Integral utilization of lignocellulosic materials; residues of the agriculture and agri-food industry

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Building Marie Curie

Luis Jiménez Alcaide→ founder of the original research line. Professor of Chemical Engineering since 1995.

Alejandro Rodríguez Pascual→ Director of the group, Lecturer of the Chemical Engineering Department.

Ana Requejo Silva→ PhD from the University of Córdoba, currently enjoys a Hub Talent scholarship at the University of Natural Resources and Life Sciences (BOKU), Austria

Fátima Vargas González→ PhD student.

Eduardo Espinosa Victor→ PhD student.

Juan Domínguez Robles→ PhD student.

RESEARCH LINE

Biorefinery of lignocellulosic materials from agricultural and agri-food activity

- Production of **cellulosic pulps** from **agricultural residues and agri-food industry** (cereals straw, vine shoots, sorghum stalks, sugar cane bagasse, olive tree prunnings, orange tree prunnings, empty fruit bunches (EFB), and **plants of rapid growth** (leucaena, tagasaste, paulownia, hesperaloe, etc.)

- **Fractionation processes** in order to obtain two fractions from the lignocellulosic materials: one rich in **cellulose and lignin** and other one rich in **hemicellulose**.

- Production of **bioethanol**.

- **Black liquor** (rich in lignin) separation and characterization

- Production of **lignocellulosicnanofibres** from fibers of cellulose of agro-industrial waste.

PROPER USE OF NATURAL RESOURCES

SUSTAINABLE ECONOMY → **THE BEST QUANTITY OF WASTE IS 0**

SOCIAL ASPECTS

INDUSTRIAL ACTIVITY

ECONOMIC BENEFITS

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LIGNOCELLULOSIC BIOMASS

- Forest-based materials, 70 % of the total lignocellulosic materials
- Agricultural origin
- Agro-Industrial origin
- Urban origin, papers or paperboard of cellulosic composition

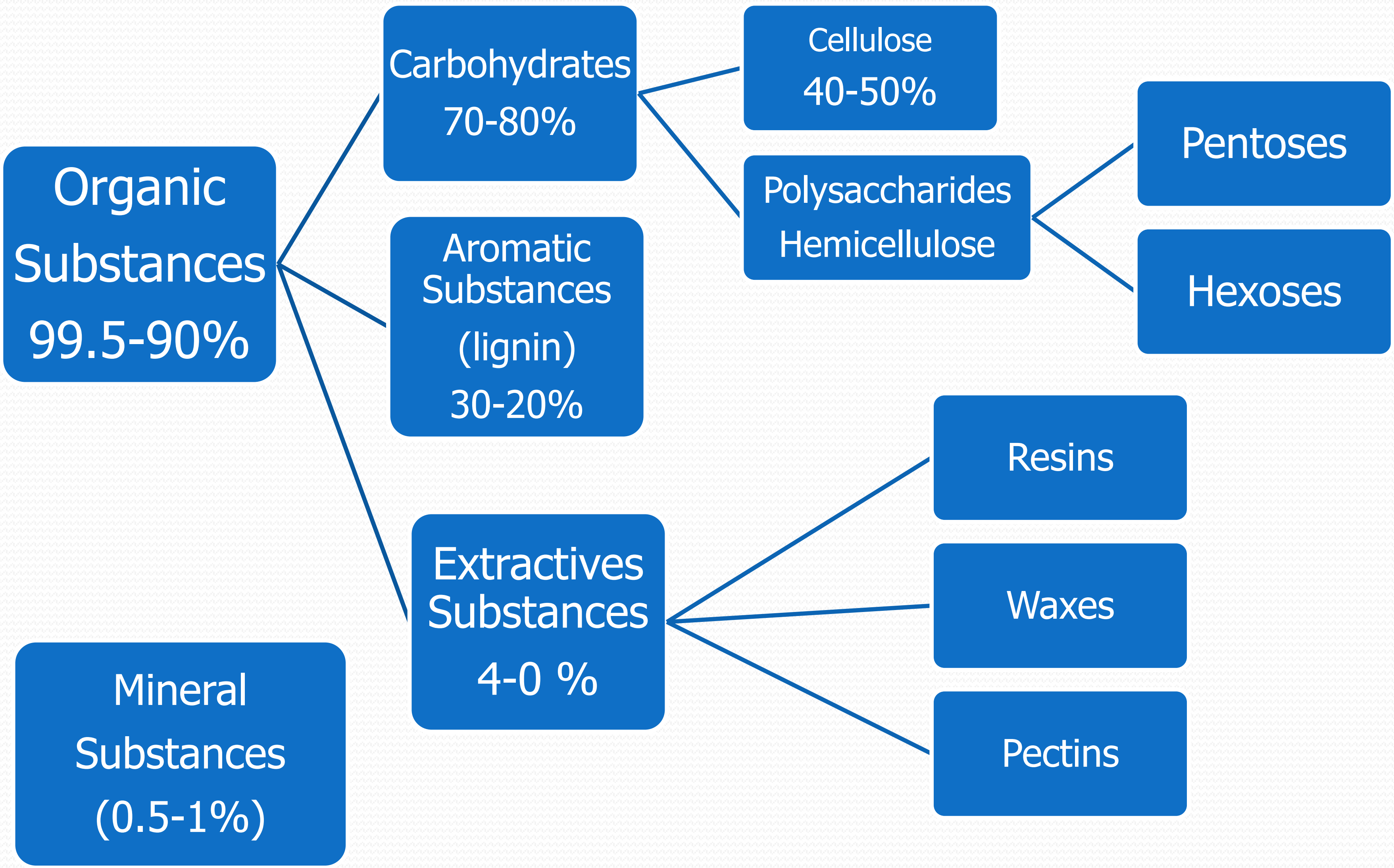
LIGNOCELLULOSIC BIOMASS
Agricultural and industrial origin

