



Diseño de procesos de biorrefinería sostenible

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Grupo de investigación “Procesos de Biorrefinería”



EL DESARROLLO INSOSTENIBLE: LA SITUACION ACTUAL

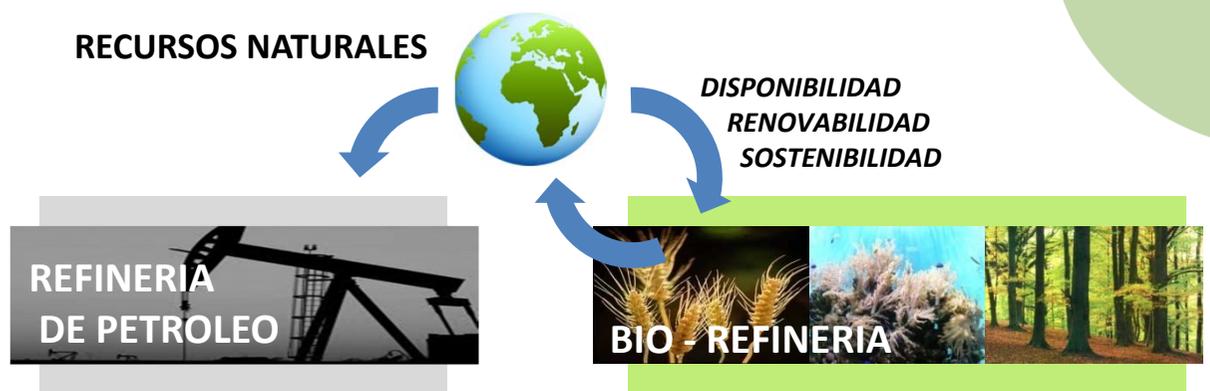
MASIVA DEPENDENCIA DE LAS FUENTES FÓSILES

IMPORTANTES REPERCUSIONES ECONÓMICA, SOCIALES Y AMBIENTALES

¿PUEDE LOGRARSE UN DESARROLLO SOSTENIBLE?

- MEJORANDO LAS TECNOLOGÍAS ACTUALES
- MAXIMIZANDO LOS RENDIMIENTOS DE CONVERSIÓN
- RECONSIDERANDO EL CONSUMO DE MATERIAS PRIMAS
- MINIMIZANDO LA GENERACIÓN DE RESIDUOS
- USO DE RECURSOS ALTERNATIVOS (Sol, viento, mareas, biomasa, ...)

USO SOSTENIBLE DE LOS RECURSOS NATURALES



SUSTITUIR LOS PRODUCTOS PETROQUIMICOS POR BIOPRODUCTOS



PRODUCTOS QUÍMICOS: Tamaño actual del mercado

Productos químicos en base a fuentes fósiles:
330 millones de toneladas

Principales moléculas:

metanol, etileno, propileno, butadieno, benceno,
tolueno y xileno

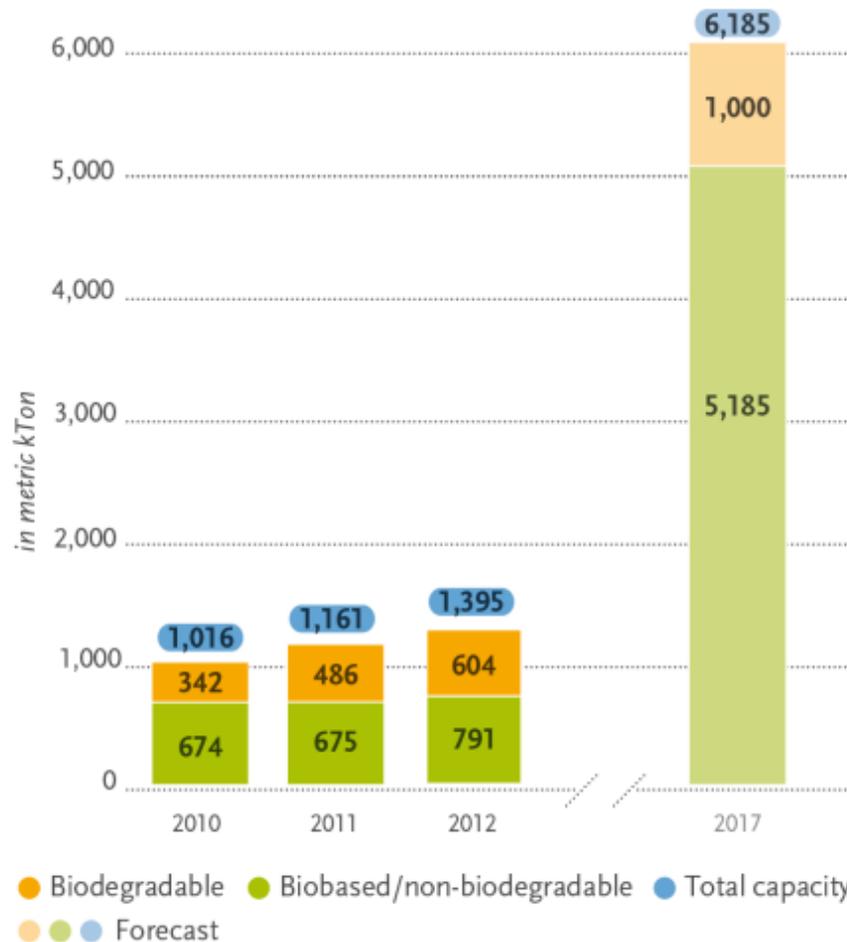
Productos químicos y Materiales de base biológica:
50 millones de toneladas

Principales moléculas:

Almidón no-alimentario, fibras/derivados de la
celulosa, ácidos grasos y productos de fermentación,...

LOS BIOPLÁSTICOS: Tamaño del mercado actual

Global production capacities of bioplastics



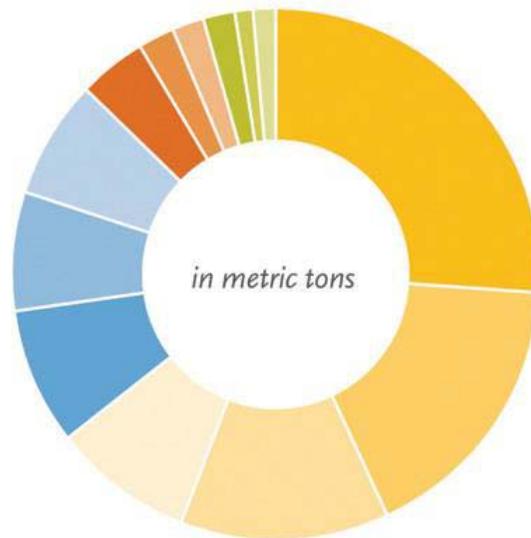
Source: European Bioplastics | Institute for Bioplastics and Biocomposites (December 2013)

Los bioplásticos se utilizan en:

- ✓ embalaje,
- ✓ abastecimiento de productos,
- ✓ automóviles,
- ✓ productos electrónicos de consumo,
- ✓ agricultura/horticultura
- ✓ juguetes
- ✓ textiles
- ✓ otros segmentos

CAPACIDAD DE PRODUCCIÓN DE BIOPOLÍMEROS

Biopolymers production capacity 2015 (by type)



● Bio-PE	450.000	26 %
● Bio-PET	290.000	17 %
● PLA	216.000	13 %
● PHA	147.100	9 %
● Biodegradable Polyesters	143.500	8 %
● Biodegradable Starch Blends	124.800	7 %
● Bio-PVC	120.000	7 %
● Bio-PA	75.000	5 %
● Regenerated Cellulose ¹	36.000	2 %
● PLA-Blends	35.000	2 %
● Bio-PP	30.000	2 %
● Bio-PC	20.000	1 %
● Others	22.300	1 %
Total	1.709.700	100 %

¹ only hydrated cellulose foils

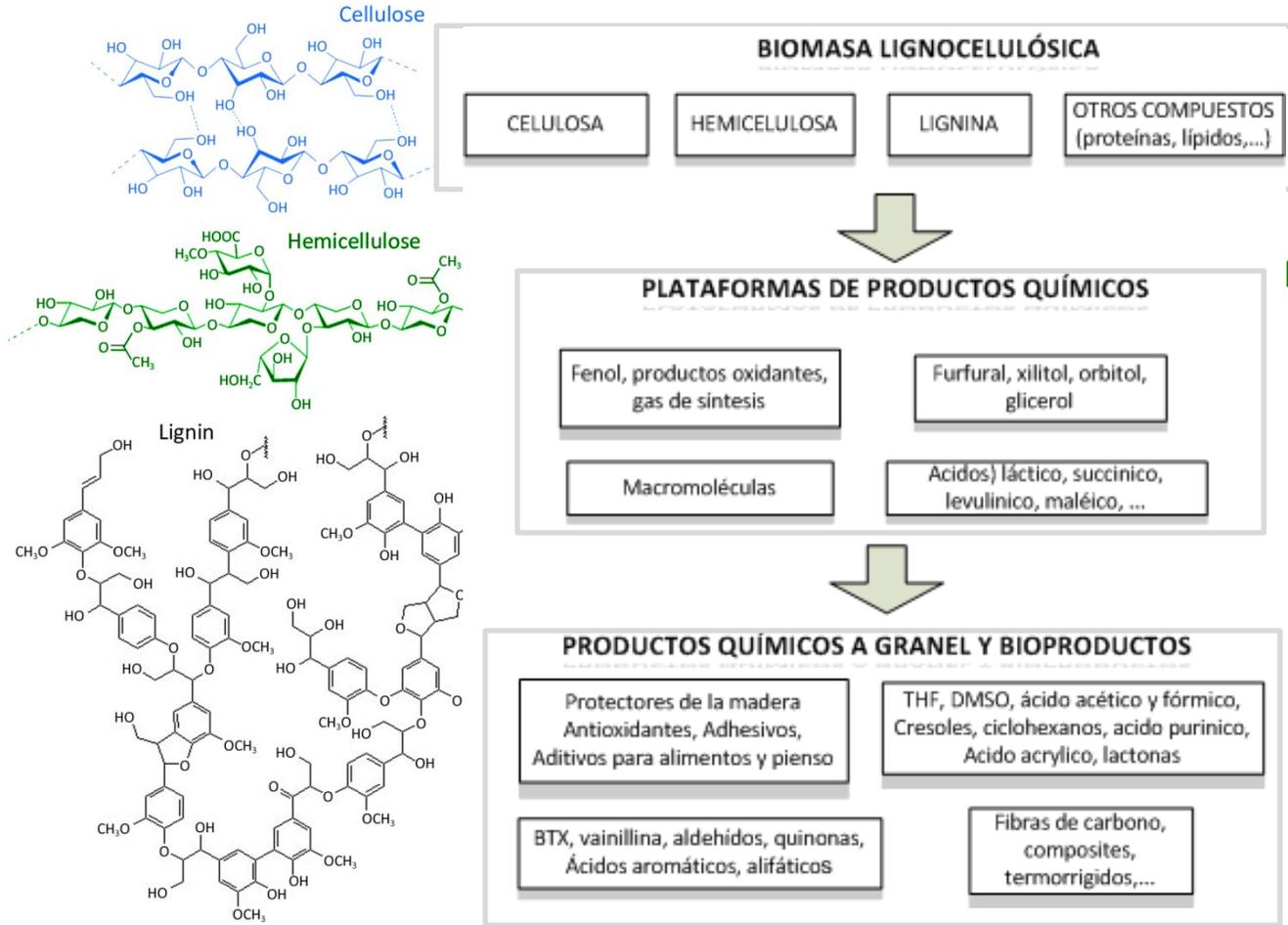
Plastics Europe anticipated biopolymer production capacity (tonnes) by 2015

PE: Polietileno, PET: Polietileno Tereftalato, PLA: Poliláctico Acido , PHA: Polyhydroxyalkanoates, PVC: Cloruro de polivinilo, PA: Poliamida



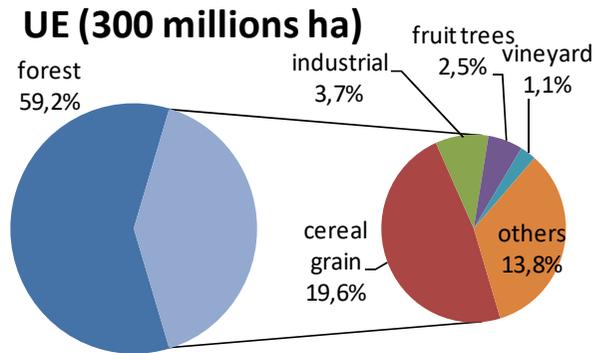
BIOMASA LIGNOCELULÓSICA: UNA POSIBLE SOLUCIÓN

COMPOSICIÓN Y ADECUADA EXPLOTACIÓN



FUENTES DE LA BIOMASA CELULÓSICA: PROS ...

MATERIAS PRIMAS RENOVABLES
DISPONIBLE EN TODO EL MUNDO
MINIMIZAR/REUTILIZAR RESIDUOS
(agrícola, industrial, forestal)



Países que han publicado patentes

Primer trimestre de 2016

Número de orden	País	Nº referencias
1	China	1337
2	PCT (solicitudes internac.)	156
3	EE.UU.	113
4	Corea	68
5	Japón	37
6	Alemania	34
7	India	17
8	Rusia	7
...	España	7

(Fuente: <http://www.oepm.es/>)



¿BIORREFINERÍA CONCEPTO VIEJO O NUEVO?

