Waste biorefinery technologies for accelerating sustainable energy processes

Fractionation of lignocellulosic biomass: status, challenges and opportunities

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Laboratório Nacional de Energia e Geologia

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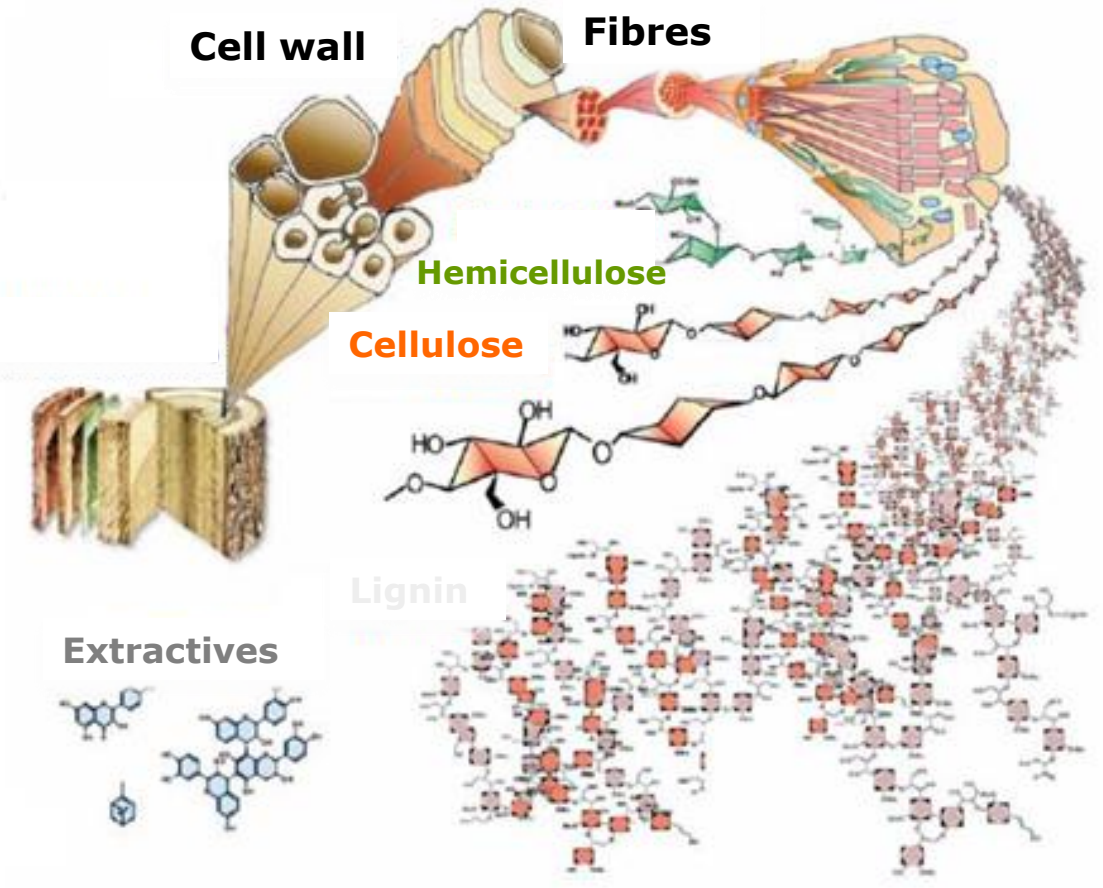
Biomass composition

