Conceptos Modernos de Fraccionamiento de Biomasa en Biorefinerias

Modern Concepts for Biomass Deconstruction Under Biorefineries

Florbela Carvalheiro

2nd SMIBIO Workshop

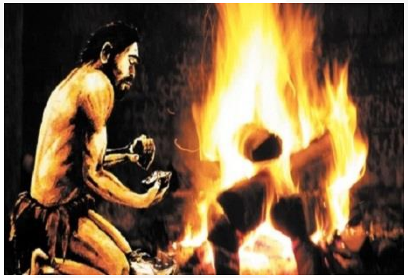
Small-scale Biorefineries for Rural Development in Latin America and Europe

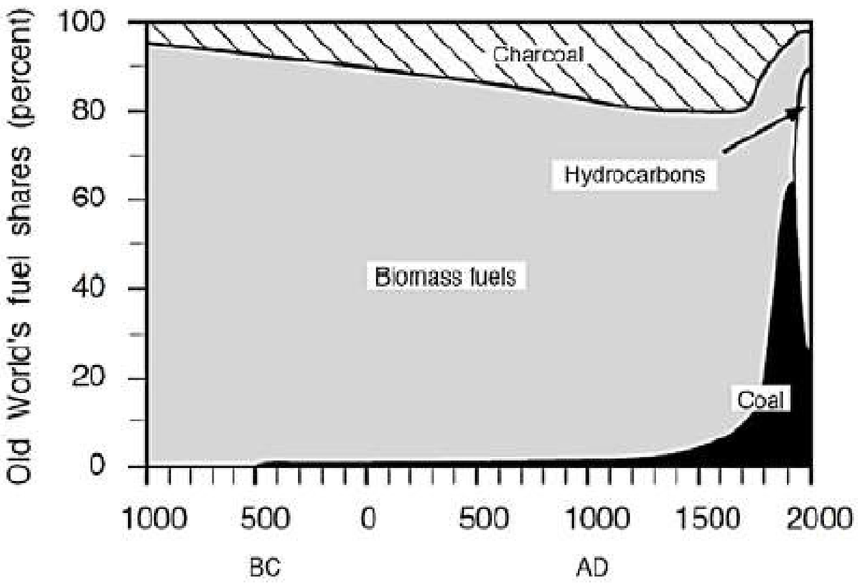
30th May 2017
Manizales, Colombia

BIOREFINERY BACKGROUND

➢ Biomass to Bioenergy

Approximate shares of global fuel consumption



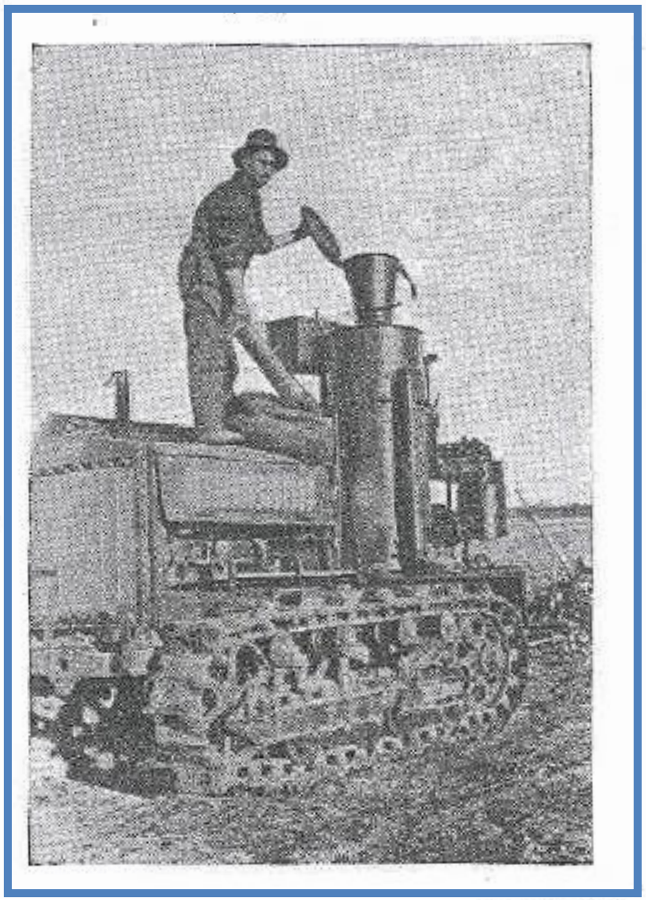


- **Biomass** was the main **energy** source in the ancient times
- Biomass has been progressively replaced by **fossil fuels**

BIOREFINERY BACKGROUND

➢ Wood gas as fuel

First farm tractor in **Portugal** working with charcoal (vineynard prunings), **Chamusca** (**1925**)



Prof Ruy Mayer

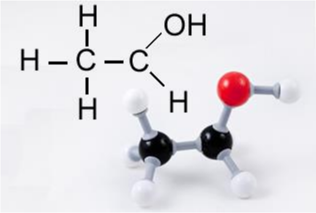
Cars equipped with gazogene, during the 2nd World war