Example: Perstorp

The origin of the chemicals manufacturer Perstorp, in the south of Sweden, was a company established in the 1880's with the intention to produce acetic acid, tar, charcoal and wood alcohol. The products were successively developed into new product lines. In 1907, formalin production started and formed the basis of a long line of products. Formalin based products are still produced by Perstorp, but now with natural gas as the feedstock basis (Perstorp 2012).

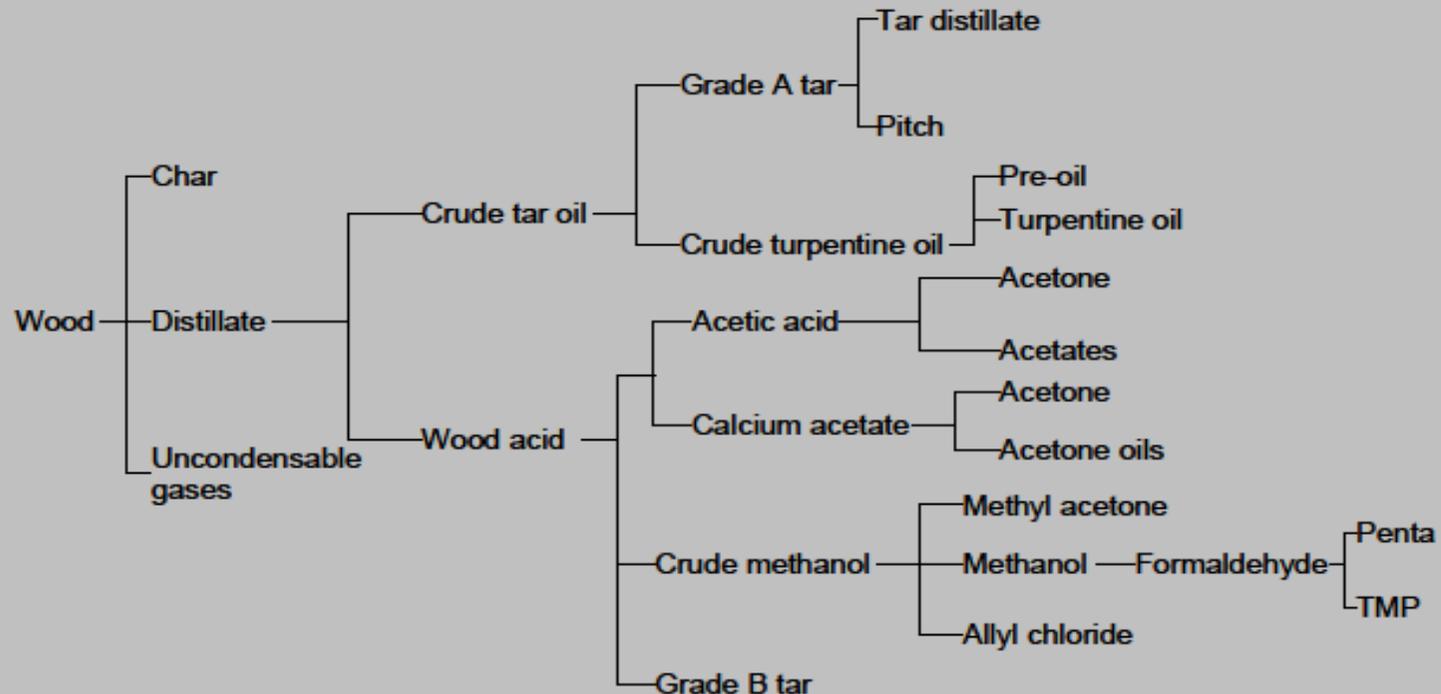


Figure 2. Historic production lines of Perstorp. Redrawn and translated from (Rex 2012).



Investigación & Invención

Los procesos de investigación e invención son limitados y a menudo se encuentran con barreras financieras
Con frecuencia la fabricación de un producto o servicio tienen dificultades para penetrar en el mercado

En consecuencia a la investigación le cuesta penetrar en el mercado

Fabricación

Problemas con el producto

- Mejores productos
- Efectos innovadores
- Rendimientos más elevados

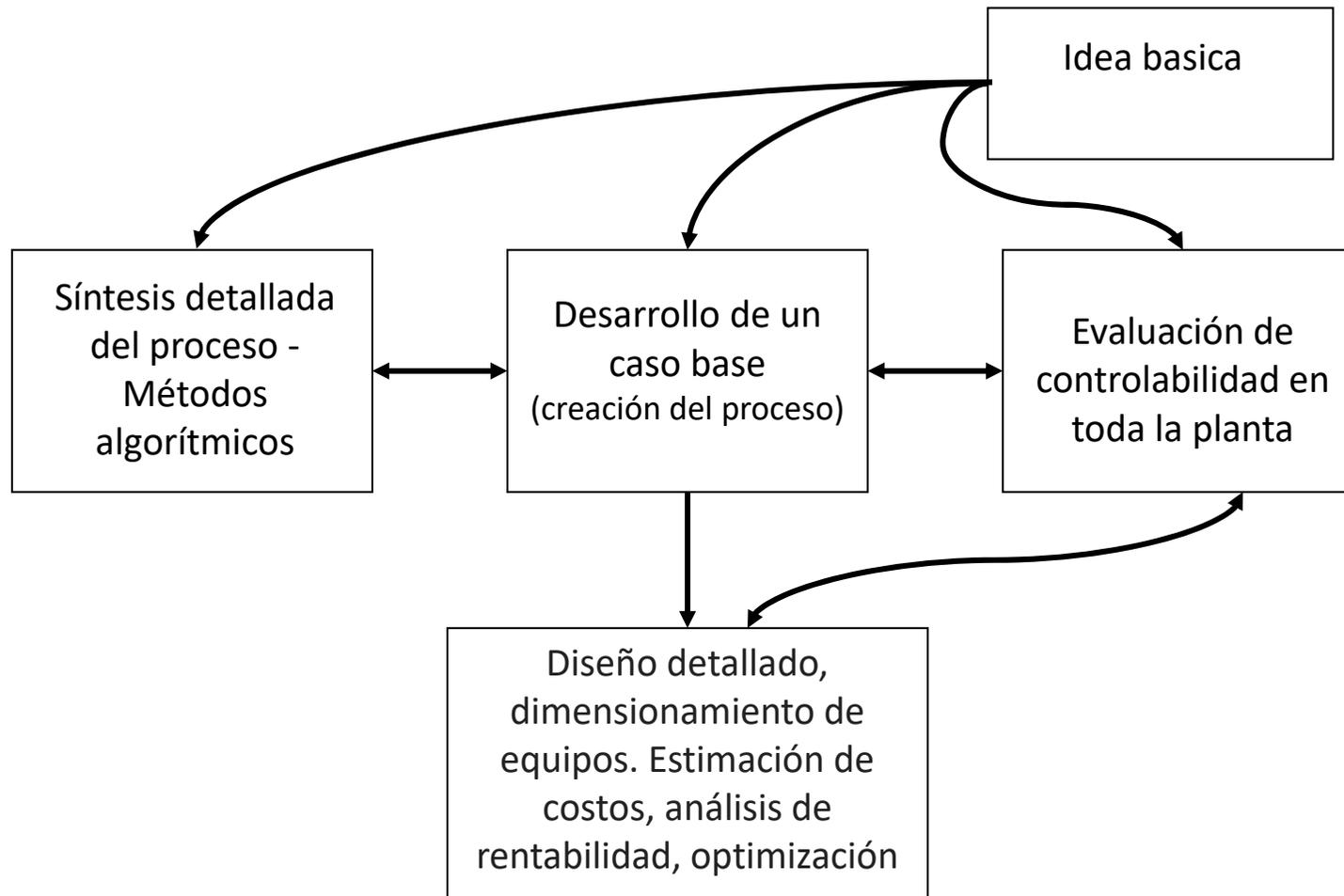
Desafíos

- Productos inferiores, oportunidades, costes fijos
- Tasas de producción más rápidas
- Productos más sostenibles



THE VALLEY OF DEATH







Producción de nano-celulosa



Nanowhiskers celulosa

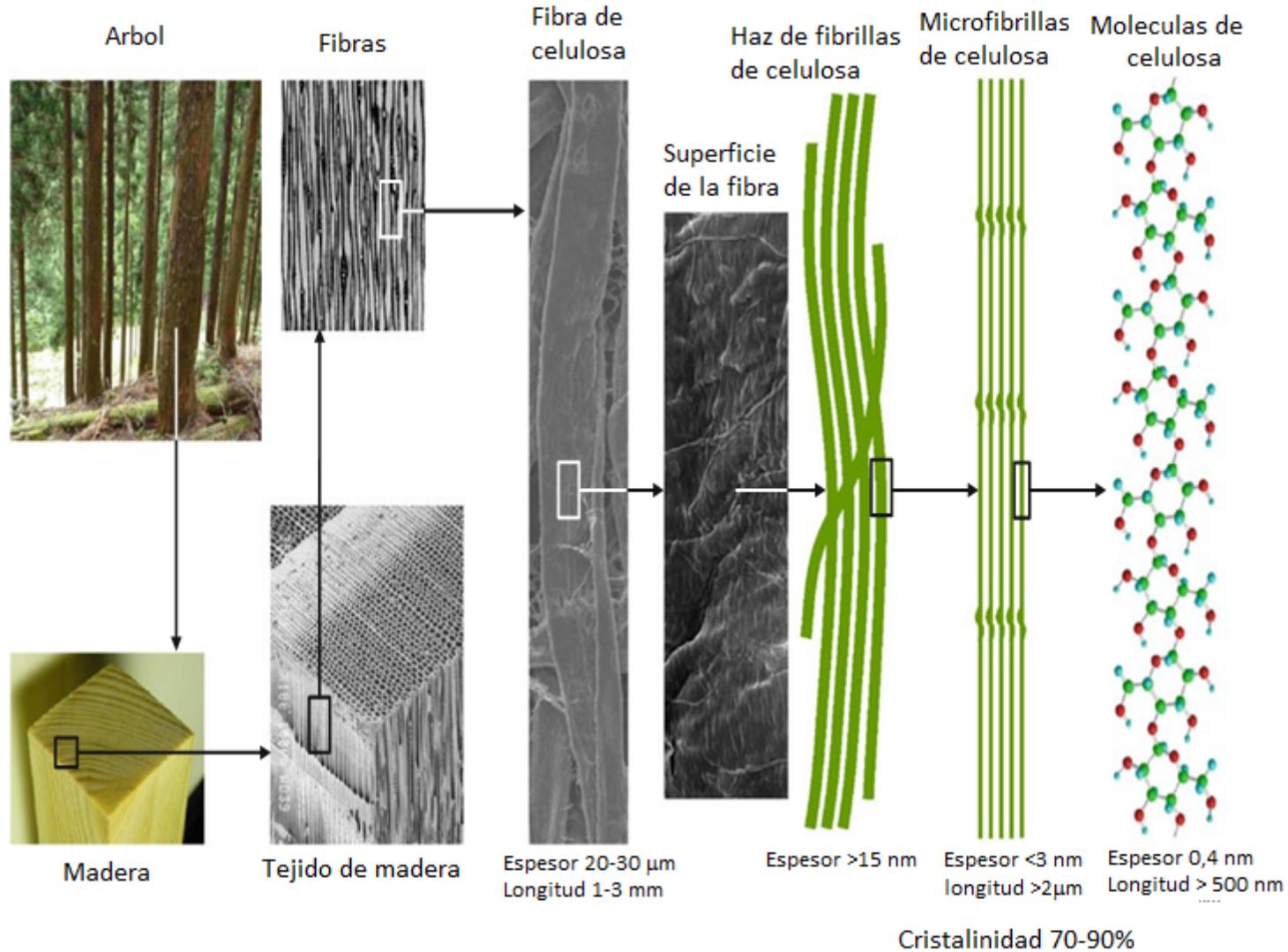
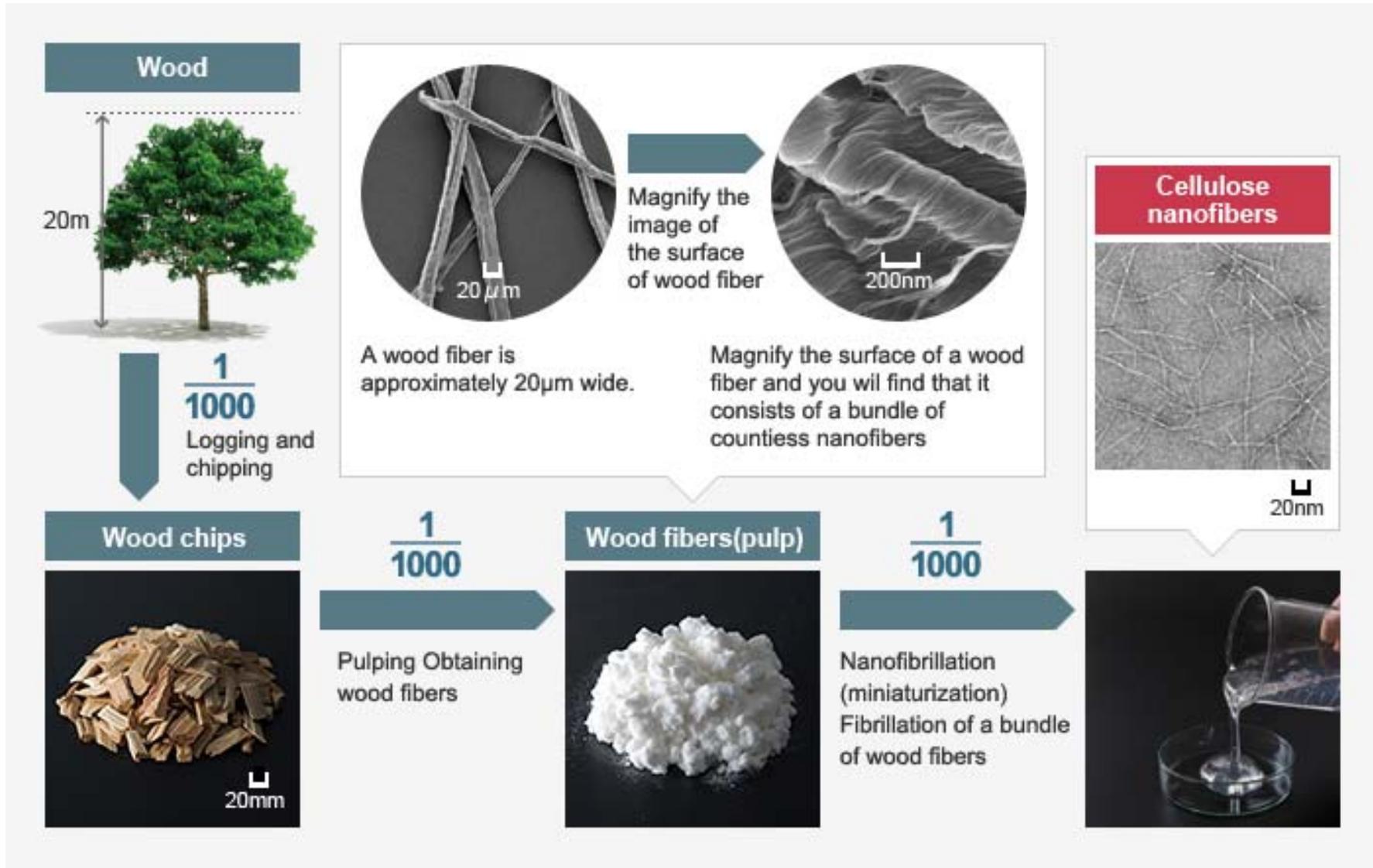