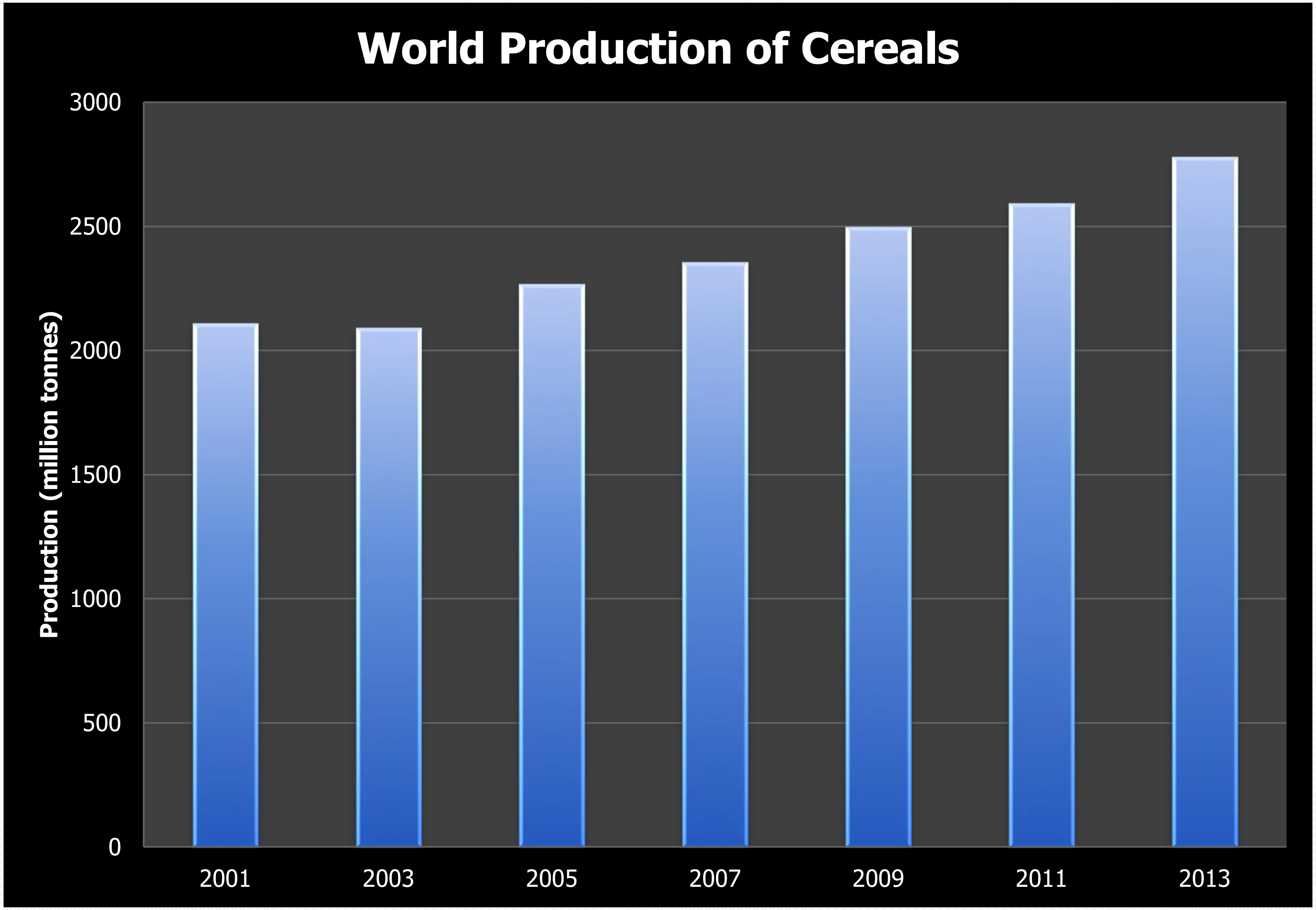
- Agricultural waste, such as cereals straw, pruning of fruit trees, etc.
- Species of rapid growth such as paulownia, tagasaste, hesperaloe, etc.
- Residues of agro-alimentary industries as, sugar cane bagasse, empty fruit bunches, etc.
- No tree species, as flax, jute, hemp, etc.