BIOREFINERY BACKGROUND

➢ Ethanol

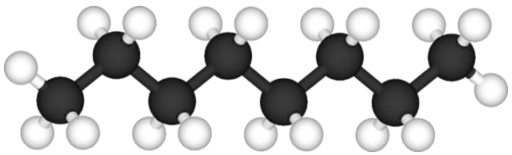
The first car moved by ethanol (Brazil, 1979)

Fiat 147



BIOREFINERY

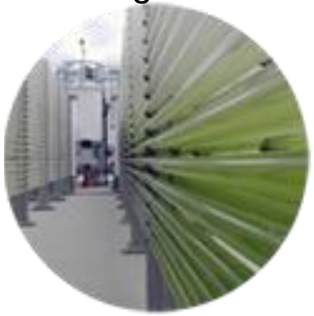
➢ Advanced biofuels



Aviation fuels with particular specifications

Lignocellulosic biomass

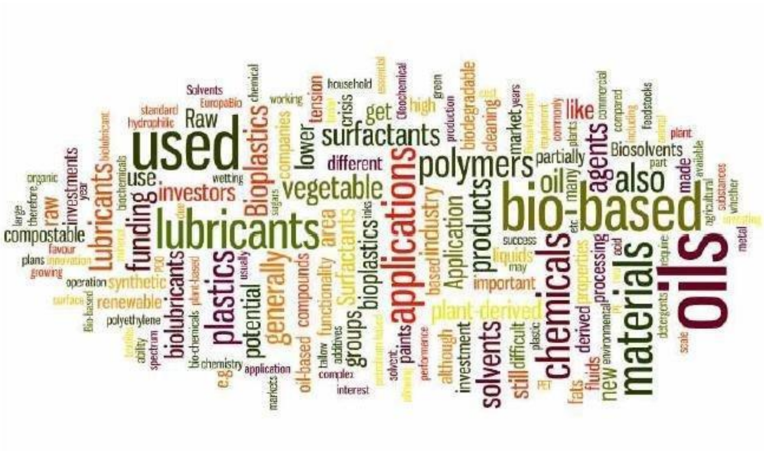
Algae



www.A4F.pt

BIOREFINERY

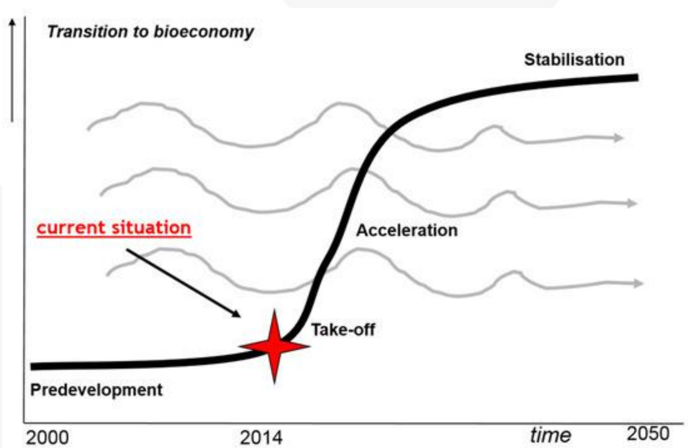
➢ Bioproducts



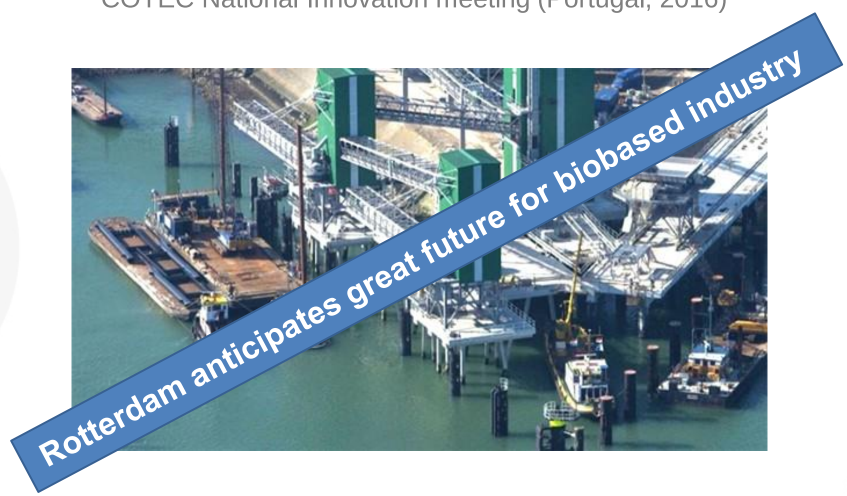
Many other products from biomass

Bio-based economy

COTEC National Innovation meeting (Portugal, 2016)