Fig. 1 Hierarchical structure of wood cellulose, forming crystalline cellulose microfibrils. Some photos are used from the Web site of Forestry and Forest Products Research Institute

Dimensiones de los materiales de celulosa aislados de las fibras naturales micro - y nano-escala

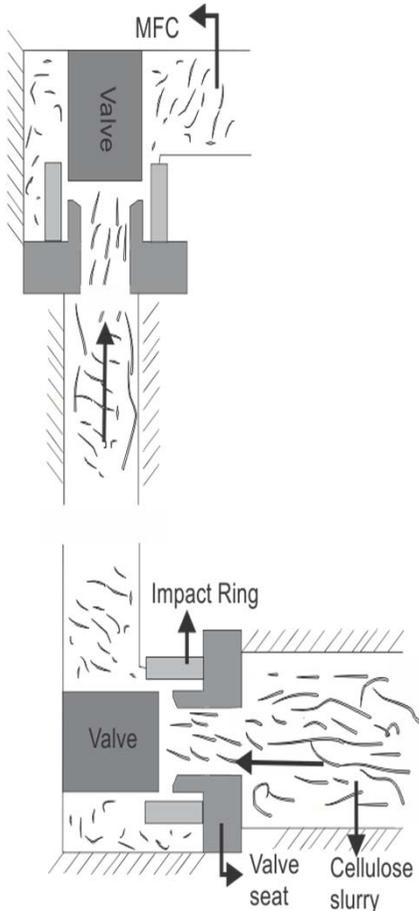
Tipo	Diámetro d [nm]	Longitud L [μm]	Relación aspecto (L/d)
MCC	>1,000	>1	~ 1
Microfibrillas	2-10	>10	>1,000
MFC/NFC	4-40	5-10	100-150
CNC	3-5	0.1-0.6	10-100

Nano fibras de Celulosa (NF)





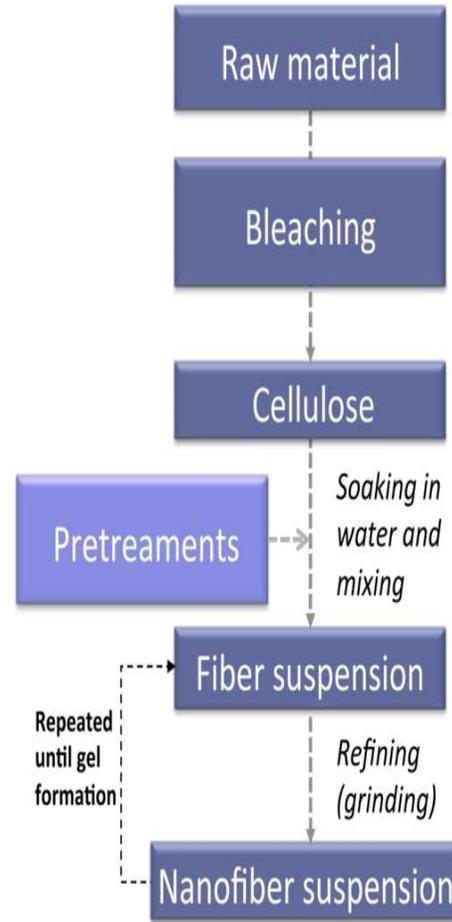
Producción de CNF



Esquema de un homogenizador de dos etapas a alta presión



Homogenizador



Purification

Isolation process



Molino



Producción de CNC

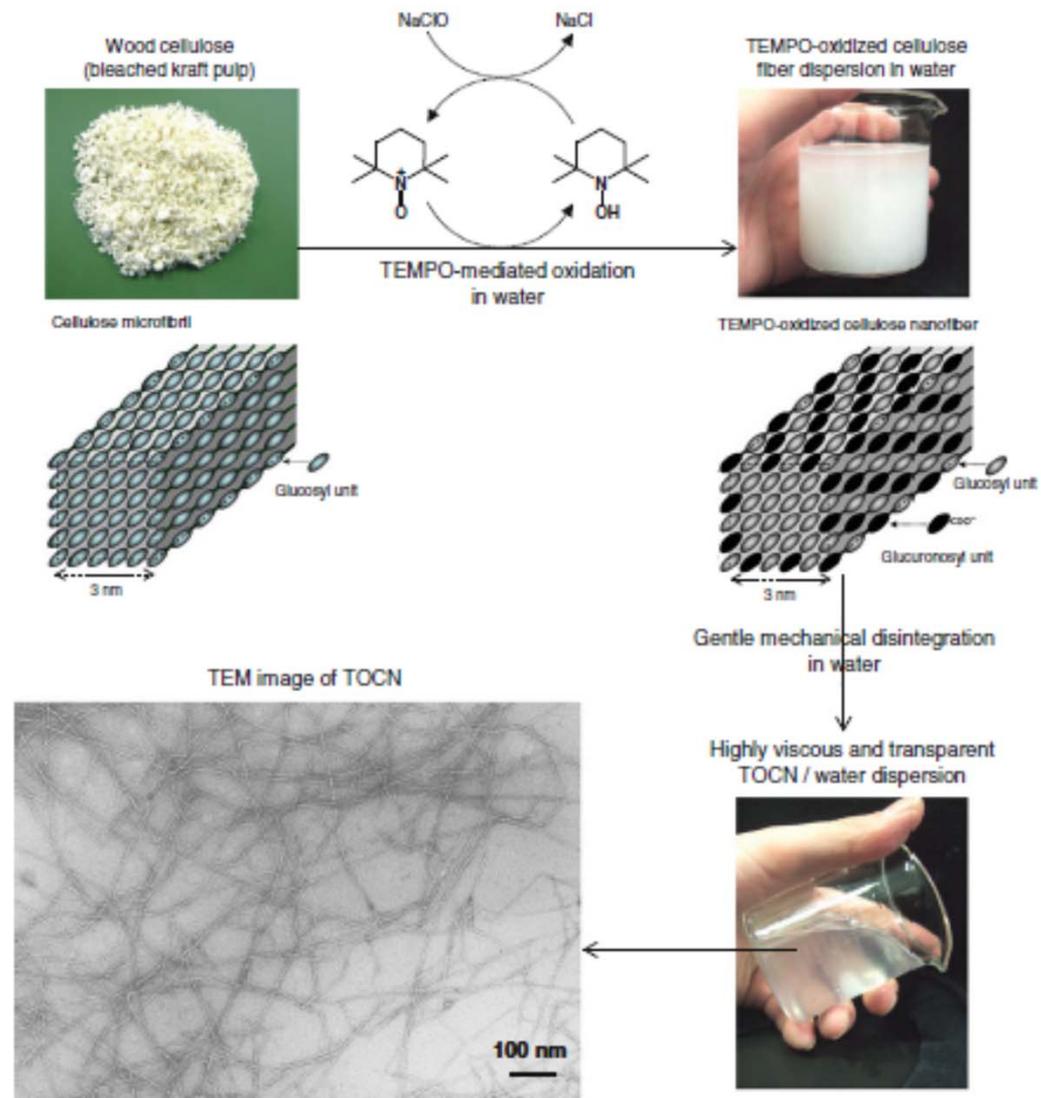
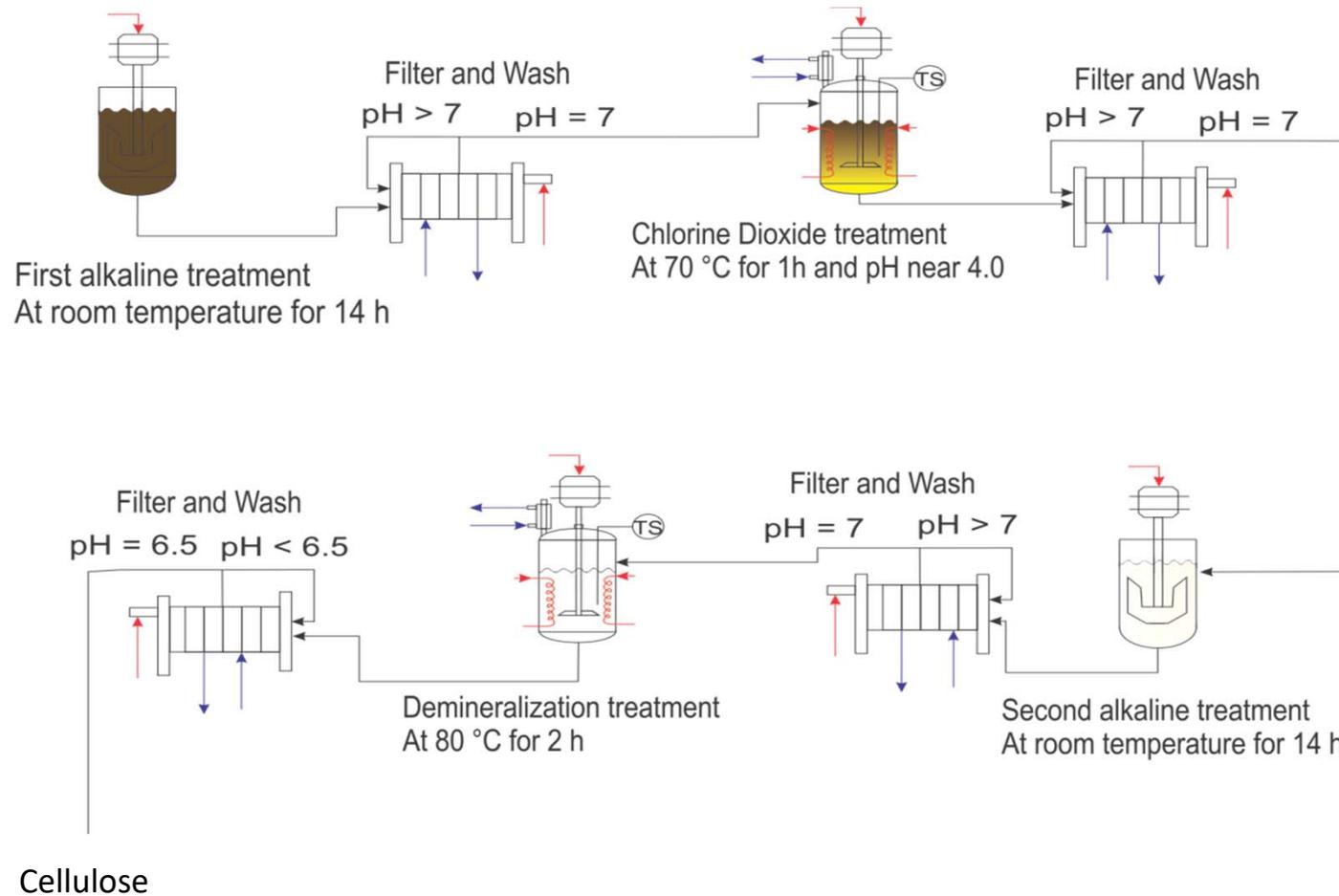