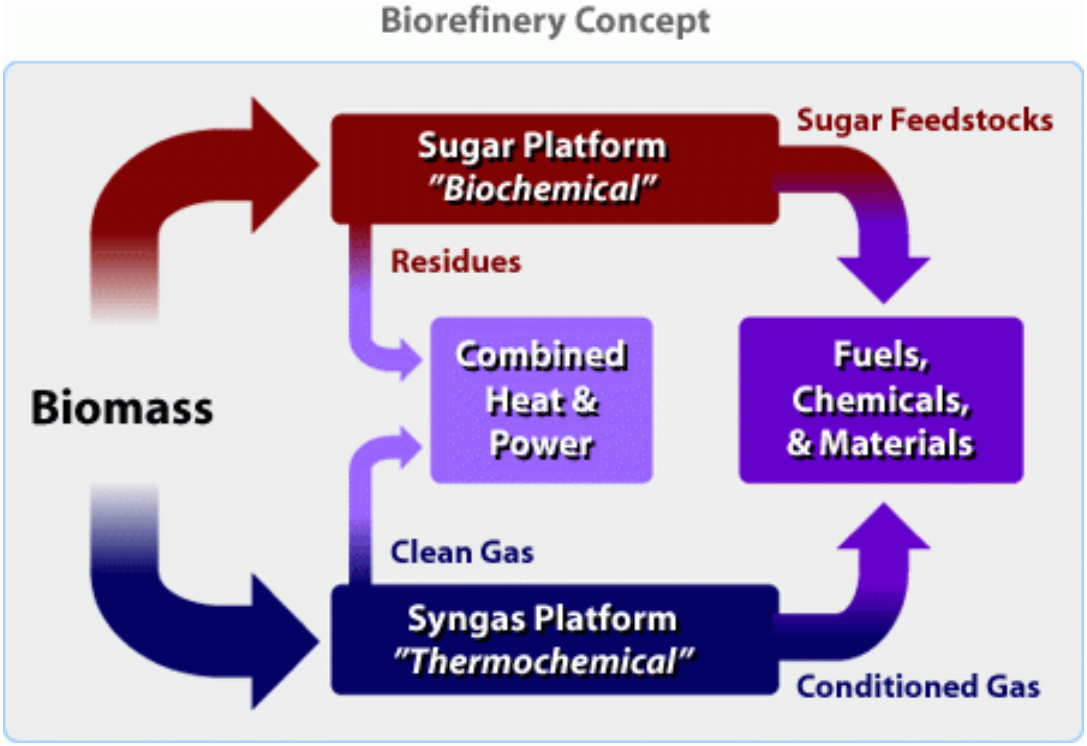


Per Hoffmann, Oskar Faix and Ralph Lehnen

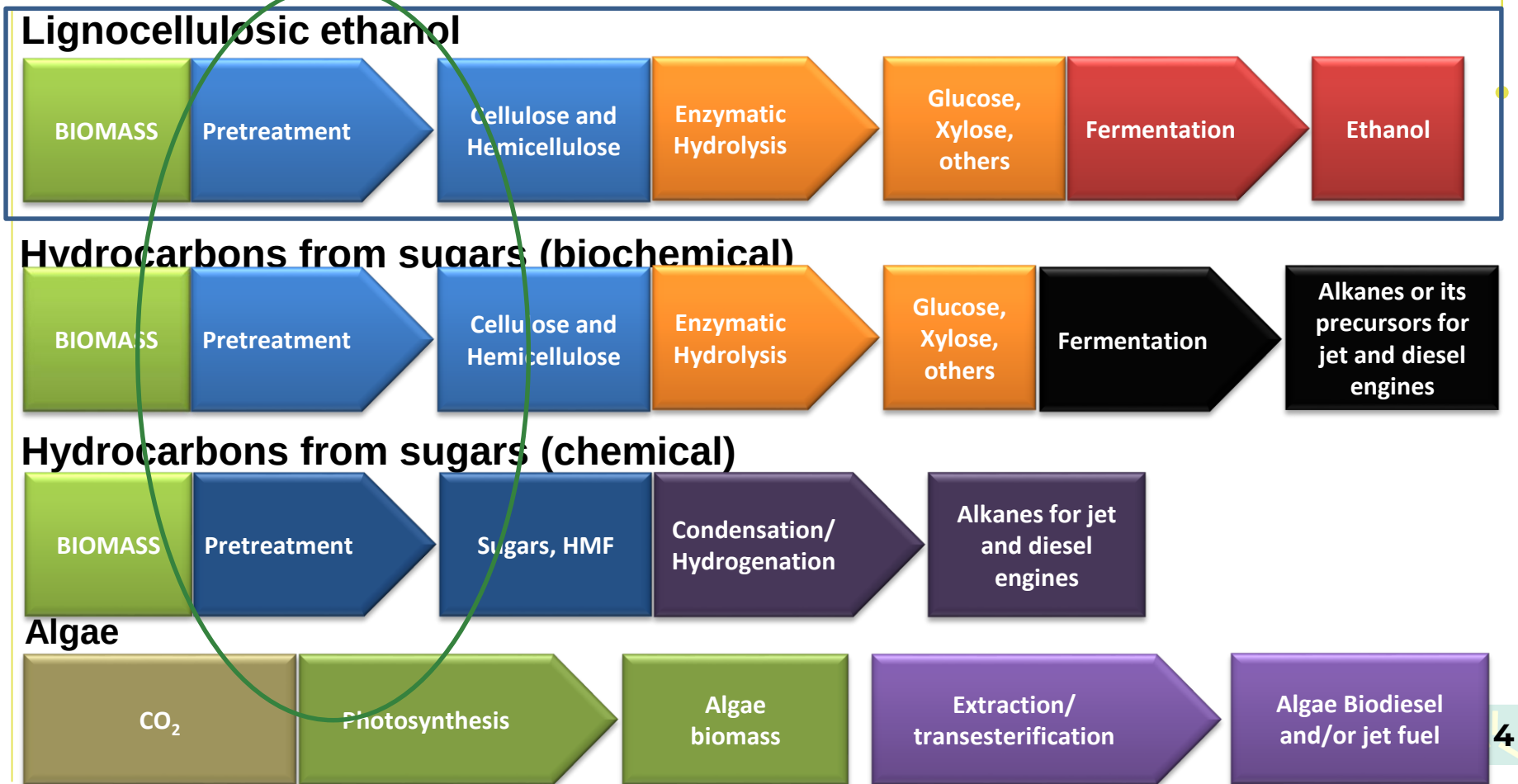
Typical chemical composition of lignocellulosic materials (in %)

