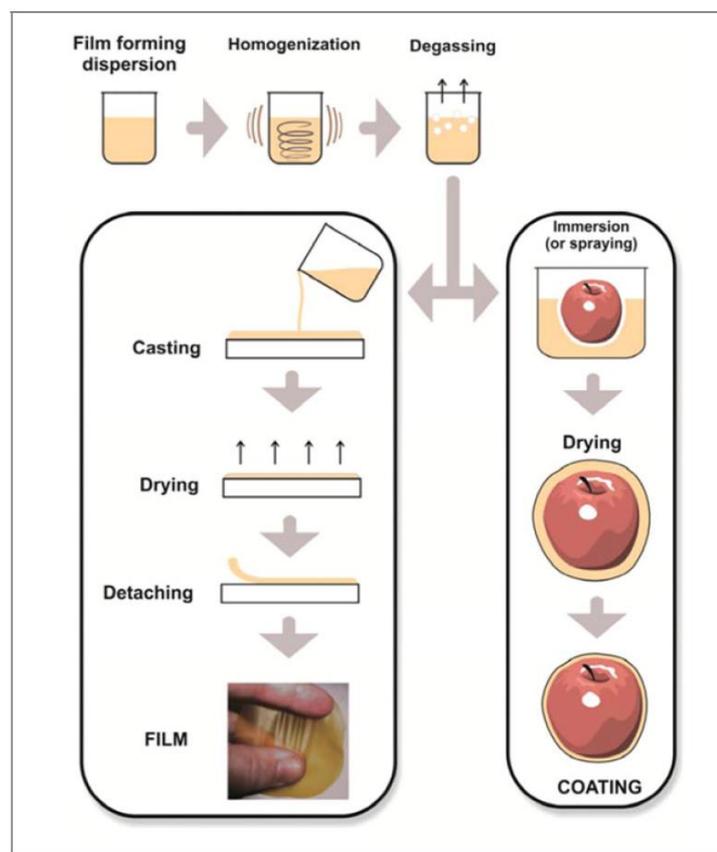


Figure 1–Schematic representation of production of films and coatings.

Otoni et al 2017

Biofilms

- Es una barrera eficaz contra el oxígeno, la grasa y el aroma.
- Prolongar la vida útil de los alimentos sensibles.



<http://www.xylophane.com/>

Properties of sorbitol-plasticized (40 wt.-%) GGM films

Tensile strength (RH 50%)	12 MPa
Elongation at break (RH 50 %)	6 %
Glass transition temperature (RH 50%)	-4 °C
Light transmittance (550 nm)	88 %
Water vapor permeability (RH 0/54%)	1–2 [g·mm/(m ² ·d·kPa)]
Oxygen permeability (RH 50-75%)	7 [cm ³ ·µm/(m ² ·d·kPa)]

Mikkonen et al. Int. J. Polym. Sci. 2012
Mikkonen et al., Carbohydr. Polym., 2010

Biofilms

Para mejorar las propiedades físico-mecánicas se siguen diferentes estrategias:

- Crosslinking
- Agregado de plastificantes
- Uso de diferentes niveles de deacetilización y de ramificación por la biomasa de partida y por los tratamientos realizados