Fig. 3 Preparation of TEMPO-oxidized cellulose nanofibrils (TOCNs) from wood cellulose and the corresponding structural model of TOCN



Proceso de producción de la celulosa

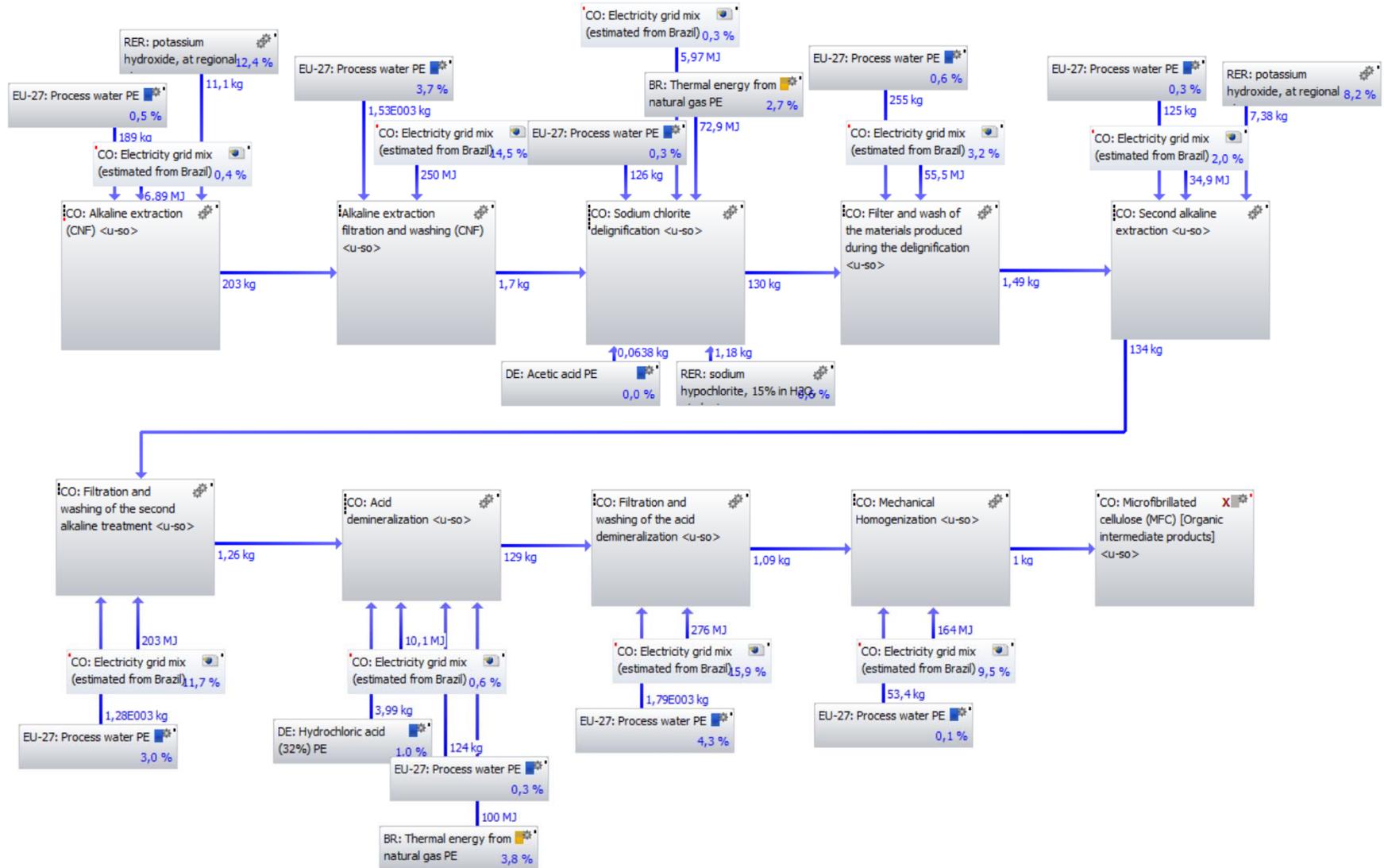




LCA del proceso de producción de NF de celulosa

Cellulose nanofiber (UBP)

Process plan: Reference quantities
LCIA preview: CML2001 - Nov. 2010, Global Warming Potential (GWP 100 years)
The names of the basic processes are shown.



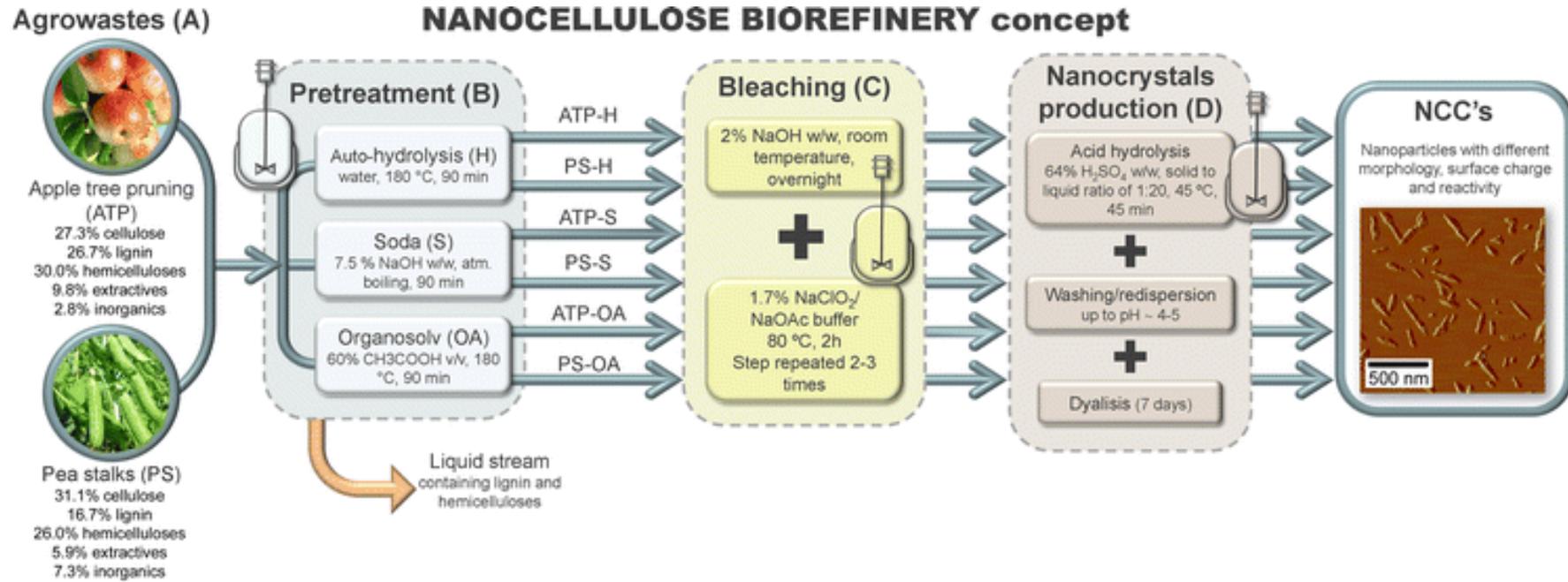


LCA del proceso de producción de NF de celulosa

Cargas ambientales relativas asociadas con la producción de 1 kg Nanofibras de celulosa

	Total	01_Alkaline extraction	02_filtration washing	03_delignification	04_Filter and wash	05_Second alkaline extraction	07_Filtration and washing	08_Acid demineralisation	09_Filtration and washing	10_Mechanical Homogenisation
Primary energy										
Primary energy demand from ren. and non ren. resources (net cal. value) [%]	100	12,82	18,41	3,79	3,90	10,35	15,03	5,28	20,53	9,89
Primary energy from non renewable resources (net cal. value) [%]	100	20,53	14,19	5,92	2,86	14,78	11,64	8,03	15,98	6,06
Primary energy from renewable resources (net cal. value) [%]	100	2,26	24,19	0,86	5,31	4,30	19,68	1,51	26,76	15,13
ReCiPe 1.08 (H)										
Agricultural land occupation [%]	100	36,08	8,59	5,37	1,59	24,40	7,11	4,97	9,85	2,04
Climate change, default, excl. biogenic carbon [%]	100	13,32	18,00	4,06	3,81	10,65	14,71	5,68	20,08	9,68
Climate change, incl. biogenic carbon [%]	100	13,22	18,10	4,04	3,82	10,57	14,79	5,65	20,21	9,60
Freshwater eutrophication [%]	100	56,22	0,74	3,80	0,12	37,50	0,62	0,09	0,87	0,03
Ozone depletion [%]	100	58,35	0,05	2,57	0,01	38,92	0,04	0,01	0,05	0,00
Photochemical oxidant formation [%]	100	16,71	16,71	4,25	3,47	12,63	13,67	5,68	18,71	8,18
Terrestrial acidification [%]	100	13,43	19,09	2,20	4,09	10,94	15,57	2,61	21,24	10,82
Water										
Blue water consumption [%]	100	2,82	25,61	1,40	5,07	3,62	21,05	1,66	28,98	9,79

Esquema para la producción de NCC a partir de residuos agrícolas



García et al. "Cellulose, 24, 2017"



Aplicaciones de la nanocelulosa



Los pioneros en el desarrollo industrial de la nanocelulosa



En España no existe ninguna iniciativa similar

Company	Country	Unit	Type of CN	Capacity
FP Innovation	Canada	Pilot plant	CNC	10 kg/week
US Forest Service's Forest Products Laboratory	USA	Pilot plant	CNC	35 - 50 kg/day
Alberta Innovates—Technology Futures	Canada	Pilot plant	CNC	100 kg/week
Cellulforce Inc.	Canada	Demonstration plant	CNC	1 tonne/day
Biovision Technologies Inc.	USA	Pilot plant	CNC	4 tonnes/year
Inventia	Sweden	Demonstration plant	CNF	100 kg/day
The Us Forest Service	USA	Demonstration plant	CNF	500 kg/day

MERCADO POTENCIAL

HIGH VOLUME	LOW VOLUME	NOVEL and Emerging APPLICATIONS
Cement	Wallboard Facing	Sensors – medical, environmental, industrial
Automotive Body	Insulation	Reinforcement fiber - construction
Automotive Interior	Aerospace Structure	Water filtration
Packaging Coatings	Aerospace Interiors	Air filtration
Paper Coatings	Aerogels for the Oil and Gas Industry	Viscosity modifiers
Paper Filler	Paint-Architectural	Purification
Packaging Filler	Paint-Special Purpose	Cosmetics
Replacement -Plastic Packaging	Paint -OEM Applications	Excipients
Plastic Film Replacement		Organic LED
Hygiene and Absorbent Products		Flexible Electronics
Textiles for Clothing		Photovoltaics
		Recyclable Electronics
		3D printing
		Photonic Films

Fuente: Vireo Advisors S.L:



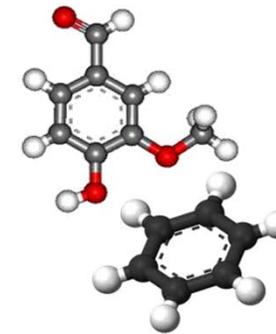
La lignina



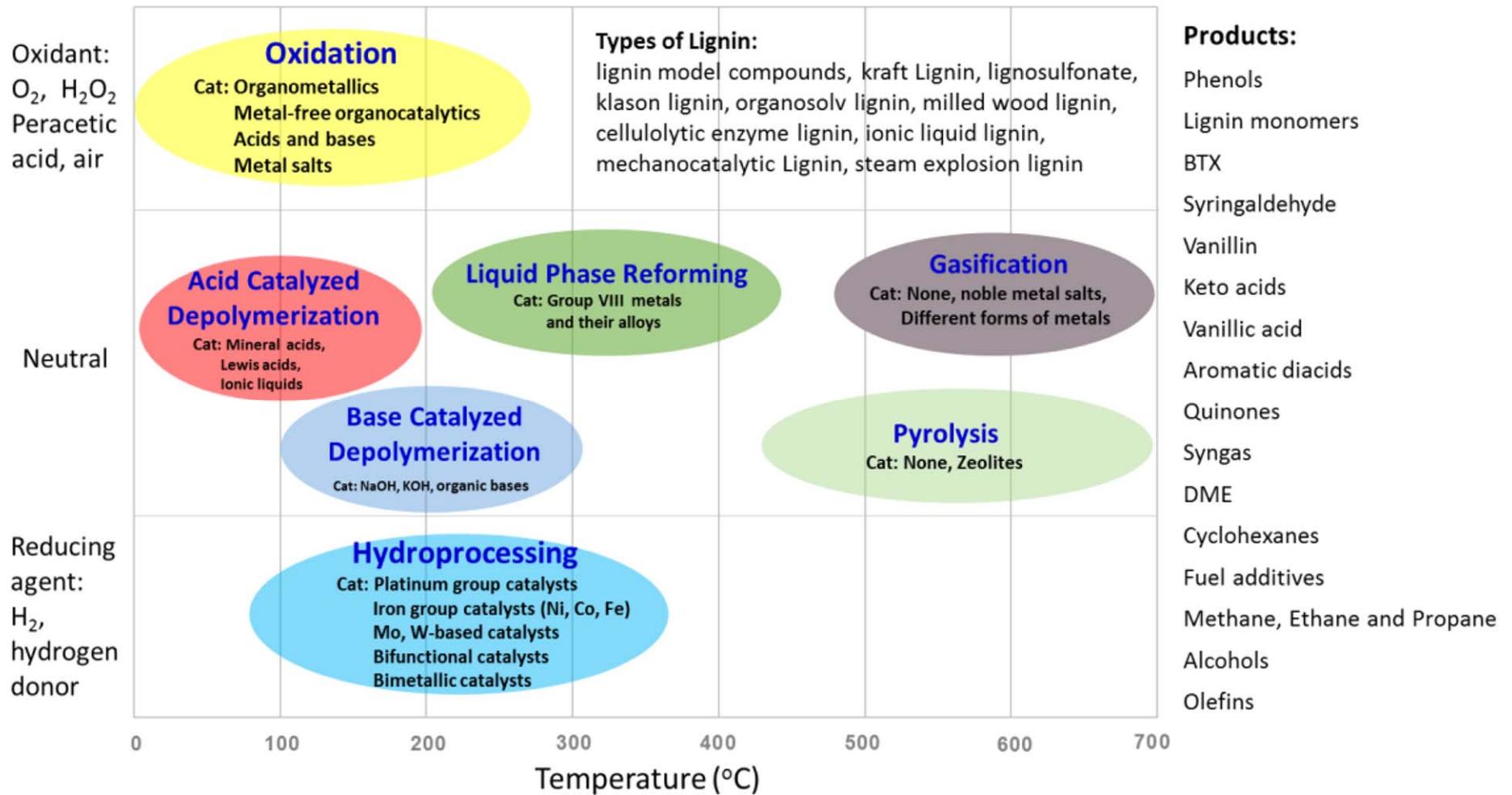


LA LIGNINA

APLICACIONES ACTUALES Y POTENCIALES DE LA LIGNINA



Resumen de los procesos de conversión de la lignina



(1) Catalytic Transformation of Lignin for the Production of Chemicals and Fuels. Changzhi Li et al. Chemical reviews (2015)

Productos potenciales de lignina

Comparación entre varios posibles productos de la lignina en términos de volumen de mercado, el precio y el máximo rendimiento gravimétrico de lignina, suponiendo un polímero lineal de unidades de monómero de G en 196 g mol^{-1} . Aunque los precios de mercado están en constante fluctuación, los datos sin embargo sirven para comparar tamaños aproximados y rendimientos de las industrias potenciales de la lignina. Cualquier carbón residual se supone que se utiliza para reformar al hidrógeno.

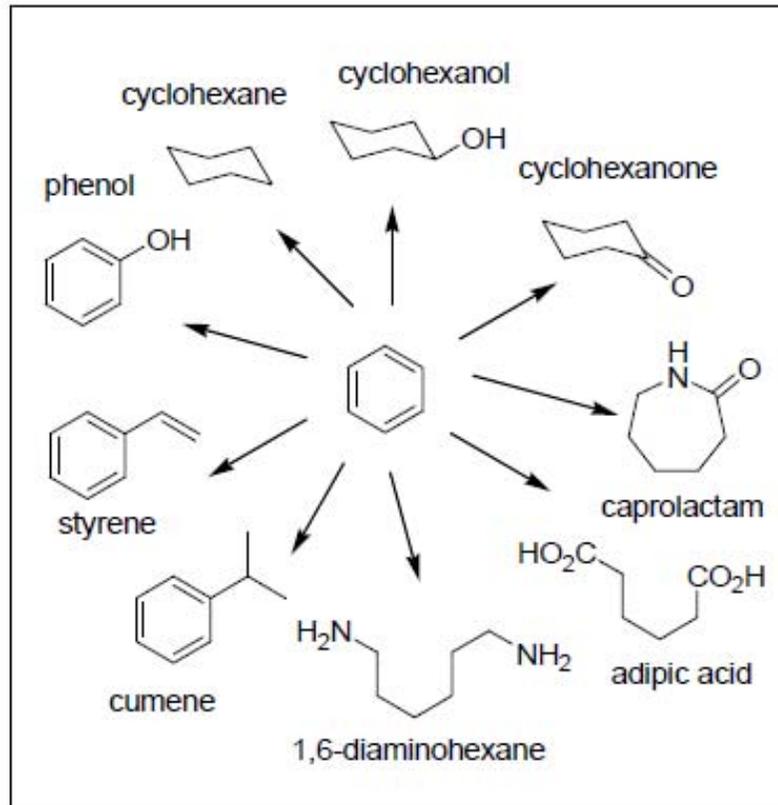
Compuesto	Volumen (10^3 kg y^{-1})	Precio (\$ kg^{-1})[a]	Rendimiento máximo teórico de lignina (wt %)	H ₂ producido (kg por kg producto)	CO ₂ producido (kg por kg producto)
Benceno		1.49	40 %	0.181	2.254
Tolueno	80 000 000 (combined)	1.38	47 %	0.088	1.433
Xileno		1.36	54 %	0.019	0.829
Fenol	8000 000	1.54	48 %	0.172	1.871
Vanillina	20 000	10–15	78 %	0.066	0.579
4-Propylguaicol	none	no (current) market	85 %	-0.036	0.000[b]

[a] benceno, tolueno, xileno y fenol los precios son FOB U.S. Gulf as of 30th October 2012. La referencia, el precio del petróleo (WTI futuro para entrega diciembre) era \$85,66 por barril en esa fecha. [b] excepto fuentes de carbón necesarias para producir hidrógeno externo.

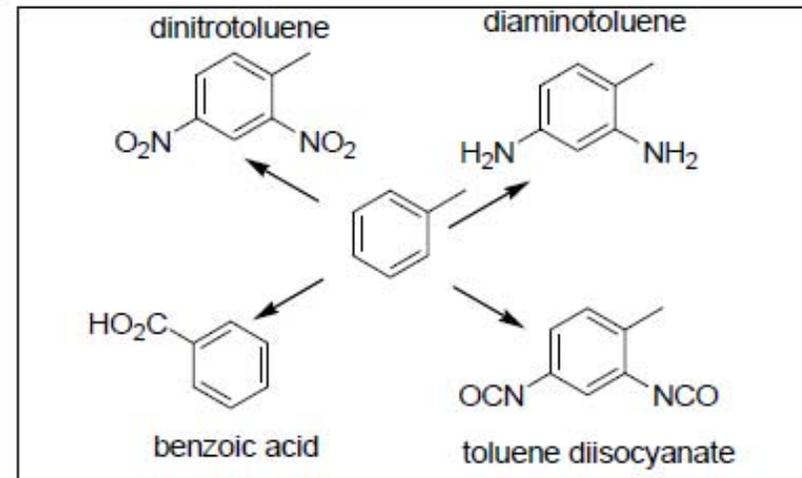
Angew. Chem. Int. Ed. 2016, 55, 8164–8215