	Softwood	Hardwood	Herbaceous
Cellulose	45-50	45-55	25-40
Hemicellulose	25-40	25-35	25-50
Lignin	18-25	25-35	10-30

Biorefineries



Biorefineries: Biochemical platform



Pre-treatment/fractionation

Objectives

- Selective fractionation
- Aiming to RECOVER ALL fractions
- To get VALUE from ALL biomass components
- By their SELECTIVE conversion to biofuels and bioproducts

Limitations

- Selectivity (weak)
- Inhibitors formation
- High use of energy and/or chemicals
- It is not a mature technology

Pre-treatment/fractionation

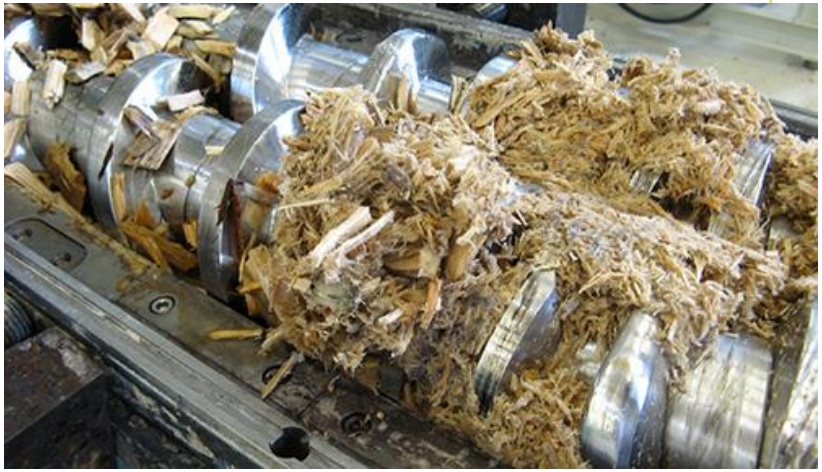
Main pretreatment options

Physical	Chemical	Physico-chemical	Biological
Milling	Acid processes	Autohydrolysis/ Liquid hot water	Brown-, white- and soft-rot fungi
Grinding	Alkaline processes	Steam explosion	
Extrusion	Organosolv	Wet oxidation	
Ultrasound	Ozonolysis	Sub- and supercritical fluids	
Irradiation (microwaves, ɣ-irradiation)	Ionic liquids		
	Deep euctetic solvents		

*Carvalheiro, F., Duarte, L.C., Bogel-Lukasik, R., Moniz, P. (2013) Boletim de Biotecnologia., Série 2, **3**, 7-10*

Pre-treatment/fractionation

Physical processes



✘ High energy demanding

✓ No chemicals are (generally) required

However,

- ❑ Milling/grinding cannot be used as a sole pre-treatment
- ❑ Extrusion can be effective, but mainly if combined with chemicals
- ❑ The interest in **ultrasound** and **irradiation** is growing: effective for specific applications (e.g., removal of extractives) or when combined with chemicals (as **physico-chemical** processes)