Assuming that 1 kilogram of product generates between 0.8-1 kg of waste

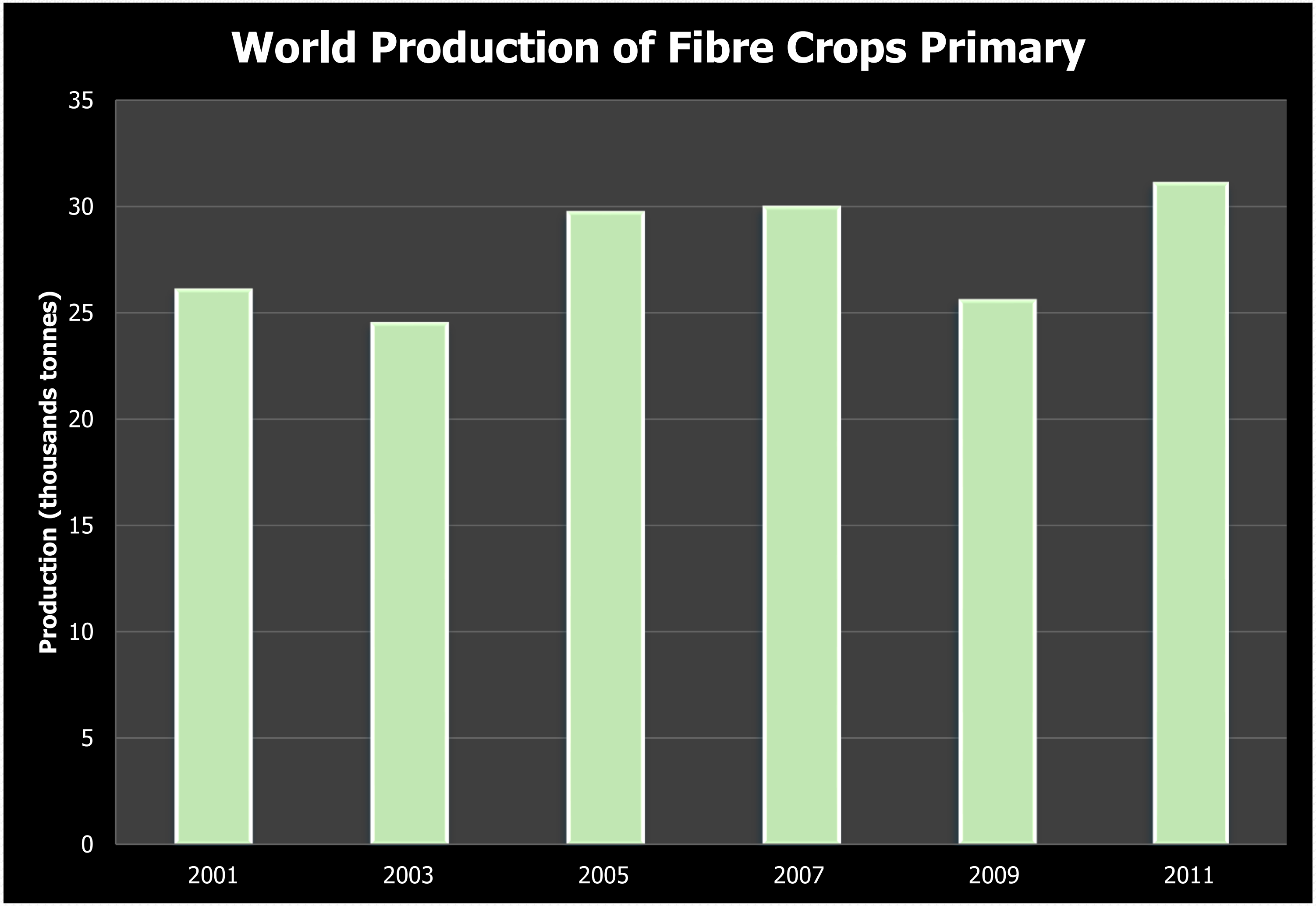
Each year are generated large amounts of waste, with a great potential of application due its composition