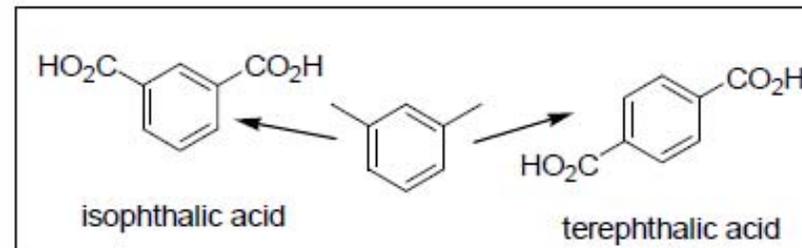
Ejemplos de tecnologías existentes



Examples of Benzene Derived Chemicals

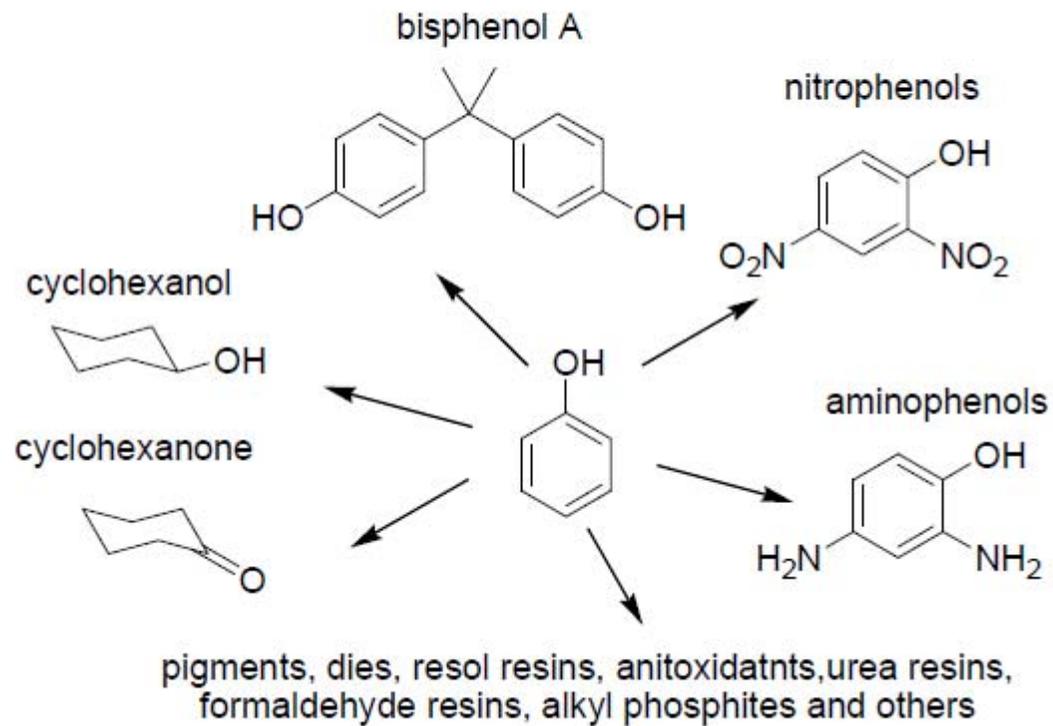


Examples of Toluene Derived Chemicals



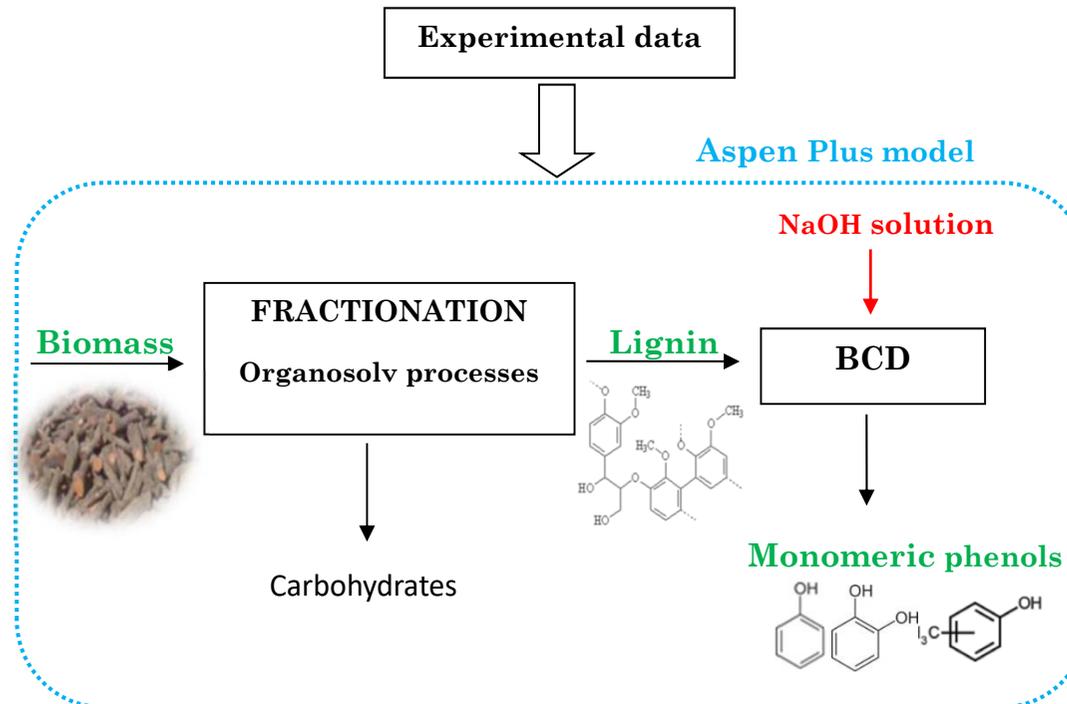
Examples of Xylene Derived Chemicals*

Derivados del fenol



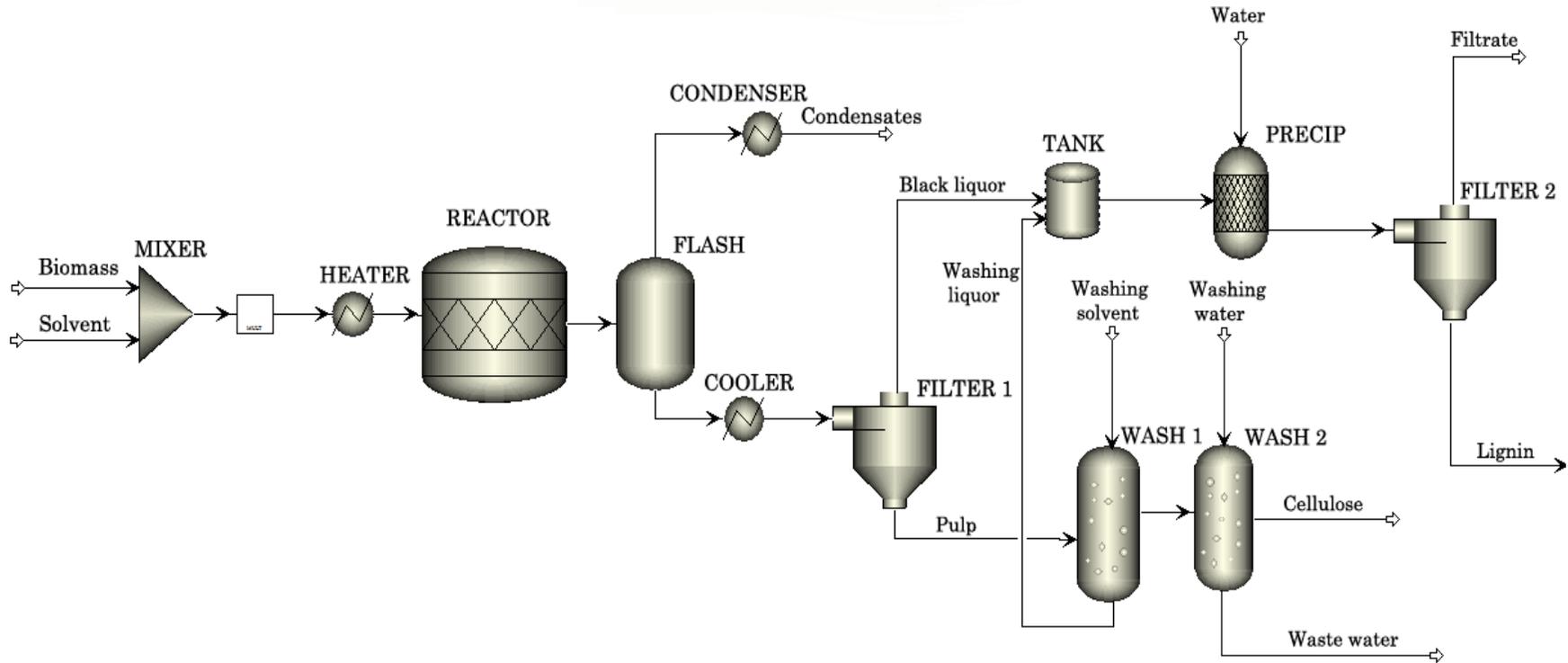
Proceso de conversión de la lignina por catálisis homogénea

- Caudal: **100 kg/h.**
- Modelos de los compuestos (Celulosa, hemicelulosa, Lignina) Base de datos del **National Renewable Energy Laboratory (NREL).**
- Modelo termodinámico: **NRTL-RK** (Non-Random, Two Liquids-Redlich-Kwong)
- Extracción liquido-liquido: **UNIQUAC**



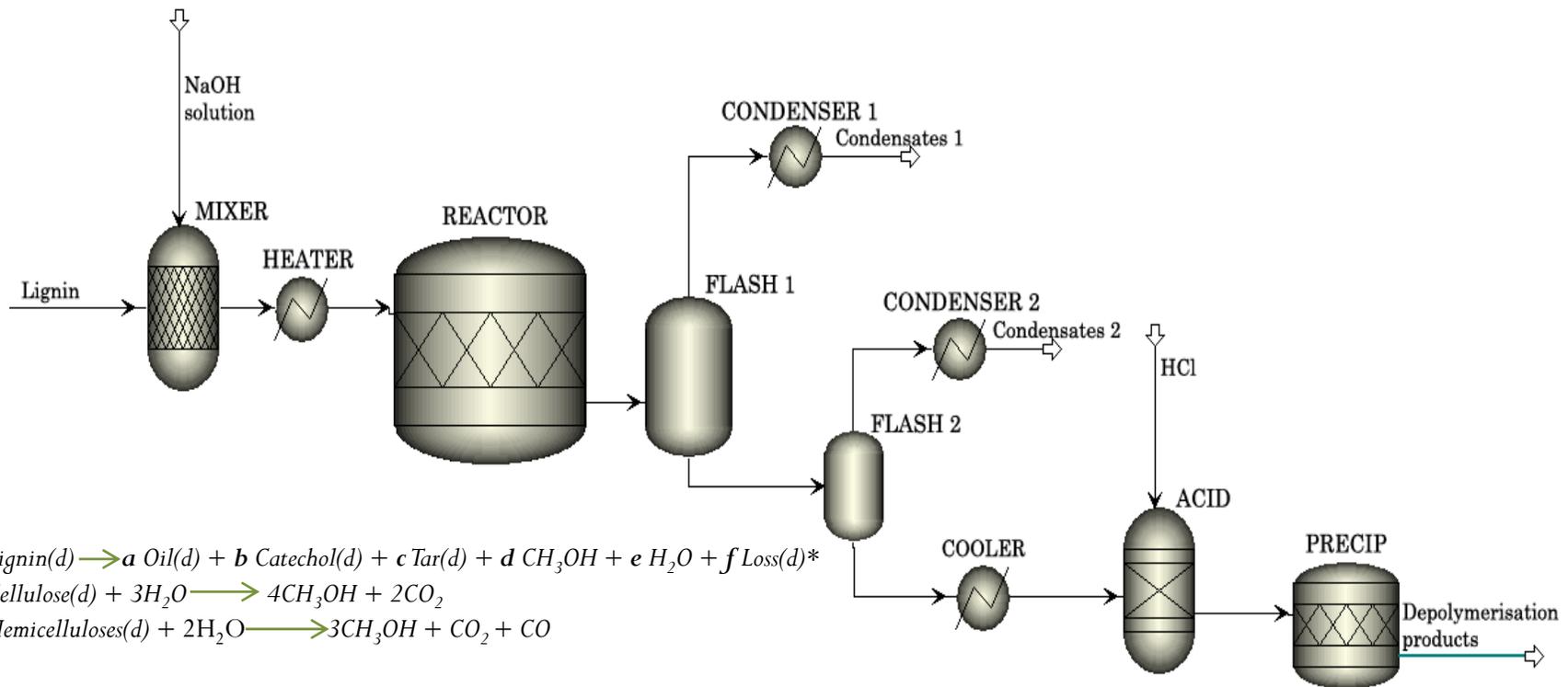


Fraccionamiento de la biomasa



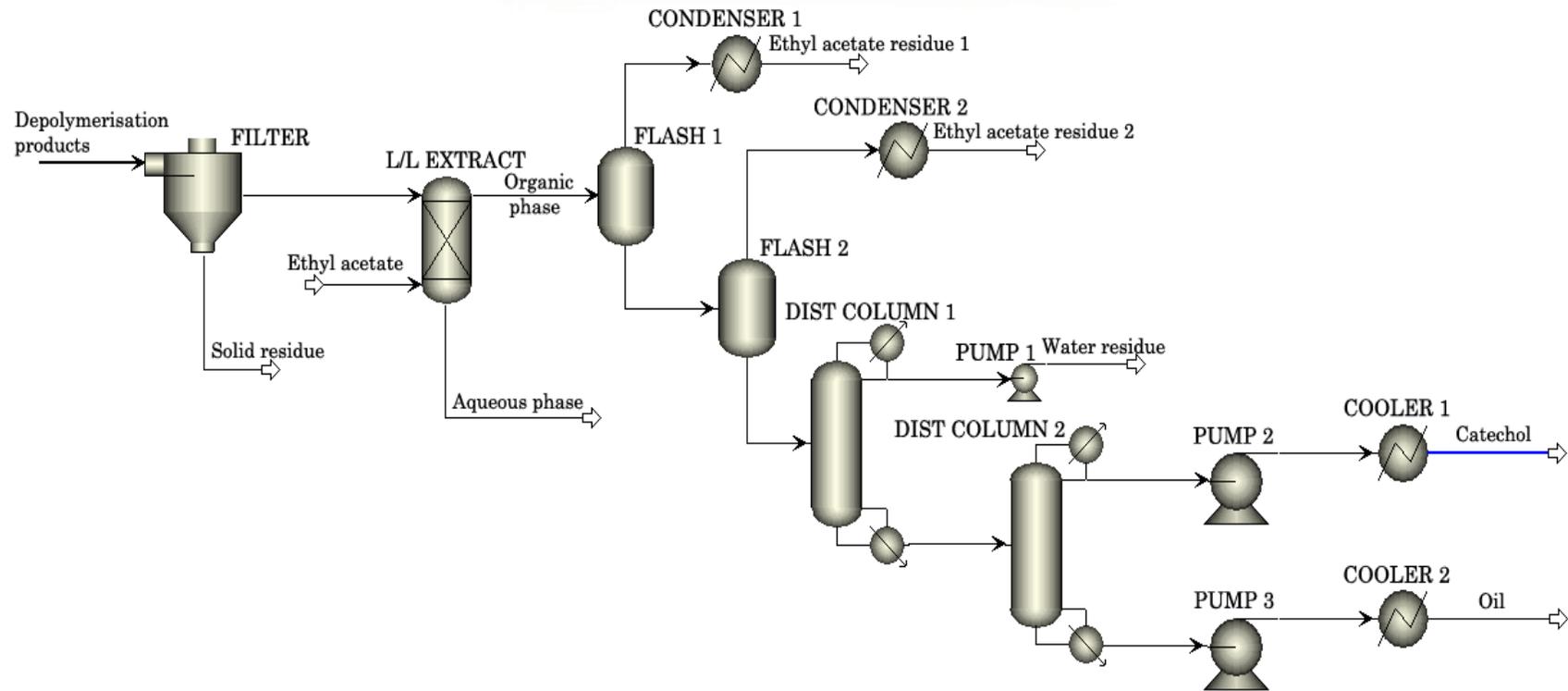
- 1) Cellulose(s) \longrightarrow Cellulose(d)
- 2) Cellulose(d) + H_2O \longrightarrow Glucose(d)
- 3) Hemicelluloses(s) \longrightarrow Hemicelluloses(d)
- 4) Xylan(d) + H_2O \longrightarrow Xylose(d)
- 5) Lignin(s) \longrightarrow **a** Lignin1(d) + **b** Lignin2(s)
- 6) Extractives(s) \longrightarrow Extractives(d)
- 7) Ash(s) \longrightarrow Ash(d)