Pre-treatment/fractionation

Chemical & Physico-Chemical processes

Selected (first) fraction	Lignin		Hemicelluloses				Cellulose
Process	**Organosolv**	**Alkali**	**LHW**	**Steam explosion**	**Dilute acid**	**Conc. acid**	**Enzymatic hydrolysis**
Selectivity	++	+	+++	++	++	+	+++
Recovery	+++	+++	+++	+	+++	++	++
Enzymatic digestibility	+	+	++	+++	++	N.A.	N.A.
Equipment protection	0 / +	---	++	0	---	- / 0	+++
Energetic efficiency	+++	+++	++	+	+	++	+++
Catalyst recovery	+	---	N.A.	N.A.	---	---	++
Residues prevention	+++	---	+++	+++	---	---	+++
Energy requirements	++	+	++	++	++	+	0
Pilot scale	Yes	Yes	Yes	Yes	Yes	Yes	Yes

LHW- liquid hot water/autohydrolysis

Processes for HC extraction first

Dilute acid hydrolysis

i) Acid type

- H_2SO_4, HCl, HNO_3, TFA, H_3PO_4, CH_3COOH (and other carboxylic acids)

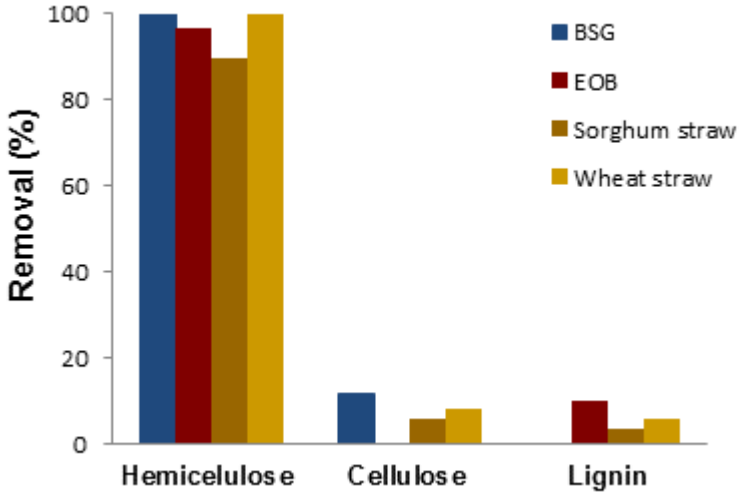
√ **Main process option amongst acid processes**

✗ **Industry tends to avoid them (high equipment corrosion)**

Processes for HC extraction first

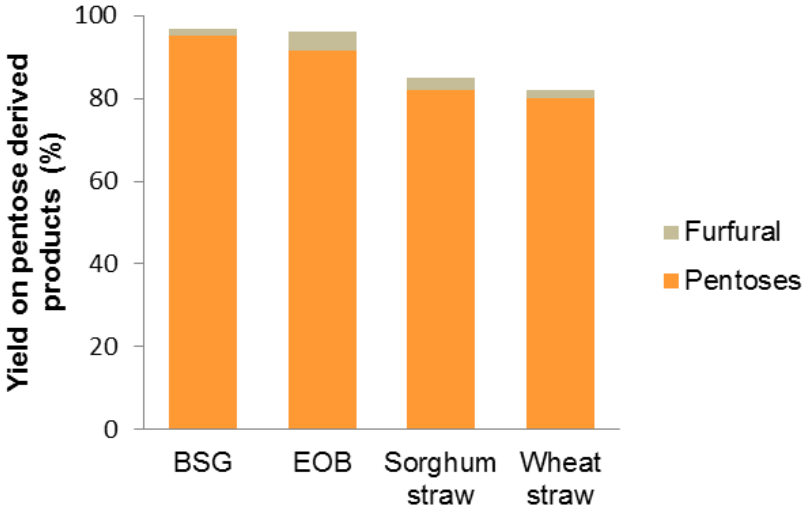
Dilute acid hydrolysis

Polymers solubilization



BSG – Brewery's Spent Grains; EOB – Olive Oil Bagasse

Hemicellulose derived products



Data from: *Carvalheiro et al. (2004); Silva-Fernandes et al. (2009); Morais et al. (2012); Torrado et al. (2012)*

- Mainly produces the **hydrolysis of hemicelluloses** with **high pentose yield**
- **Cellulose** and **lignin** recovered in the solid phase ate high yield