Biopolymer	Plasticizer	References
Cassava starch	Glycerol	Amaral and others (2010); Souza and others (2011); Farias and others (2012); Dantas and others (2015); Reis and others (2015)
	Sucrose	Hayashi and others (2006); Souza and others (2012)
	Inverted sugar	Hayashi and others (2006); Souza and others (2011, 2012)
Chitosan	Glycerol	Wang and others (2011a)
	Glycerol	Wang and others (2011b)
Carboxymethylcellulose	Glycerol	Wang and others (2011a); Wang and others (2011b); Xu and others (2017)
	Glycerol	Wang and others (2011a); Wang and others (2011b); Shin and others (2014); Tulamandi and others (2016); Liu and others (2017)
Corn starch	Glycerol	Wang and others (2011a); Wang and others (2011b); Xu and others (2017)
Gelatin	Glycerol	Wang and others (2011a); Wang and others (2011b); Shin and others (2014); Tulamandi and others (2016); Liu and others (2017)
High-methoxyl pectin	Glycerol	McHugh and Senesi (2000); Park and Zhao (2006); Rojas-Graü and others (2006); Ravishankar and others (2009); Ravishankar and others (2012); Espitia and others (2014a, 2014b); Peretto and others (2014); Azeredo and others (2016)
	Sorbitol	Park and Zhao (2006); Du and others (2008a, 2009b); Otoni and others (2014)
HPMC	–	Lorevice and others (2012, 2014); Otoni and others (2015)
Low-methoxyl pectin	Glycerol	Deng and Zhao (2011); Du and others (2008b, 2009a, 2011); Eca and others (2015); Mattoso and others (2015); Park and Zhao (2006)
	Sorbitol	Park and Zhao (2006); Otoni and others (2014)
Methylcellulose	Glycerol	Shin and others (2014)
	–	Mariniello and others (2007)
Phaseolin	Glycerol	Shin and others (2014)
Poly lactide	Glycerol	Deng and Zhao (2011)
Ticafilm® a	Glycerol	Deng and Zhao (2011); Rojas-Graü and others (2007)
Sodium alginate	Glycerol	Deng and Zhao (2011); Rojas-Graü and others (2007)

Biofilms- uso de plastificantes

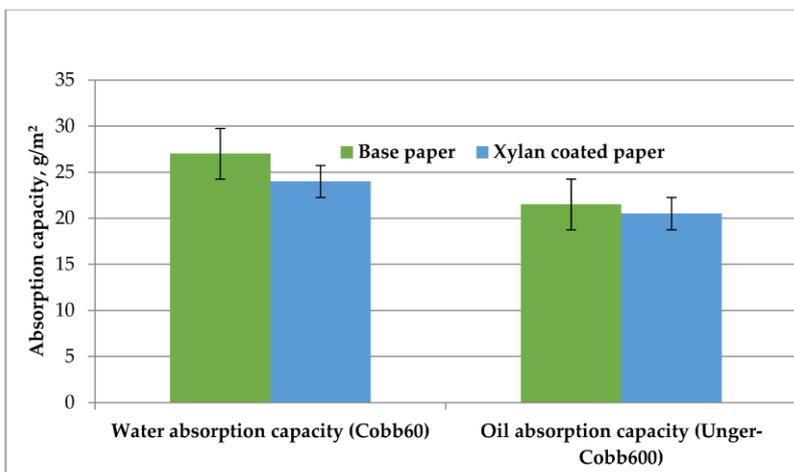
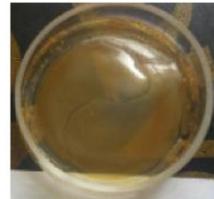


Figure 12. The images of xylan hemicellulose films.



XP1/25



XG



XHC



50XCh



70XCh



80XCh

Nechita et al, 2021

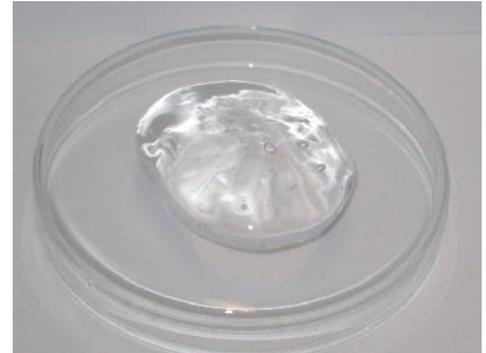
Hidrogeles

- Los denominados hidrogeles refieren a redes tridimensionales, hidrófilas y poliméricas capaces de absorber grandes cantidades de agua o fluidos biológicos.
- Reciben cada vez mayor atención debido a muchas propiedades favorables, tales como la hidrofilia, la consistencia que imita a los tejidos blandos, alta permeabilidad a los metabolitos y al oxígeno, y a su capacidad de recuperación