Proceso de despolimerización de la lignina





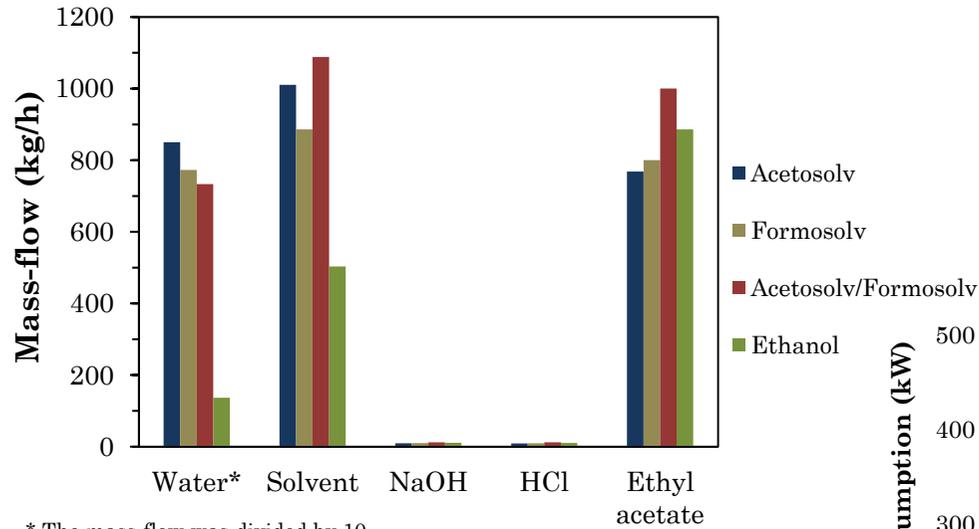
Separación de productos





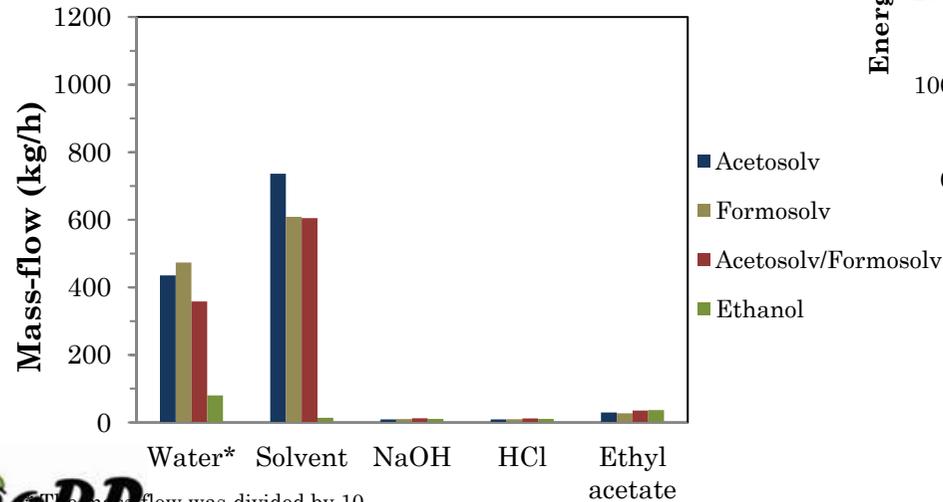
Consumos de reactivos y de energía

Sin reciclado

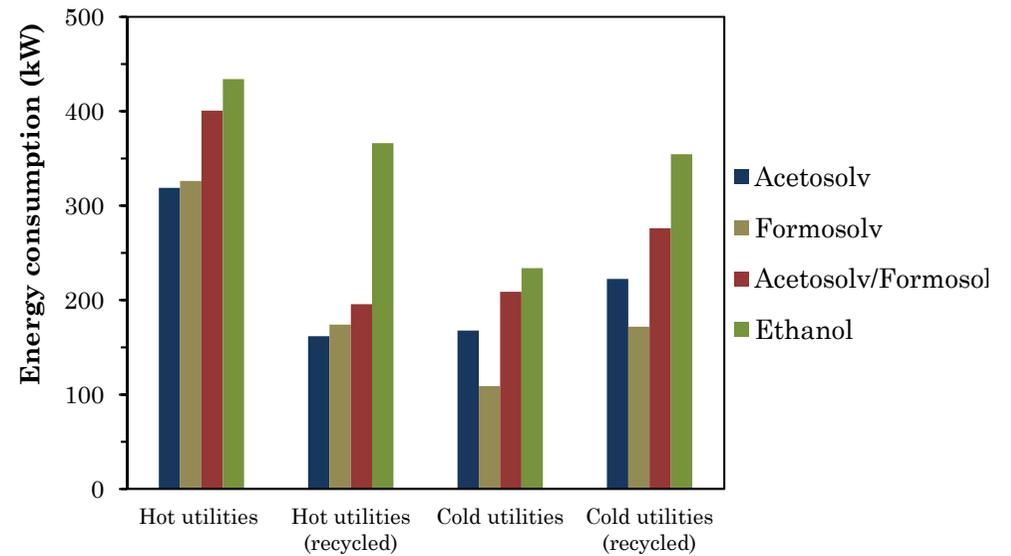


* The mass-flow was divided by 10.

Con reciclado



* The mass-flow was divided by 10.





Simulación de procesos de fermentación



HYDROLYSIS, SACCHARIFICATION and CULTURE

RStoic SEED
35 °C, 1 bar

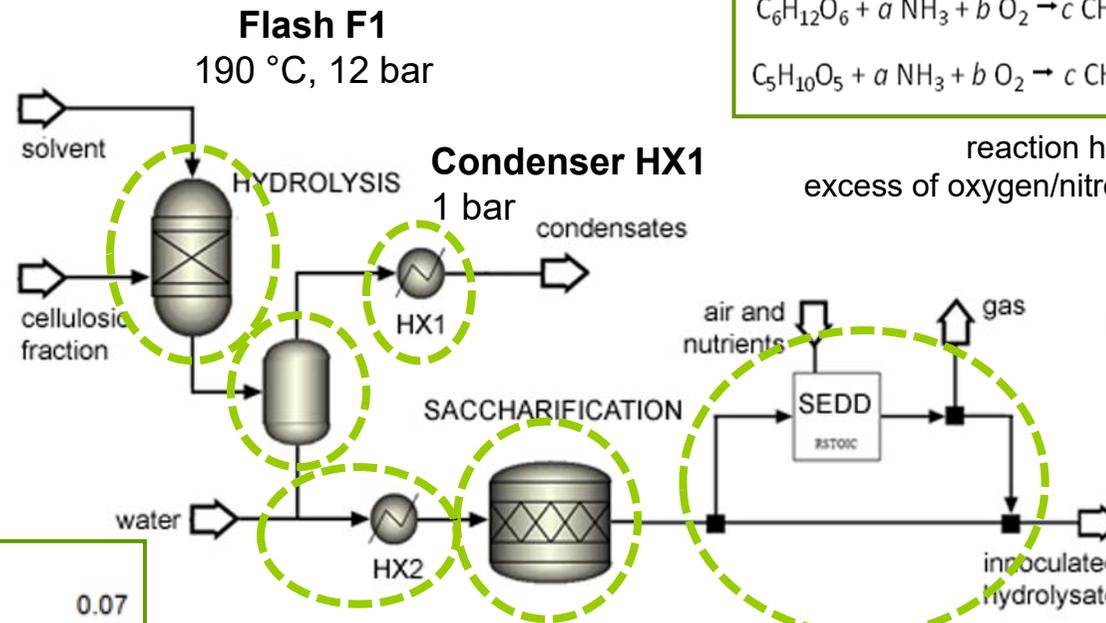
1000 kg/h of lignocellulosic feedstock
 45% cellulose
 20% hemicelluloses
 30% lignin
 5% acetate groups

(1% w/w of H₂SO₄) in a **solid to liquid ratio of 1:6**

RStoic HYDROLYZER
190 °C, 12 bar

HYDROLYSIS STEP

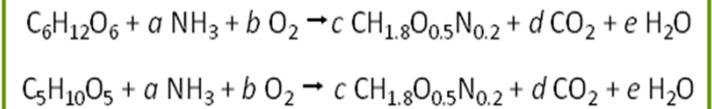
CELLULOSE(s) → GLUCAN(s)	0.07
GLUCAN(s) + H ₂ O → GLUCOSE(d)	0.90
HEMICELULOSES(s) → XYLAN(s)	0.90
XYLAN(s) + H ₂ O → XYLOSE(d)	0.90
LIGNIN(s) → LIGNIN(d)	0.05
ACETATE(s) → ACETIC(d)	1.00
GLUCAN(s) → HMF + 2 H ₂ O	0.05
XYLAN(s) → FURFURAL + 2 H ₂ O	0.05



Total solids 30 ± 0.1%
 (*DesignSpec*)

Heater HX2
 65 °C

RStoic SACCHARIFIER
 65 °C, 1 bar



reaction heat of 187300 kJ/kmol
 excess of oxygen/nitrogen source (air, NH₃)

0.3 ± 0.01% of microorganisms in the final inoculated hydrolysate
 (*DesignSpec*)

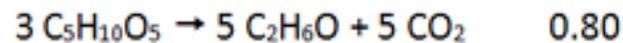
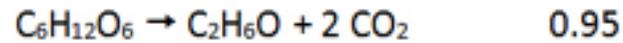
SACCHARIFICATION STEP

CELLULOSE(s) → GLUCAN(s)	0.95
GLUCAN(s) + H ₂ O → GLUCOSE(d)	0.90

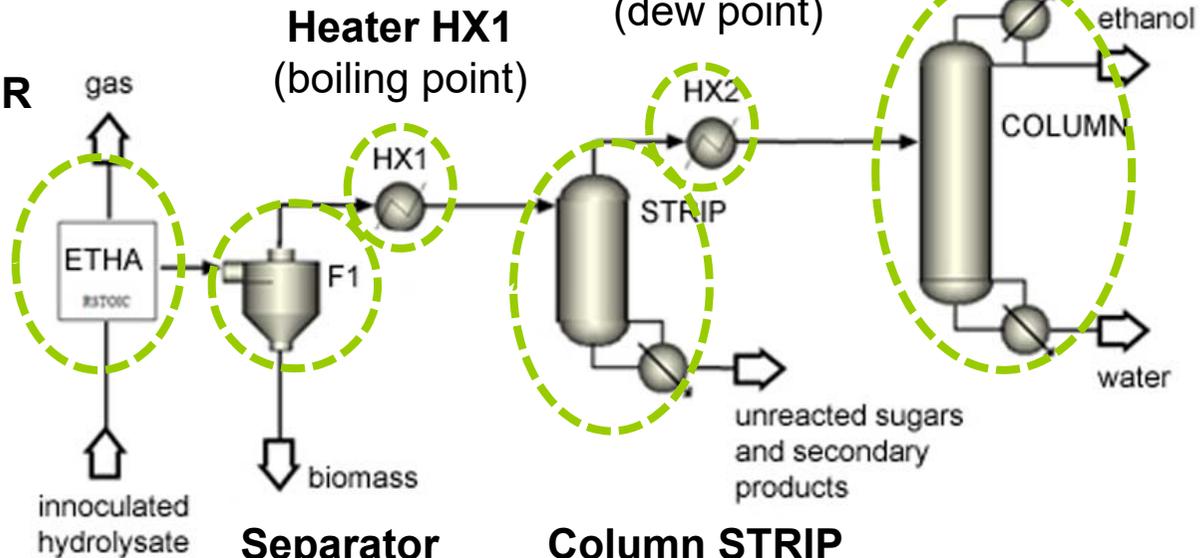


ETHANOL PRODUCTION

FERMENTATION REACTIONS



RStoic
FERMENTOR
35 °C, 1 bar



Heater HX1
(boiling point)

Condenser HX2
(dew point)

Column COLUMN
(DesignSpec)

20 stages

1 bar

mass reflux ratio 3

116 kW in the reboiler

Separator F1

(10% of liquid in biomass stream)

Column STRIP
(DesignSpec)

8 stages

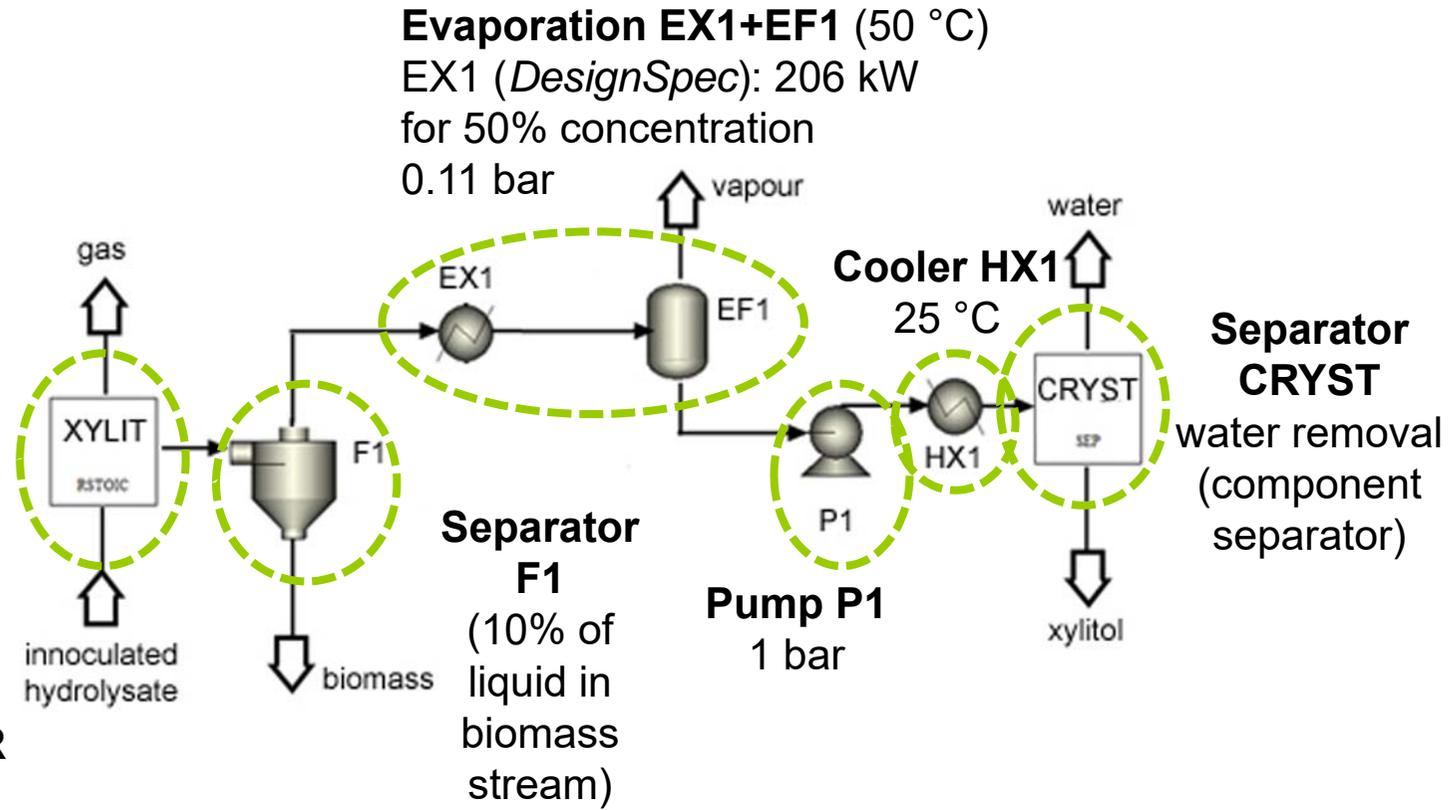
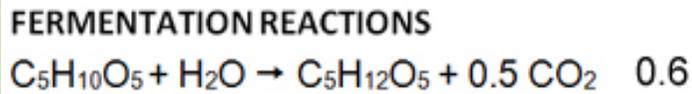
1 bar