LIGNOCELLULOSIC BIOMASS COMPOSITION

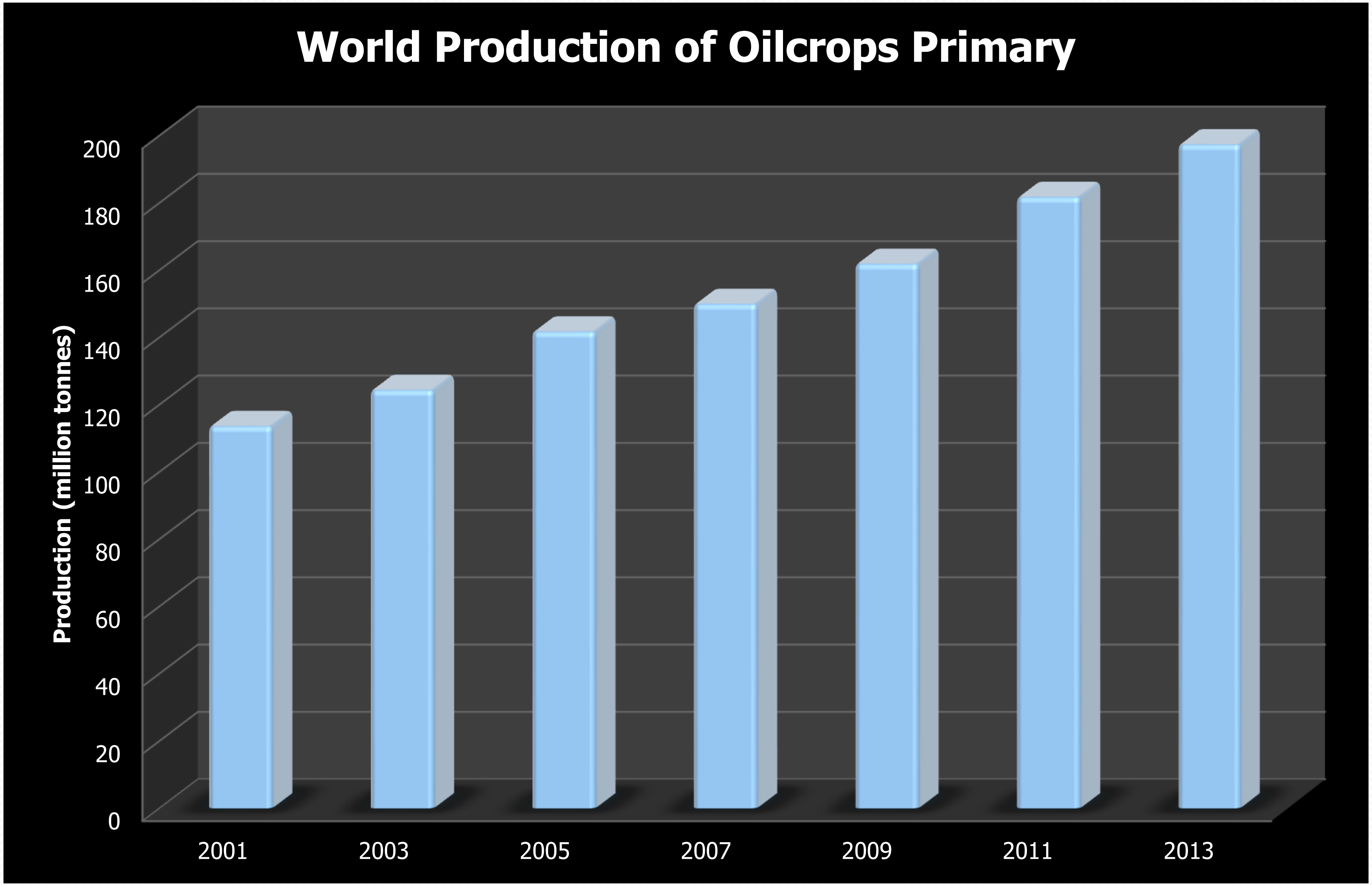




2013 → 2780,7 $*10^6$ tonnes



Jemp, flax, jute, abaca, sisal, etc.



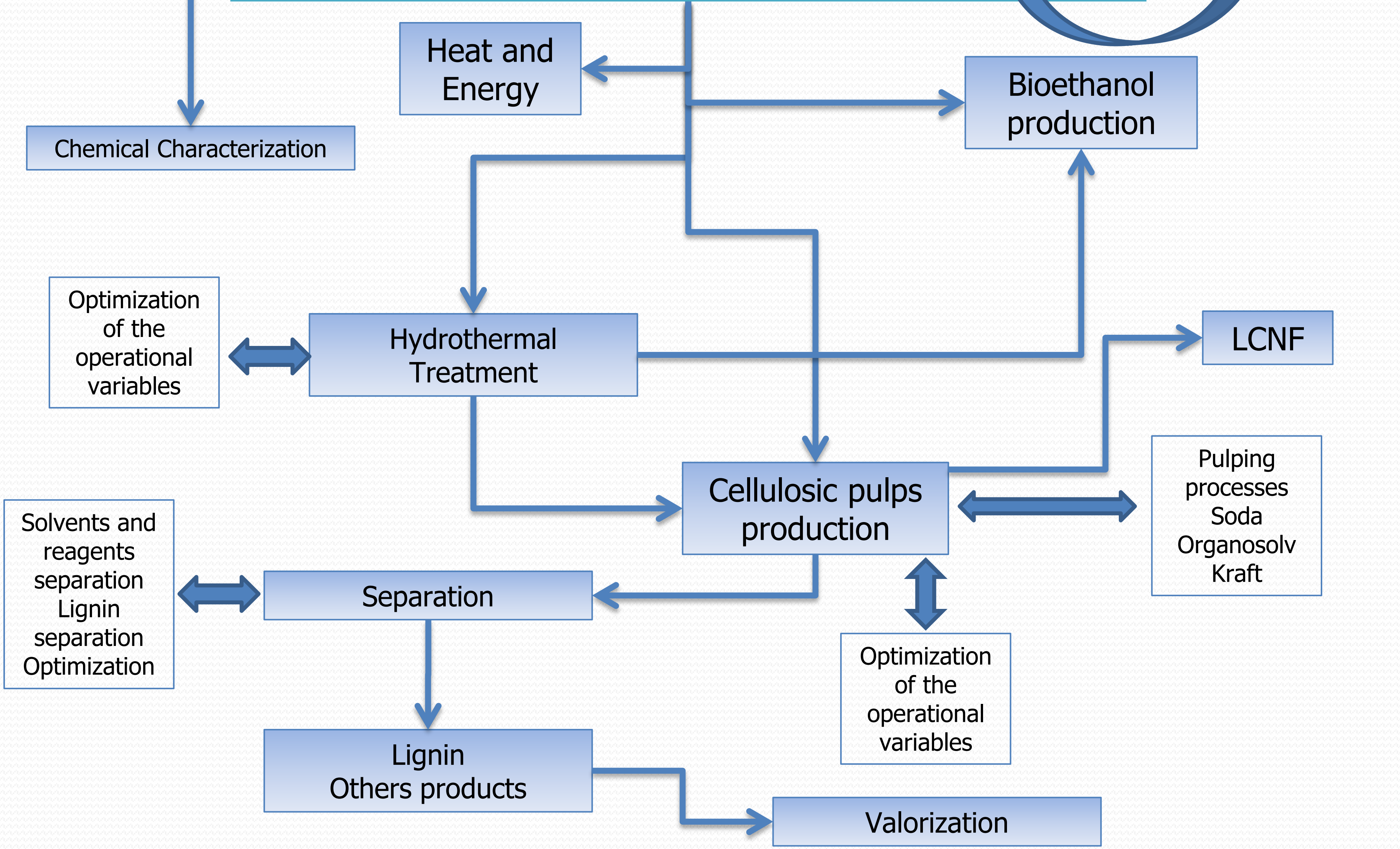
Olives, palm, jojoba, coconuts, etc.