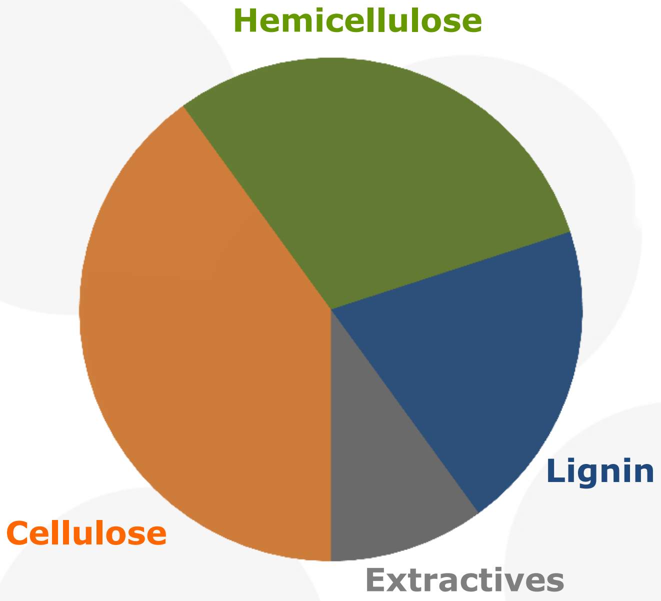


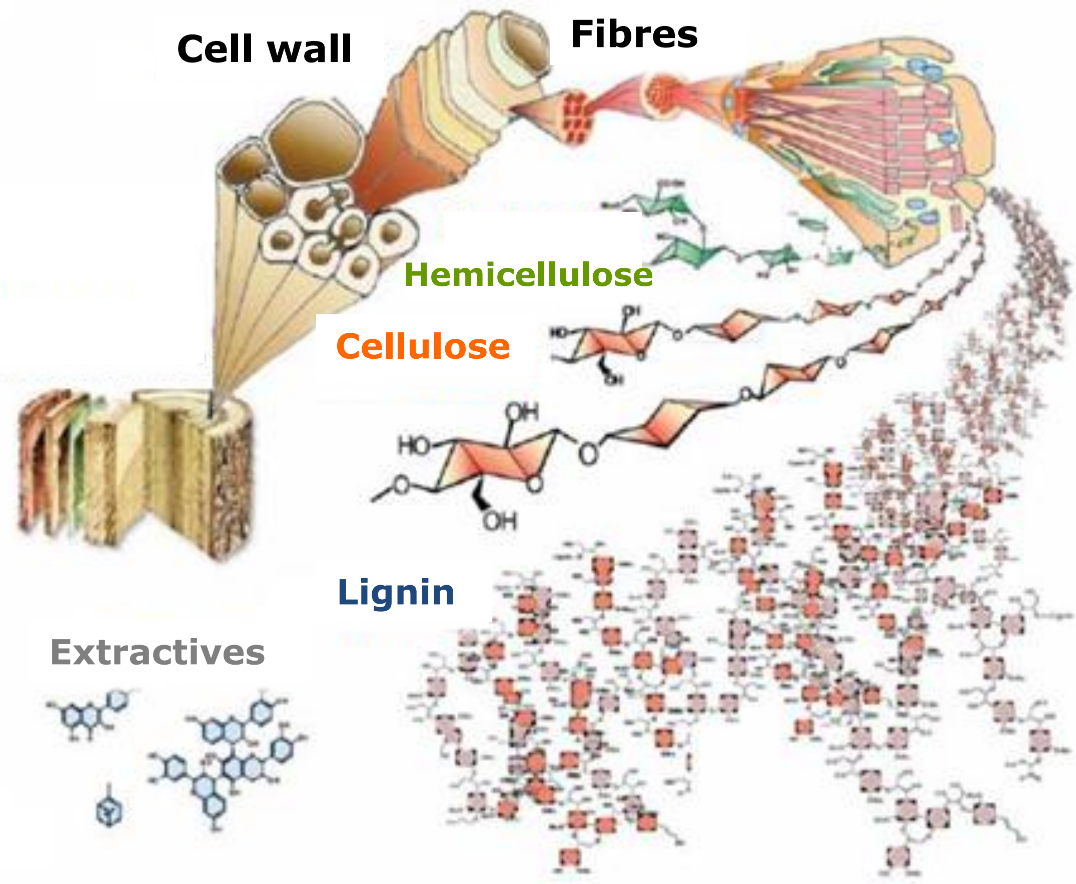
Prof. J. Routti, KE Finland WB workshop (2004)



www.green4sea.com

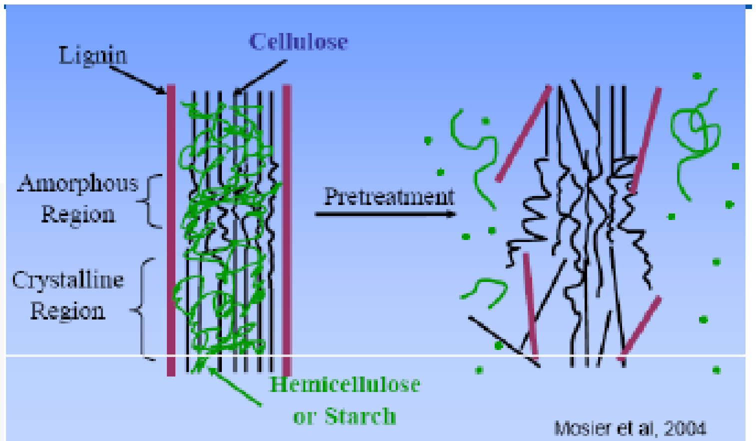
BIOMASS COMPOSITION





Per Hoffmann, Oskar Faix and Ralph Lehnen

BIOMASS PRETREATMENTS



Mosier N, Wyman C, Dale B, Elander R, Lee YY, Holtzapple M, Ladisch MR, 2004.