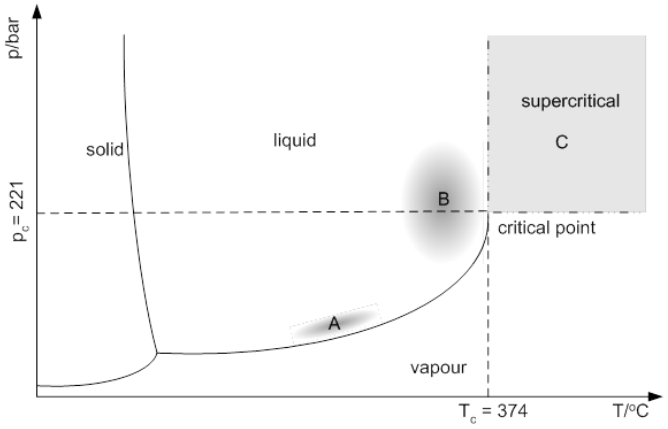
Processes for HC extraction first

Hydrothermal processes

A competitive alternative to dilute acid processes

- **Autohydrolysis (or LHW) (A)**
- **Steam (A)**
- **Steam explosion (A)**
- **Subcritical water (B)**
- **Supercritical water (C)**

Typical ranges for water based processes as a function of T, p



Catalysts oh hydrolysis

i) **hydronium** ions generated from **water** ionization

ii) **hydronium** ions generated from **acetic acid**

Processes for HC extraction first

Autohydrolysis/liquid hot water

- Biomass mixed with **water** and heated to a defined temperature
- Temperatures are usually in the range 150-230ºC, minutes-hours

LNEG infrastructure (BBRI 1 facility)

Steam explosion

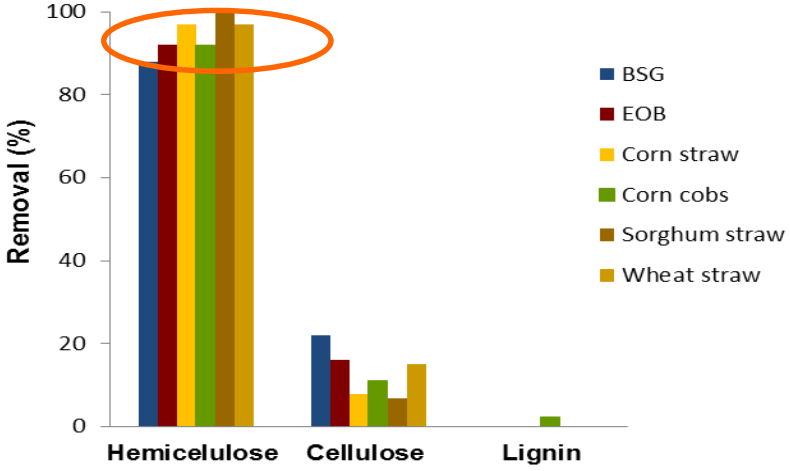
Thermo-mechano-chemical process

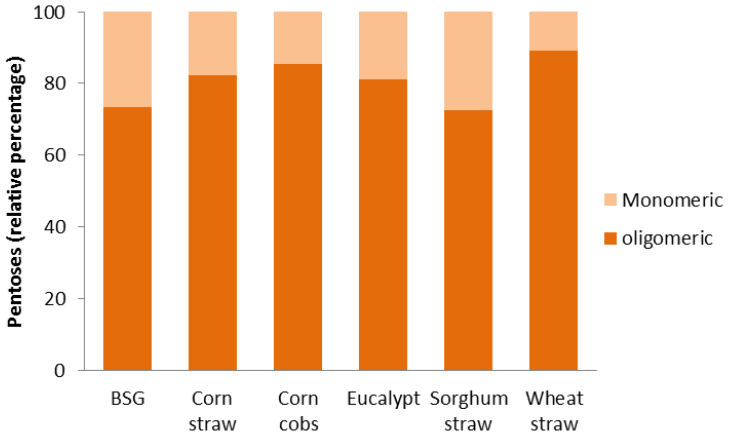
Steam (heat)	Shear forces (expansion)	Hydrolysis (chemical)

- **Saturated steam** (< 240ºC), few seconds to several minutes
- Biomass is wetted by steam and **exploded** leading to **disaggregation** of lignocellulosic matrix and **ultrastructure modification**

Processes for HC extraction first

Hydrothermal (Autohydrolysis/liquid hot water)