200 $*10^6$ tonnes

LIGNOCELLULOSIC BIOMASS
(agricultural and industrial origin)

- Organic soil amendment
- Feed for animals
- Burnt in the field causing pollution and risk of fire (CO_2 emissions)

RESIDUES FROM AGRICULTURAL ACTIVITY AND AGRI-FOOD INDUSTRY



CELLULOSE

Analysis (%, dry matter basis)	Vine shoots	Olive trimmings (Jiménez et al., 1996)	Wheat straw (Jiménez et al., 1996)	Sunflower stalks (Jiménez et al., 1996)	Cotton stalks (Jiménez et al., 1996)	Rice straw (Alonso, 1976)	Sugar-cane bagasse (Alonso, 1976)
Moisture	8.08 (0.15)	7.14	8.27 (0.51)	10.64	8.89	9.83	7.75
Ash	3.49 (0.28)	1.04	7.22 (1.03)	7.90	2.17	15.39	2.10
Cold-water solubility	12.83 (0.57)	15.5	11.44 (1.85)	22.26	3.41	10.53	4.20
Hot-water solubility	16.09 (0.81)	12.76 (6.37)	13.80 (2.16)	22.72	3.33	16.57	4.40
1% soda solubility	39.21 (3.39)	30.04	43.58 (2.95)	47.81	20.34	46.94	33.92
Ethanol–benzene extractables	4.87 (0.88)	11.49 (1.07)	4.26 (0.35)	4.07	1.42	1.40	1.73
Holocellulose	67.14 (1.65)	64.74 (6.23)	74.78 (2.01)	71.76	72.86	70.60	80.20
α-Cellulose[a]	41.14 (2.03)	59.04 (4.07)	53.12	58.67	58.48		
β- and γ-Cellulose[a]	58.86 (3.47)	43.33	48.78	41.33	42.00		
Lignin	20.27 (0.93)	18.94 (1.97)	17.85 (0.81)	13.44	21.45	25.23	19.80

Analysis (%, dry matter basis)	Esparto (Alonso, 1976)	Flax fibres (Alonso, 1976)	Flax stalks (Alonso, 1976)	Reed (Alonso, 1976)	Eucalyptus (Jiménez et al., 1996; Alonso, 1976)	Pine (Jiménez et al., 1996; Alonso, 1976)
Moisture	7.33	7.88	7.47	8.69	7.36 (0.00)	7.27 (0.00)
Ash	2.30	5.06	2.10	4.87	0.53 (0.06)	0.45 (0.13)
Cold-water solubility	7.32	15.23	4.35	13.52	2.52 (0.14)	1.58 (1.20)
Hot-water solubility	8.48	15.39	5.10	15.82	2.88 (0.05)	1.95 (0.06)
1% soda solubility	34.01	30.86	23.54	38.90	12.62 (0.28)	9.94 (2.76)
Ethanol–benzene extractables	3.24	3.57	1.21	4.40	1.28 (0.18)	1.75 (1.17)
Holocellulose	75.95	75.65	82.39	72.77	79.97 (0.71)	68.59 (1.41)
α-Cellulose[a]					66.01	81.53
β- and γ-Cellulose[a]					34.61	19.93
Lignin	18.01	13.27	19.62	19.02	20.60 (0.91)	27.54 (1.86)

Jiménez *et al*., 2006, Industrial Crops and Products 23, 122-130

CELLULOSE

Soda process

NaOH 12%
170 ºC
60 min
L/S 6

VINE SHOOTS

Kraft process

NaOH 12%
Sulphity 20%
170 ºC
60 min
L/S 6

Yield 32.1 %
Ash 4.36 %
Holocellulose 79.4 %
α-cellulose 70.0 %
Lignin 24.1 %

Yield 29.2 %
Ash 3.93 %
Holocellulose 84.2 %
α-cellulose 73.7 %
Lignin 17.2 %

Jiménez *et al.*, 2006, Industrial Crops and Products 23, 122-130

CELLULOSE

Physical properties of papersheets made with vine shoots as raw material

Pulp	Schopper Riegler ºSR	Breaking length m	Stretch %	Burst Index, kN/g	Tear Index, mNm^2/g
Soda	21	659	1.89	1.01	0.9
Kraft	25	1316	4.72	1.63	1.59

Jiménez *et al*., 2006, Industrial Crops and Products 23, 122-130

CELLULOSE

Holocellulose 61.5 %
α-cellulose 35.7 %
Lignin 19.7 %

OLIVE TREE PRUNINGS

NaOH 15%
180 ºC
60 min
L/S 6

Yield 49.1 %
Kappa Number 109.7
Breaking length 556.7 m
Burst Index 24.20 kN/g
Tear Index 0.9 mNm^2/g