Biomass **pretreatments** have been developed as a treatment step prior to the enzymatic saccharification and fermentation in cellulosic **ethanol** production process

The **aim** is to adequately **access the sugars** contained in plant cell wall carbohydrates

- **Not selective**
- Mainly focussed on **a single product**

Biomass

Pretreatment Processes

Cellulose Hydrolysis

Fermentation

Purification

Bioethanol

BIOMASS PRETREATMENT/FRACTIONATION

Objectives

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

- Improvement of environmental and economic performance
- Better meeting the requirements of downstream processes
- Improving the properties/value of the **products** obtained

Limitations

- **Selectivity**
- **High use of energy and/or chemicals**
- **It is (still) an expensive process ("is not a mature technology")**

PRETREATMENTS

➢ Main pretreatment options

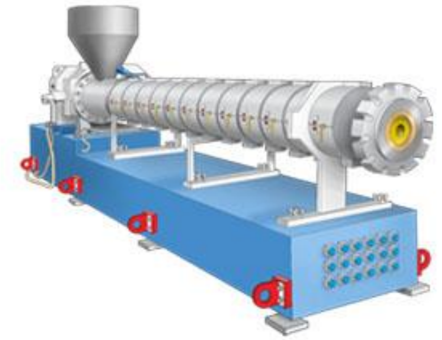
Physical	Chemical	Physico-chemical	Biological
Milling	**Acid processes**	**Autohydrolysis/ Liquid hot water**	Brown-, white- and soft-rot fungi
Grinding **Extrusion**	**Alkaline processes**	**Steam explosion**	
Ultrasound	Wet Oxidation	**Sub- and supercritical fluids**	
Irradiation (microwaves, ɣ-irradiation)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

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

- ➢ Alternatives to the more establish processes are being proposed

PHYSICAL PROCESSES: extrusion

- Heating, mixing and shearing
- Disruption of lignocellulose structure (screw speed, temperature), defibrilation, fibrilation and shortening of fibres



✘ **High energy demanding**

	Extrusion temp. (ºC)	Sugar yield (%)	
		Glucose	Xylose
Physical[a]	40-180	41-95	25-79
Acid[a]	60-230	41-60	84
Alkali[b]	68	90	71
Alkali combined treatment[a]*	Room-140	88-92	Xylan removal: 95 Lignin removal: 87

*Ionic liquids; organic solvent; steam explosion; LHW

[a]Zheng, J & Rehmann, L. (2014) *Int. J. Mol. Sci., 15*, 1867-1898
[b]Duque et al. (2013) *Proc Biochem*., 48, *775-781*

✓**Can produce high sugar yields**

✓**Can be operated at mild temperatures**

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CHEMICAL PROCESSES

➢Acid Hydrolysis

	Dilute acid	Concentrated acid
Acids	H_2SO_4, HCl, HNO_3, TFA, H_3PO_4, CH_3COOH	H_2SO_4, HCl, HNO_3, TFA
Temperature	**High**	**Low/moderate**
Acid concentration	Low	High
Hemicellulose hydrolysis	**High**	**High***
Cellulose hydrolysis	Low; (alternative 2 step hydrolysis)	**High***
Enzymatic digestibility	**High**	
Alteration of lignin structure	Minor	
Inhibitors formation	High	Low**
Equipment corrosion	Low	High
Energy requirements	High	Low
Acid recovery	-	Mandatory (economy)
Waste generation	High (neutralization)	
Proven at pilot scale	**Yes**	**Yes**

* less specific; **highly dependent on the temperature

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CHEMICAL PROCESSES

➢ Dilute acid hydrolysis

Advanced Biofuels

Aerial view of POET-DSM's Project Liberty cellulosic ethanol plant in Emmetsburg, Iowa

Commercial plant

Feedstock: Corn stover

Pre-treatment: Two-stage dilute acid pre-treatment

C5+C6 fermentation

Products: Ethanol + Biogas + lignin (CHP)

NOVEL CHEMICAL PROCESSES

➢ Solid (Super)Acids

Solids which can donate protons or accept electrons during reactions

"acids stronger than 100% sulphuric acid" (Brønsted superacids), "acids stronger than anhydrous aluminum trichloride" (Lewis superacids)