116 kW in the reboiler



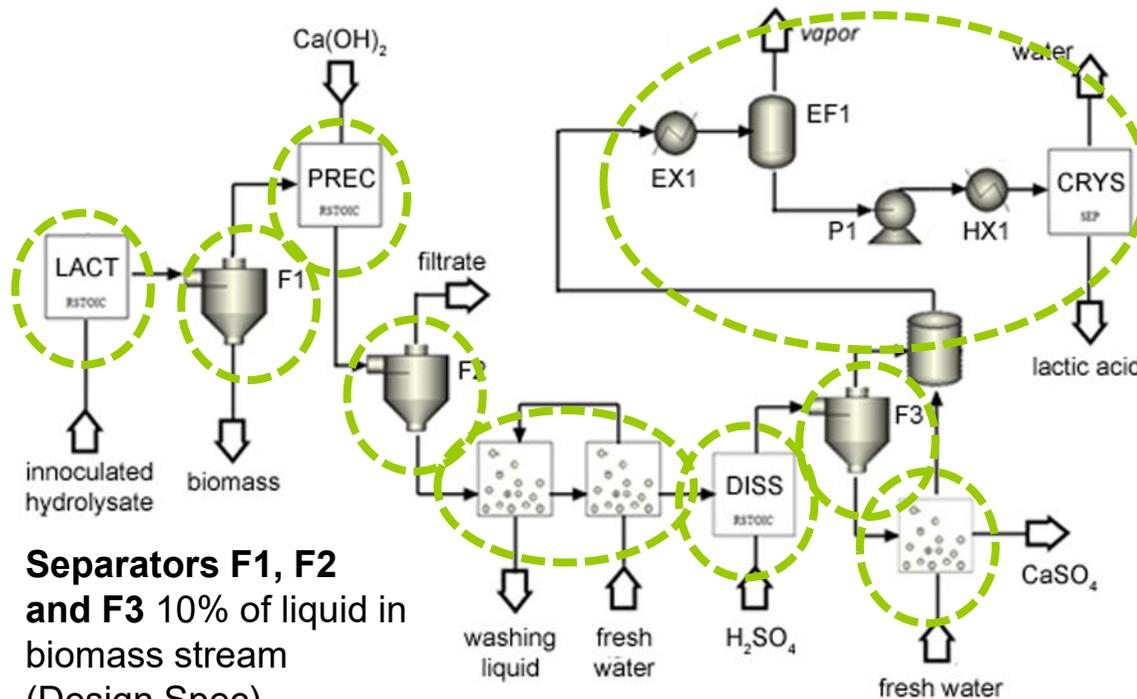
XYLITOL PRODUCTION

**RStoic
FERMENTOR**
35 °C, 1 bar





LACTIC ACID PRODUCTION



Separators F1, F2 and F3 10% of liquid in biomass stream
(Design Spec)

Washers W1, W2 and W3 less than 1% solids in the liquid part
(Design Spec)

Evaporation EX1+EF1 (60 °C). EX1 (*DesignSpec*): 1043 kW for 50% concentration. 0.17 bar

Pump P1: 1 bar

Cooler HX1: 25 °C

Separator CRYST

RStoic FERMENTOR

30 °C, 1 bar

FERMENTATION REACTIONS



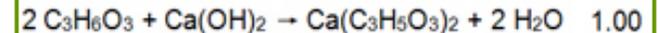
Rstoic PREC

15:85 w/w lime-water

(*DesignSpec*)

95 °C, 1 bar

PRECIPITATION REACTIONS



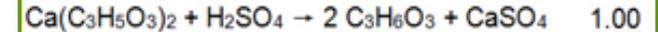
Rstoic DISS

15:85 w/w sulfuric-water

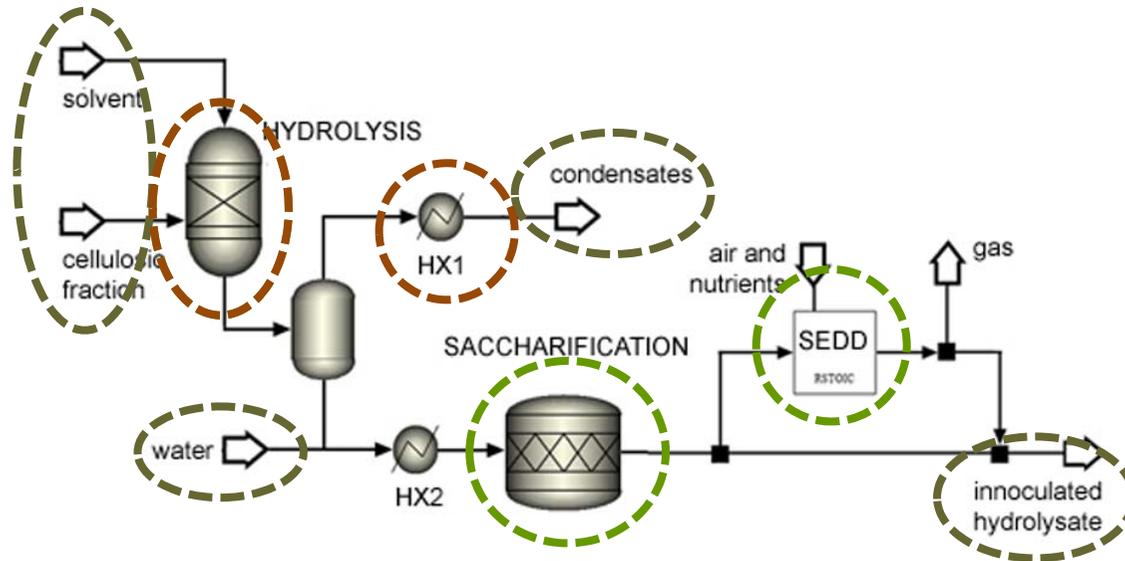
(*DesignSpec*)

20 °C, 1 bar

REDISSOLVING REACTIONS



HYDROLYSIS, SACCHARIFICATION and CULTURE



ENERGY REQUIREMENTS

4633 kW for heating during hydrolysis
4063 kW for condensation
 4 kW for cooling in HX2
 1 kW for heating during saccharification
 8 kW for cooling during culture

YIELDS

26 % of raw material was hydrolyzed
 (7% of cellulose, 100% of hemicellulose, 5% of lignin and 100% of acetate)
95% of cellulose was dissolved into glucose during saccharification
12.1% of glucose and xylose consumed during culture step

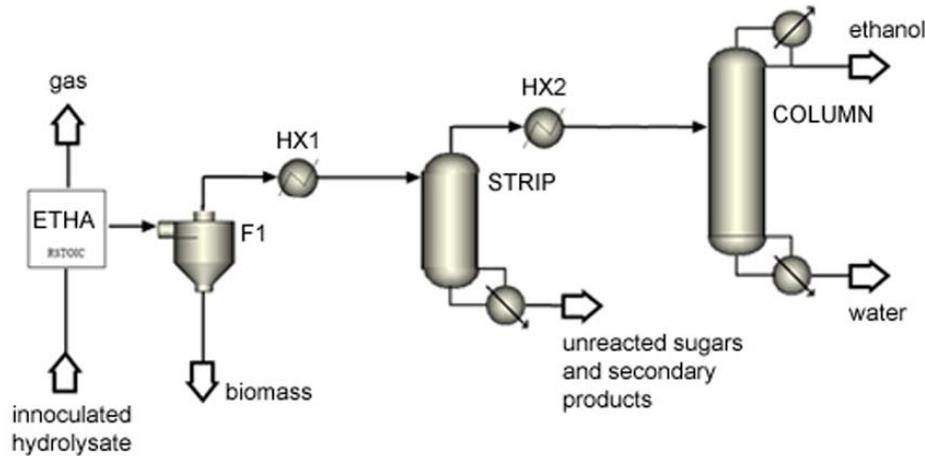
INPUT STREAMS

1000 kg/h lignocellulosic feedstock
6000 kg/h solvent
181 kg/h water for stream conditioning

OUTPUT STREAMS

6413 kg/h condensates
 (recovery of 99 % of furfural and acetic acid and 20% of HMF)
753 kg/h of inoculated hydrolysate
 (for subsequent bio-transformation steps)

ETHANOL PRODUCTION PROCESS



OUTPUT STREAMS

133 kg/h ethanol (92.5% purity)
242 kg/h biomass
1088 kg/h of syrup
(24.6 kg/h of unreacted sugars)
181 kg/h of water from column

ENERGY

164 kW for heating
314 kW for cooling

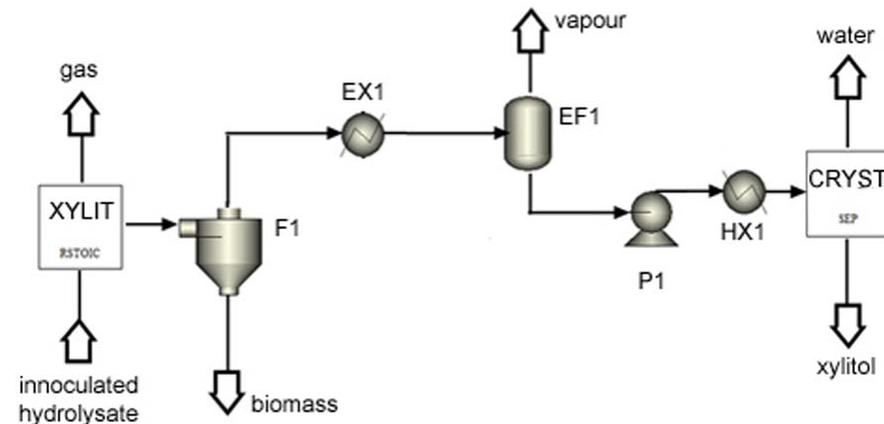
OUTPUT STREAMS

310 kg/h xylitol (14.3% purity)
340 kg/h biomass
790 kg/h of condensate vapour
310 kg/h of water from crystallizer

ENERGY

543 kW for heating
489 kW for cooling

XYLITOL PRODUCTION PROCESS





LACTIC ACID PRODUCTION PROCESS

INPUT STREAMS

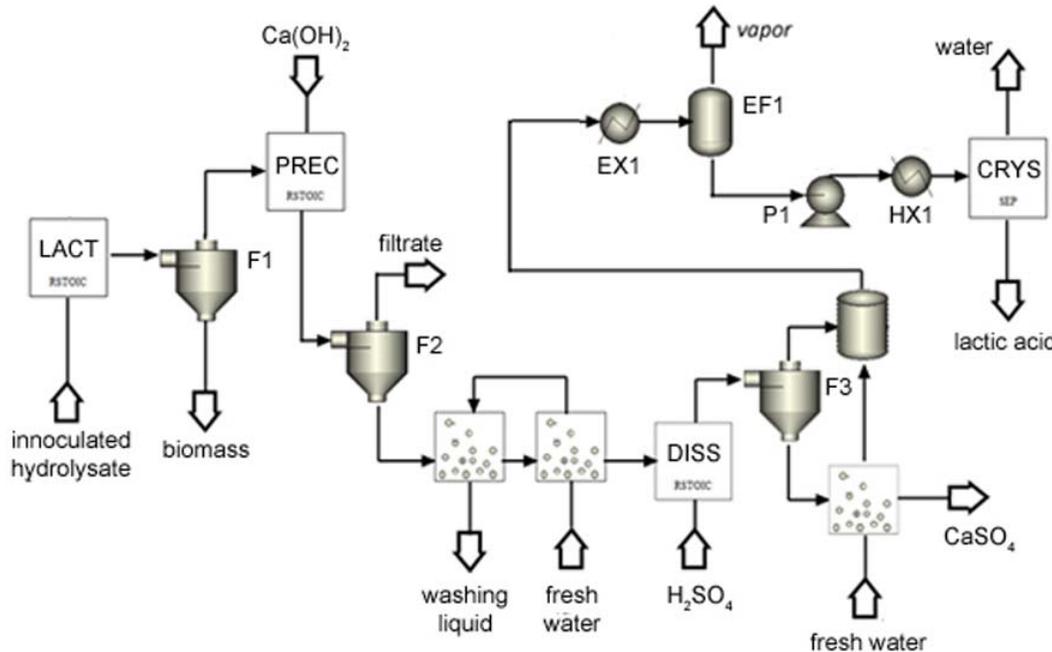
448 kg/h lime 15%
593 kg/h sulphuric acid 15%
898 kg/h water for washing

OUTPUT STREAMS

162 kg/h lactic acid (94% purity)
264 kg/h biomass
1686 kg/h of filtrates
(90% of unreacted sugars)
122 kg/h of washing liquid
235 kg/h of sulphate
1079 kg/h condensed vapour
162 kg/h of water from crystallizer

ENERGY

763 kW for heating
655 kW for cooling



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4th IBEROAMERICAN CONGRESS ON BIOREFINERIES

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Gracias

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