Jiménez *et al*., 2004, Holzforschung, 58pp 122-128

CELLULOSE

Ash 3.4 %
Holocellulose 73.2 %
α-cellulose 48.0 %
Lignin 19.95 %

ORANGE TREE PRUNINGS

Soda-AQ process

NaOH 10-16%
155-185 ºC
40-90 min
L/S 8
AQ 1%

Kraft-AQ process

NaOH 10-16%
Sulphity 20%
155-185 ºC
40-90 min
L/S 8
AQ 1%

AFTER REFINING PROCESS

Soda-AQ:
Yield 51.7 %
ºSR 51.5
TI 62.76 Nm/g
TeI 2.83 mNm^2/g

Kraft-AQ:
Yield 53.8 %
ºSR 64.6
TI 91.1 Nm/g
TeI 3.19 mNm^2/g

González *et al.*, 2013, BioResources, 8(4), 5622-5634

CELLULOSE

ABACA

Raw material	Ash, %	Lignin, %	Holocellulose, %	α-cellulose, %
Abaca	1.35	10.4	87.9	67.9

"Soda process"

5-10% NaOH

150-170ºC

15-45 min

L/S ratio = 6:1

Raw material	Yield %	Kappa Number	Viscosity mL/g	Breaking length m	Stretch Index %	Tear Index mNm^2/g
Abaca	72.8-78	10.6-35.7	1121-1411	4874-5231	4.30-4.76	14.2-18.3

Jiménez *et al*., 2005, Bioresource

CELLULOSE

Hesperaloe funifera

Raw material	Ash, %	Lignin, %	Holocellulose, %	α-cellulose, %
Hesperaloe funifera	5.9	7.9	74.1	52.3

10 % NaOH, 1% AQ
155ºC, 30 min
L/S 8

Raw material	Yield %	Kappa Number	Viscosity mL/g	Tensile index Nm/g	Stretch index %	Burst index kN/G	Tear index mNm^2/g
Hesperaloe funifera	48.3	15.2	737	83.6	3.8	7.34	3.20

Sánchez *et al*., 2010, Biomass and Bioenergy 34, 1471-1480

CELLULOSE

TAGASASTE

Raw material	Ash, %	Lignin, %	Holocellulose, %	α-cellulose, %
Tagasaste	0.9	18.5	80.3	40.4

16% NaOH
180ºC, 60 min
L/S 8:1

Raw material	Yield, %	Kappa Number	Brightness, %
Tagasaste	41.2	26.5	30.3

Alfaro *et al.*, 2010, Bioresource Technology, 101, 7635-7640

CELLULOSE

EFB

Raw material	Ash, %	Lignin, %	Holocellulose, %	α-cellulose, %
EFB	3.2	24.5	67.0	47.9

10-20% NaOH
155ºC – 185ºC
30 - 90 min
L/S 4:1 - 8:1
% AQ 0 - 1

Raw ma-terial	Yield, %	Kappa Number	Visco-sity, mL/g	Tensile index, Nm/g	Stretch, %	Burst index, Kpam^2/g	Tear index, mNm^2/g	Bright-ness, %
EFB	29-46.3	15.8-74.3	282-849	8.7-25.8	1.24-2.97	0.49-1.90	0.26-0.55	44.7-65.1