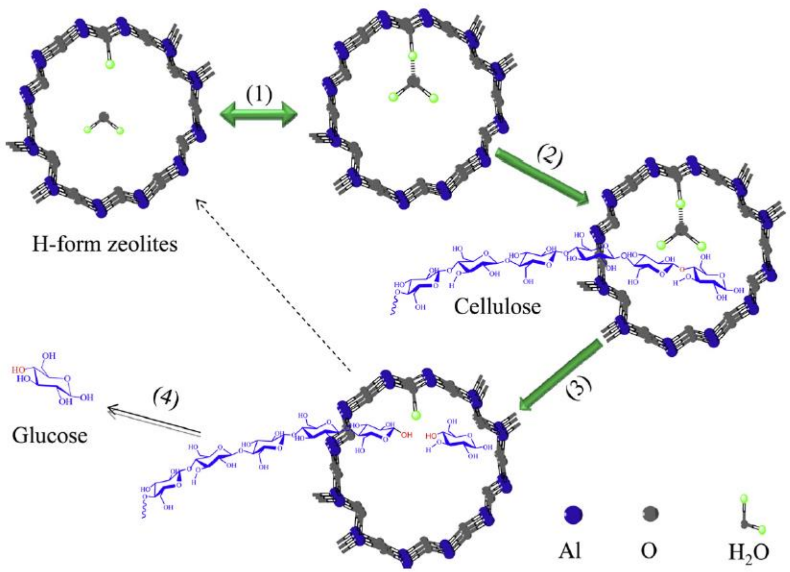
Main classes

- **H-FORM ZEOLITES** *(microporous aluminosilicates minerals)*
  - H-mordenite, H-ZSM-5, …, but also bentonite, kaolin
- **TRANSITION-METAL OXIDES** *(mesoporous Single or Mixed metal oxides)*
  - Nb_2O_5, Zr-TMS, TiO_2, CeO_2, $HNbMoO_6$, Ta_2O_5-$W0_3$, Zn-Ca-Fe oxide, …
- **CATION-EXCHANGE RESINS**
  - Amberlyst-15 (polystyrene-based cation-exchange resin with SO_3H), Dowex 50wx8-100, NKC-9, Nafion® NR50 (perfluorosulfonated ionomer)

NOVEL CHEMICAL PROCESSES

➢ Solid (Super)Acids

- Temperature: room and up ~180ºC
- Hydrolysis of both **cellulose** and **hemicellulos**e (mono and oligosaccharides)
- Lignin mainly remain insoluble (depends on the catalyst)
- Integration with Microwave / Ultra-sounds / Nanotechnology is possible/desirable



(2005) Biores Technol., **96**, 2007-2013

NOVEL CHEMICAL PROCESSES

➢ Solid (Super)Acids

Compared to liquid catalysts:

- ✓ **Limited problems associated to equipment corrosion, safety and waste generation**
- ✓ **Easy separation/recovery without loss of activity**
- ✓ **Long catalyst life**
- ✓ **High Selectivity**
- ✘ Costs, reaction time
- ✘ Thermal stability
- ✘ **Solid-solid interaction required (mass transfer limitations, pore diameters, …) may limit accessibility**

Kim and Lee (2005) Biores Technol., **96**, 2007-2013

Factors determining efficiency still *unknown* as similar catalysts can yield quite different results, e.g. for different raw materials

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NOVEL CHEMICAL PROCESSES

➢ Inorganic salts

- $FeCl_3$, $FeSO_4$, $Fe(NO_3)_3$, $Al_2(SO_4)_3$, $AlCl_3$, $MgSO_4$, KCl, $CaCl_2$
- Alternative to acid hydrolysis; **Brønsted acids**
- Catalysts: H^+ from dissociation of salts; metal ions
- Hydrolysis of **hemicelluloses** (high) and solubilisation of **lignin**
- Increase of **enzymatic digestibility of cellulose**

	$Fe(NO_3)_3$	$Fe(NO_3)_3$	$FeSO_4$	$FeCl_3$	$FeCl_3$
Raw material	Corn stover sillage	Corn straw	Corn stover	Wheat straw	Wheat straw
Temperature (ºC)	**150**	**180**	180	**140**	**120**
Concentration (mM)	50	45	100	100	200
Salt (mg/100 g feedstock)	45	36	90	10	20
pH	n.r.	2.77	3.64	n.r.	1.73
Time (min)	10	0	20	20	120
Xylose yield	**91.8**	**60**	**89.6**	**89.0**	**20.6**
Xylose yield (oligomers)	8.9	2.2	10.4	n.r.	n.r.
Furfural yield		2.2			**62**
	Sun et. al. (2011)	Santos et al (2014)	Zhao et al. (2010)	Liu et al. (2009)	Marcotullio et al. (2010)

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NOVEL CHEMICAL PROCESSES

➢ Inorganic salts

- ✓ **High reaction rate, less corrosive than acids**
- ✓ **Easy to recycle**
- ✓ **Neutralisation of the hydrolysates can even be avoided (mild pH)**
- ✘ **Salts can be incorporated into biomass (?)**