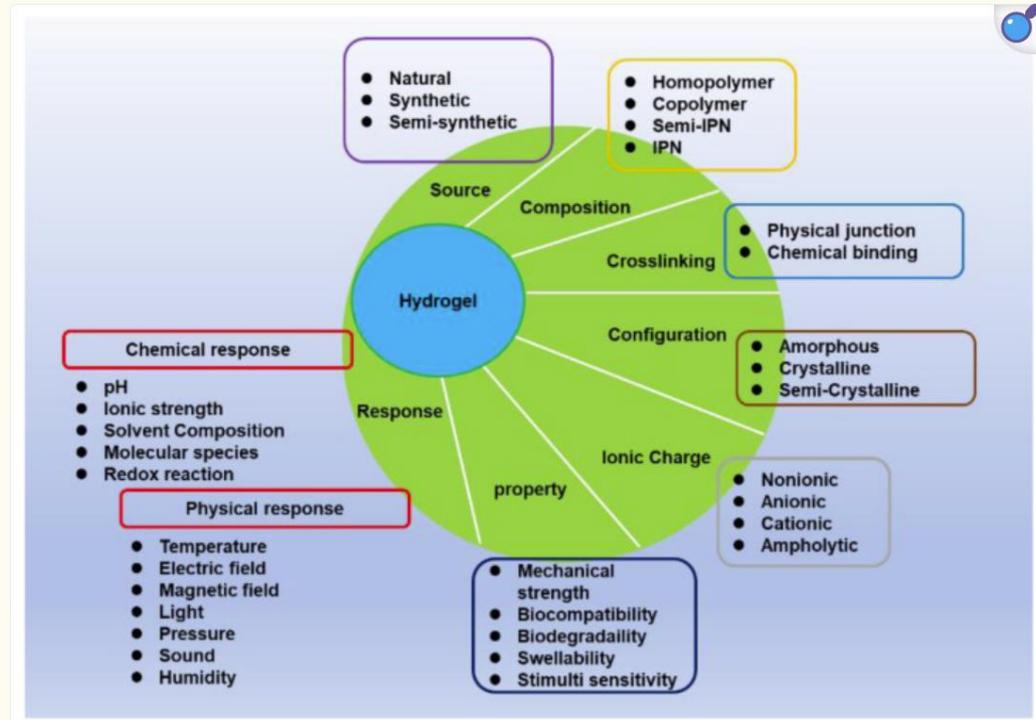
Hidrogeles

- Otra característica interesante es que las diferentes funcionalidades pueden ser incorporadas en el reticulado, física o químicamente, para producir hidrogeles “inteligentes” Estos hidrogeles exhiben múltiples respuestas a los cambios en las condiciones externas, tales como temperatura, pH, salinidad, campo eléctrico, y el entorno químico, y por lo tanto son materiales altamente atractivos en los campos de medicina, biotecnología y medioambiente.



Hidrogeles

Figure 2.

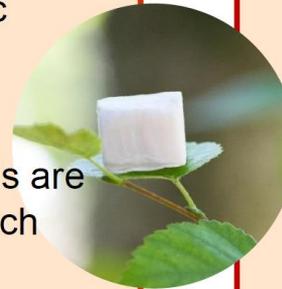


Aerogels

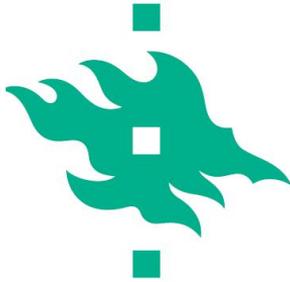


Wood-based aerogels

- Aerogels are porous solid foams with high specific surface area.
- Polysaccharide aerogels are a fascinating new research area.



- The aerogels can be used as
 - mechanical support
 - thermal insulator
 - active packaging
 - delivery media
 - biomedical applications.



Spruce galactoglucomannan (GGM) aerogels

Density: 0.02 g/cm³

Porosity: 98–99 %

Recovery after compression up to 88 %

Compressive modulus up to 200 kPa



Tenkanen M. I&S Workshop, 22-25 November 2016, Montevideo Uruguay