Jiménez *et al*., 2009, Bioresource Technology, 100, 1262-1267

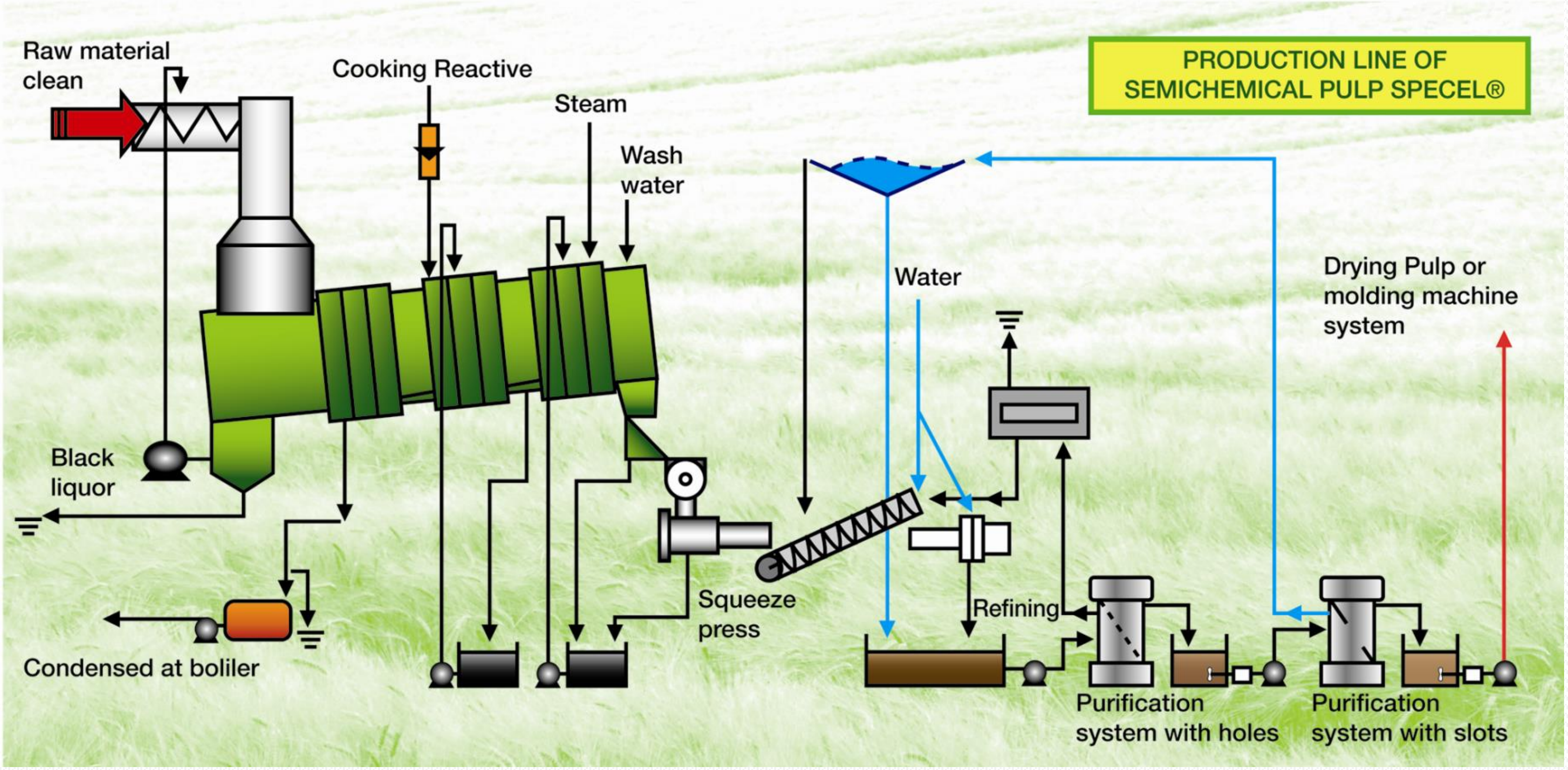
CELLULOSE

CEREAL STRAWS

Raw material	Alcohol extractives, %	Ash, %	α-cellulose, %	Hemicellulose, %	Lignin, %
Oats	6.4	7.00	37.9	37.7	16.6
Maize	6.8	5.95	44.0	30.7	18.2
Rapeseed	7.9	6.38	37.0	36.5	17.2
Barley	8.1	9.49	34.0	27.7	16.3
Wheat	5.2	7.72	39.7	30.6	17.7

CELLULOSE

CEREAL STRAWS



NaOH 7%
100 ºC
150 min,
L/S 10

CELLULOSE

CEREAL STRAWS

Raw material	Yield, %	Beating Degree, ºSR	Kappa number	Viscosity, mL/g
Oats	66.9	36	71.5	465
Maize	65.5	47	56.7	996
Rapeseed	63.1	29	115.1	184
Barley	65.6	61	57.5	468
Wheat	70.0	51	38.6	536

CELLULOSE

CEREAL STRAWS

Raw material	Tensile index, Nm/g	Stretch index,%	Burst index, kN/g	Tear index, mNm^2/g	Brightness, %
Oats	64.0	1.84	2.966	2.049	57.1
Maize	68.2	1.85	3.284	2.837	60.2
Rapeseed	42.8	1.21	1.630	2.207	64.3
Barley	63.9	1.75	3.169	2.300	55.7
Wheat	43.5	2.71	2.330	2.620	60.0