CHEMICAL PROCESSES

➢ Alkaline processes

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

Mild temperatures and pressures

ii) Ammonia

- Soaking in aqueous ammonia **(SSA)**
- Ammonia recycling percolation **(ARP)**

  Aqueous ammonia, flow-through mode at high temperature (150-170ºC)

- **<u>Ammonia fibre explosion</u> (AFEX)**

  Anhydrous ammonia (liquid), combination of alkaline and steam-explosion

  Basically a dry to dry process (no wash stream)

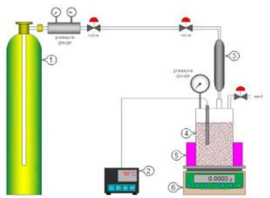

Figure 27: AFEX process (adapted from Teymouri et al. 2004) 1. Ammonia tank 2. Temperature controller 3. Sample cylinder 4. Biomass 5. Heating mantle 6. Balance

Adpt. “Lignocellulosic ethanol” (2013), D. Chiaramonti, A. Giovannini, R. Janssen, R. Mergner, WIP Renewable Energies

CHEMICAL PROCESSES

➢ Alkaline processes

	Lime	AFEX
Temperature	**Mild**	**Moderate;** High pressure
Hemicellulose removal	Minor	Minor
Lignin removal	**High***	**High**
Enzymatic digestibility	**High**	**Very High** Cellulose decrystallization
Inhibitors formation	**Low**	**Low**
Energy requirements	Low	High
Capital costs	Low	High
Alkali recovery	Easy	Mandatory (economy)
Waste generation	Low	-
Other	Salts (incorporated into biomass)	**Not attractive for softwoods**
Proven at pilot scale	Yes/No	No/**Yes**

Lignin removal can be improved by the addition oxidizing agents (O_2/H_2O_2)

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CHEMICAL PROCESSES

➢ Alkaline processes

DEINOVE
The deinococcus way

Paris, France

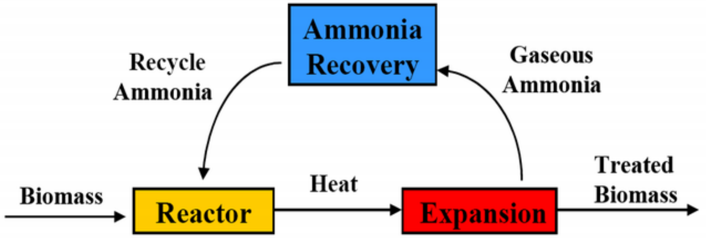
Pretreatment: AFEX

Established a partnership with **MBI** (multidisciplinary centre, Michigan, USA) and **MSU** (Michigan State University) to use **AFEX** technology for the production of 2G biofuels at **pilot scale**

Feedstocks: 'industrial biomass' (preliminary tests on corn stover)

Product: ethanol

Deinococcus bacterial strains (C6+C5, oligomers)



AFEX

CHEMICAL PROCESSES

➢ Alkaline processes

Commercial plant

Nevada - Iowa, USA

Pre-treatment: Dilute ammonia process

Feedstock: Corn stover

Products: Ethanol and CHP (from lignin)

Bacterial fermentation (recombinant *Z. mobilis*); no waste water (total water recycle)

CHEMICAL PROCESSES

➢ Organosolv

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


Fraunhofer CBP (Leuna)

✘ **Overall economy depends on the solvent recycling**

✓ **Solvents like ethanol are easily recycled (distillation)**

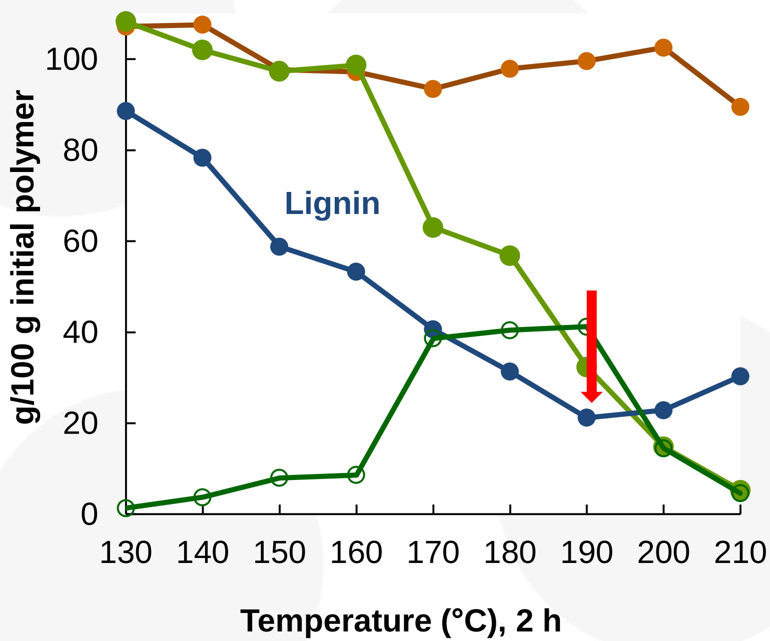
✓ **Production of high quality lignin (value added applications)**