BSG – Brewery's Spent Grains
EOB – Olive Oil Bagasse

Data from: *Bernardo (2011); Carvalheiro et al. (2005); Carvalheiro et al. (2009) Moniz et al. (2009); Moura et al. (2007): Silva-Fernandes et al. (2010)*

- Mainly produces the **hydrolysis of hemicelluloses** with **high pentose yield** (mainly in the oligomeric form)
- Recovery of cellulose and lignin in the solid phase with high yield (low degradation)

Processes for Lignin extraction first

Alkaline processes

i) Hydroxides: NaOH, KOH, $Ca(OH)_2$ (lime)

ii) Ammonia

- Soaking in aqueous ammonia (SSA)
- Ammonia recycling percolation (ARP)
- Ammonia fibre explosion (AFEX)

Processes for Lignin extraction first

i) Hydroxides (NaOH, KOH, $Ca(OH)_2$) processes

- Solubilisation of lignin (and hemicelluloses)
- **Mild temperatures** (30-130ºC) and pressures
- Increase of cellulose digestibility
- Lignin removal can be improved by the addition **oxidant agents** (O_2/H_2O_2) to $Ca(OH)_2$/ NaOH

✓ Low capital costs and energy requirements

✘ Alkali is converted to irrecoverable salts/incorporated as salts into biomass

✘ Low quality **lignin**

Processes for Lignin extraction first

ii) Organosolv

- ❑ Water/**organic solvents** (acetone, ethanol, methanol, butanol)
- ❑ Organic solvent can be used in combination with a catalyst (e.g., **acids**
- ❑ Temperature: room - 200ºC (typically 150-200ºC)
- ❑ Solubilisation of **lignin** and hydrolysis of hemicelluloses

- ✓ Organosolv processes may potentially increase the **overall yields** (**sugars** and **lignin**) obtained from biomass
- ✓ Organosolv enable the production of high pure lignins
- ✘ **Overall economy depends on the solvent recycling**
- ✓ **Solvents like ethanol are easily recycled (distillation)**