HEMICELLULOSE

Rice straw

Hydrothermal treatment

150 – 190 ºC
0 – 20 min
L/S 6 – 10

Optimal conditions

190 ºC
15 min
L/S 9

Glucose 1.92 g/L
Xylose 3.97 g/L
Arabinose 0.99 g/L
Acetic acid 1.96 g/L

Rodríguez*et al*., 2009, Bioresource Technology, 100, 4863-4866

Hesperaloe funifera

Hydrothermal treatment catalyzed

150 – 190 ºC
0 – 20 min
0 – 0.5% H_2SO_4
L/S 8

Optimal conditions

170 ºC
20 min
L/S 8

Glucose 4.62 %
Xylose 10.56 %
Arabinose 1.28 %

Sánchez*et al*., 2011, Biochemical Engineering Journal 56,130-136

HEMICELLULOSE

Olive tree prunings

Hydrothermal treatment

150 – 190 ºC
0 – 20 min
L/S 6 – 8
0.1 – 0.5% H_2SO_4

Optimal conditions

186 ºC
18 min
L/S 7
0.1 % H_2SO_4

Glucose 5.33 %
Arabinose 2.76 %

Requejo *et al*., 2012, BioResources 7(1), 118-134

Empty fruit bunches

Hydrothermal treatment catalyzed

150 – 190 ºC
0 – 20 min
0 – 0.5% H_2SO_4
L/S 6 – 8

Optimal conditions

190 ºC
15 min
L/S 6
0.1 % H_2SO_4

Glucose 3.12 g/L
Xylose 4.0 g/L
Arabinose 2.35 g/L
Acetic acid 2.28 g/L

Ferrer *et al*., 2013, Bioresource Technology, 129, 506-511

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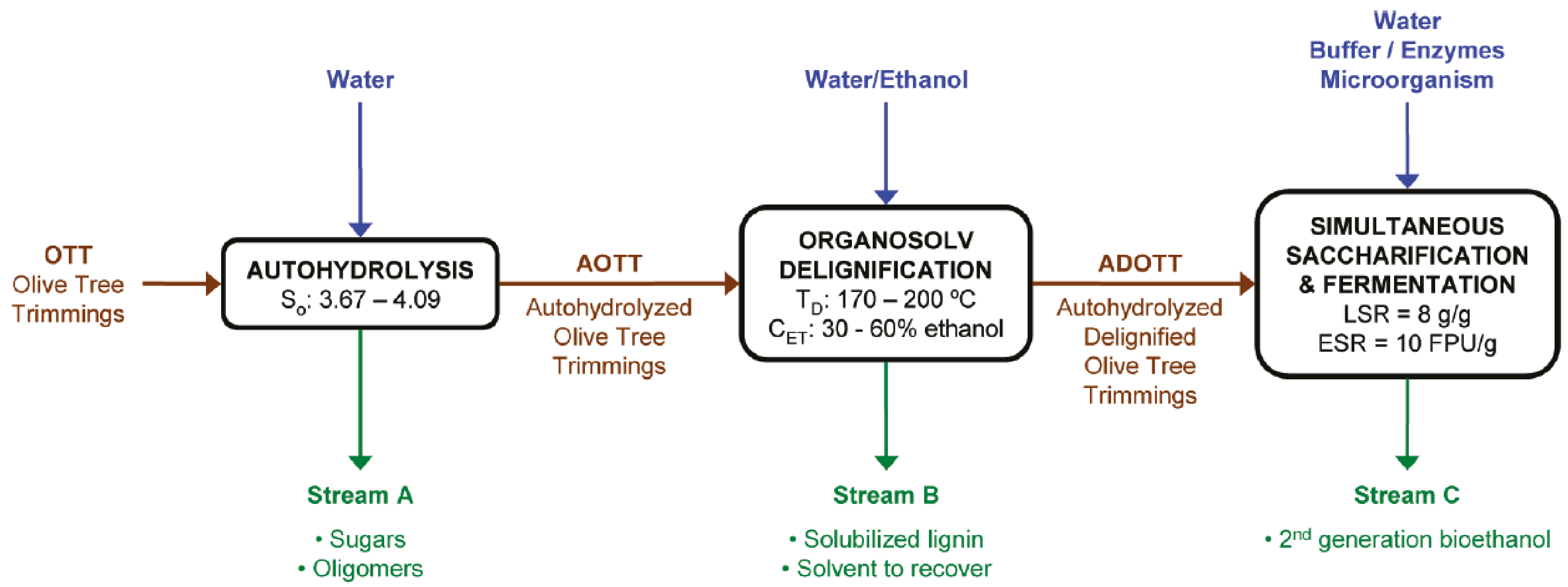
BIOETHANOL

OLIVE TREE PRUNINGS



Ethanol concentration of fermented media reached values up to 39 g/L

Requejo*et al*., 2011, Energy and Fuel, 25(10), 4803-4810

Combustion: Calorific Value (CV)

Lignocellulosic Material	kJ/kg
Main fraction of orange tree prunings	18,626
Residual fraction of orange tree prunings	16,870
Main fraction of olive tree prunings	19,110
Residual fraction of olive tree prunings	18,699
Hesperaloe funifera	17,57
EFB	19,045
Banana	17,751

Fuel	CV (MkJ/t)	Fuel cost (€/t)	Heat unit cost (€/MkJ)
Main fraction of orange tree prunings	18.63	60	3.22
Residual fraction of orange tree prunings	16.87	30	1.78
Main fraction of olive tree prunings	19.11	60	3.14
Residual fraction of olive tree prunings	18.70	30	1.60
Hesperaloe funifera	17.76	60	3.38
EFB	19.05	30	1.57
Banana	17.75	60	3.38
Mineral coke	25.94	100	3.86
Diesel heating	37.67	800	21.24
Commercial propane	43.89	1.650	37.59

LIGNONANOFIBERS

WHEAT STRAW
CELLULOSIC FIBERS
SPECEL© PROCESS

UNBLEACHED
(high lignin values
vs bleached pulps)

MECHANICAL TREATMENT
PFI refiner until 90ºSR

TEMPO OXIDATION
NaClO + TEMPO + NaBr

ENZYMATIC HYDROLYSIS
PFI refiner 4000 rpm +
endoglucanase FiberCare®

LIGNOCELLULOSIC NANOFIBERS (LCNF)

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LIGNONANOFIBERS

MECHANICAL TREATMENT

TEMPO OXIDATION

ENZYMATIC HYDROLYSIS

4 times at 300 bars
3 times at 600 bars
3 times at 900 bars

a) Enzymatic Hydrolysis, b) TEMPO, c) Mechanical Treatment

LNFC	Cost (€/kg)
TEMPO	205.61
Enzymatic Hydrolysis	13.64
Mechanical Treatment	2.24

CONCLUSIONS

It is possible to use the agriculture residues to obtain differents products

In some cases the yield of the process is not so high (but at least reduce the quantity of the residue)

It is possible to apply to a raw material the full biorefinery scheme

WEAKNESSES –> problems with the cost of harvesting and transport because the raw materials are localized in large areas. In some cases, the established processes do not allow to introduce these new processes

THANK YOU FOR YOUR ATTENTION

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