CHEMICAL PROCESSES

➢ Organosolv (Ethanol/water)

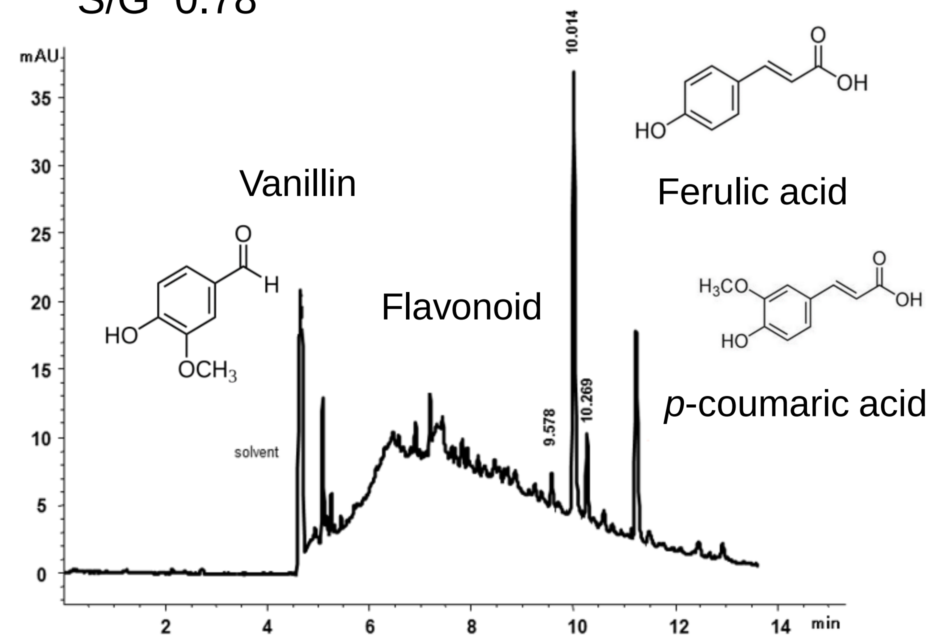
Corn cobs, rice straw

Delignification yield



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

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



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

High delignification yield, high quality lignin-added value compounds

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CHEMICAL PROCESSES

➢ Organosolv

CIMV
THE BIOREFINERY CONCEPT

Demo plant

Toulouse, France

Feedstocks: straws, bagasse, hardwoods

CIMV technology is based on the utilization of **acetic acid/formic** acid **organosolv** processes

Delmas, M. (2008). Chem. Eng.Technol. 31, 792-797
Snelders et al. (2014) Biores. Technol. 156, 275-282

CELLULOSIC PULP

- Biofuels
- Bio-building blocks
- Bioplastics
- Paper

BIOLIGNIN™

- Glues and adhesives
- Elastomers, carbon fibers
- Polyurethanes, polyesters

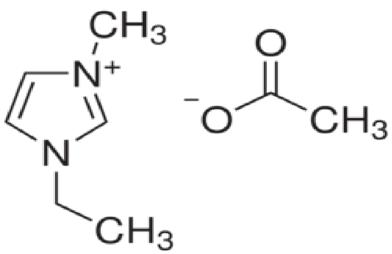
C_5 SUGARS SYRUP

- Animal feed additives
- Biofuelss
- Chemical precursor
- Furfural and derivatives

Source: www.CIMV.fr

NOVEL CHEMICAL PROCESSES

➢ IONIC LIQUIDS (ILs)



[emim][Ac]

- ILs organic salts (melting point < 100ºC)
- **High thermal stability**, great solvent power, negligible vapour pressure
- Particularly useful in dissolution of cellulose

- **Imidazolium ILs** dissolve up to 25% of cellulose (**Rogers et al., 2002**), breaking the extensive hydrogen bonding network
- **Chlorine ILs**; (Cl- strong proton acceptor in the interaction between IL and hydroxyl groups of the carbohydrate). High melting point/viscosity
- Newly **designed ILs** (1-ethyl-3-methylimidazolium dimethylphosphate ([**emim**][$(MeO)_2PO_2$]), ILs containing dialkylimidazolium cation and dicyanamide anion)
- **Two-possible approaches:**
    - **hydrolysis**
    - **complete dissolution** of biomass followed by **selective precipitation** (to recover selected fractions)