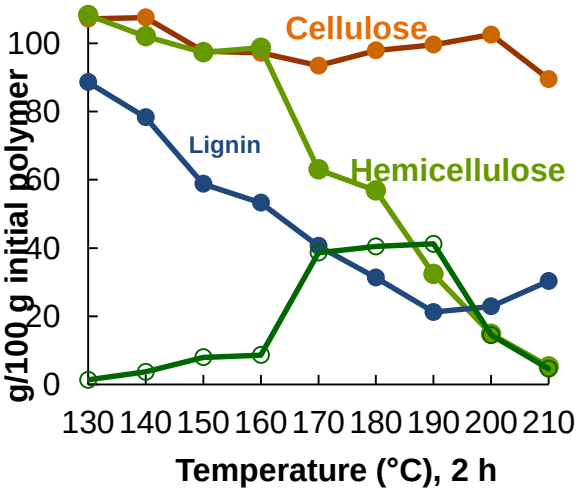
Processes for Lignin extraction first

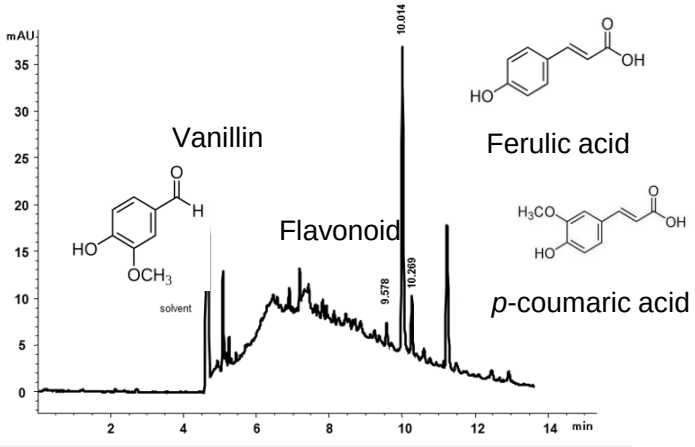
Organosolv

Feedstock: Corn cobs, rice straw

Low molecular weight lignins:
Mn < 606 g/mol
Mw < 2011 g/mol
PD < 3.3
S/G 0.78

Delignification yield





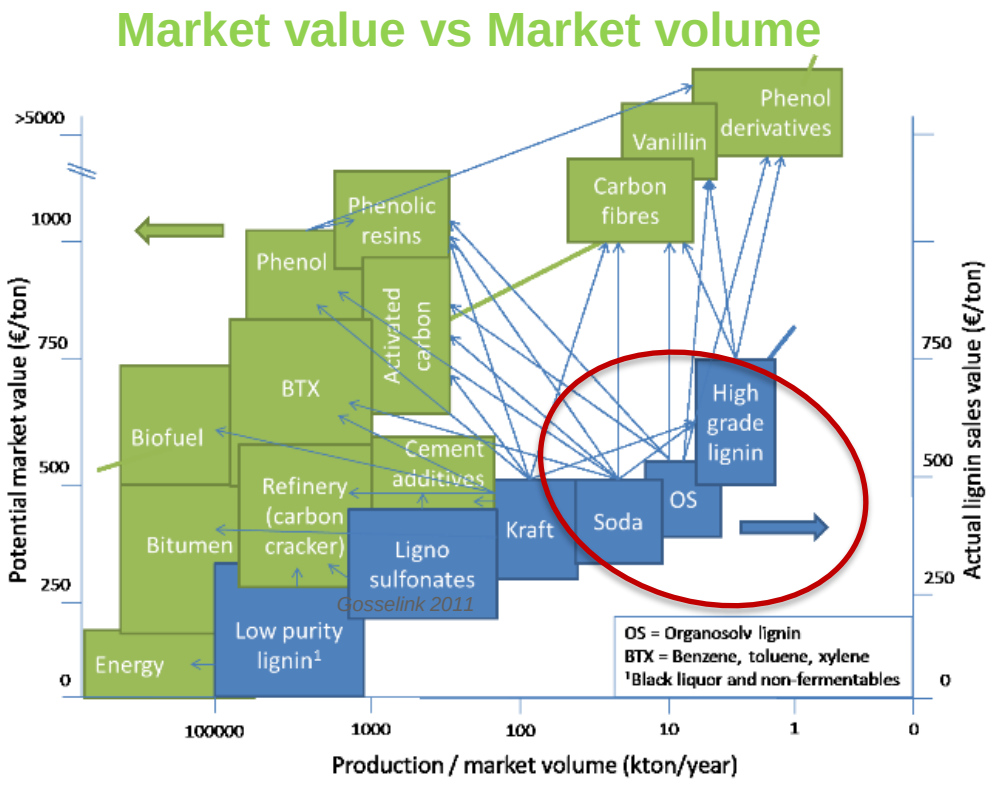
Fialho et al. (2015), 3-CIAB, Chile

Moniz et al. (2015) Bioresources, 10, 2626-2641

High delignification yield, high quality lignin and lignin-derived compounds

Processes for Lignin extraction first

Organosolv

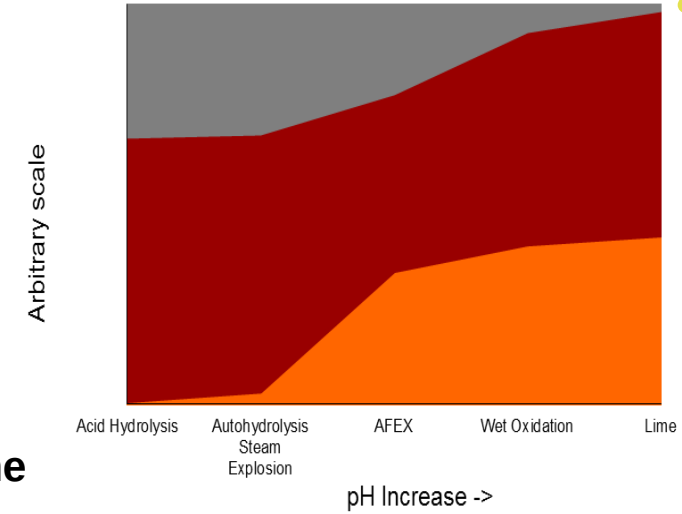


- Lignins of high value
- Different (potential) applications

CONCLUSIONS

What do we expect from a pretreatment?

- Low energy demanding
- Low cost
- Low levels of (non-harzard) catalys
- Selective
- One-pot but multireaction process



- There is no single method that can fulfill all the requirements for the effective biomass fractionation
- Use of combined/sequential processes targeting different fractions, i.e., the separate recovery of hemicellulose and lignin may be advantageous

Many Thanks

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