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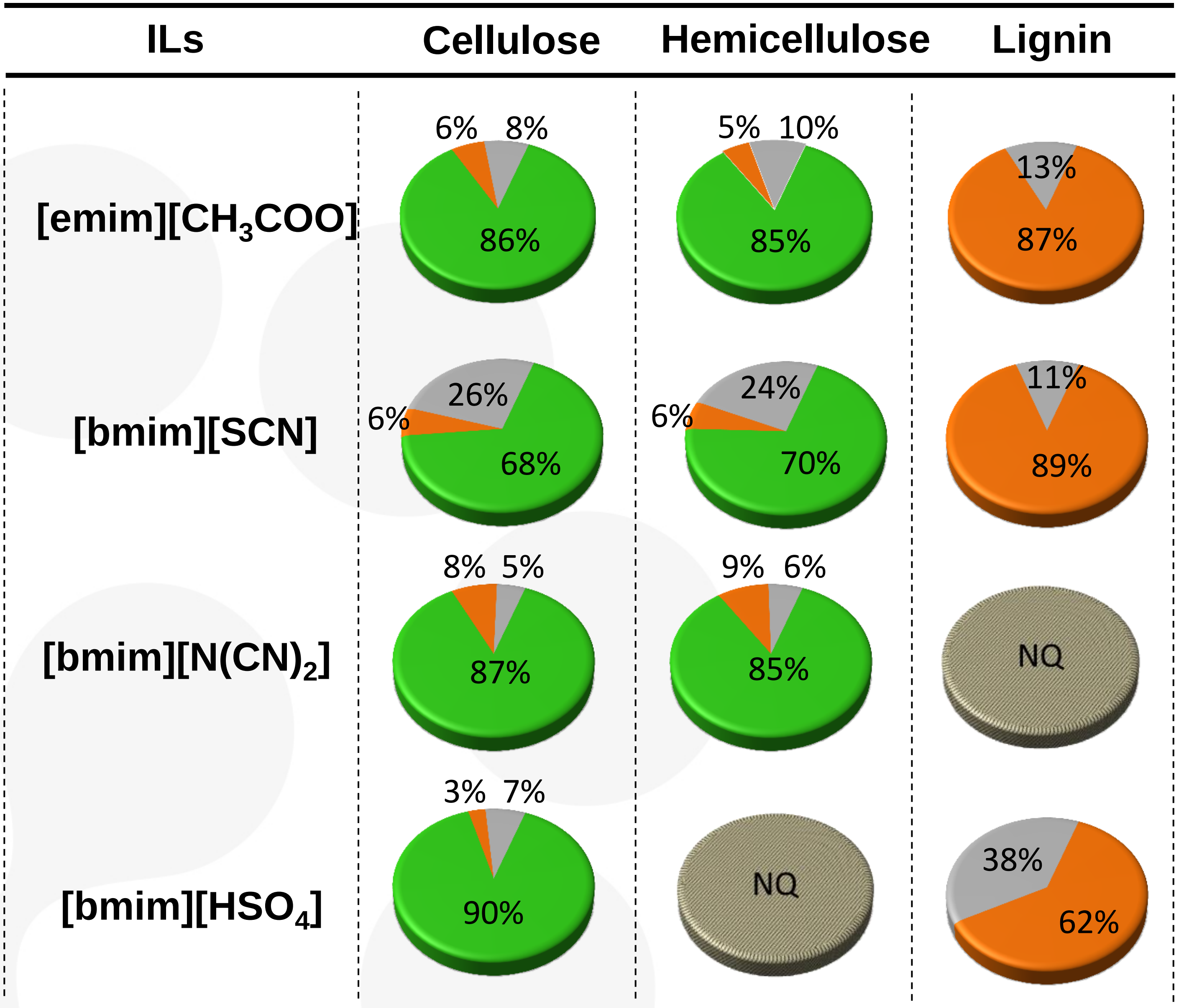
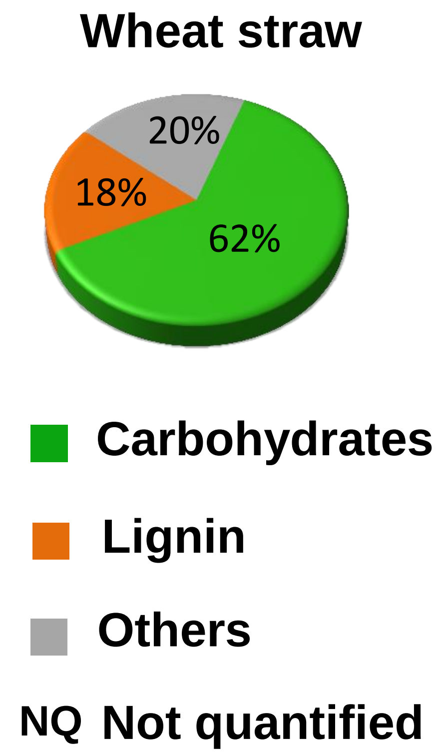
NOVEL CHEMICAL PROCESSES

➢ IONIC LIQUIDS (ILs)

- ✘ Water content of biomass can decrease the solubility of dissolved carbohydrates
- ✓ Addition of protonated solvents allows the regeneration of dissolved carbohydrates
- ✓ Important progresses in the fractionation of hemicelluloses and lignin have been reported
- ✘ Cost of ILs
- ✓ ILs can be recovered with high yield

RESULTS WITH ILs





A. M. da Costa Lopes, K. G. Joao, E. Bogel-Lukasik, L. B. Roseiro and R. Bogel-Lukasik, *J. Agr. Food Chem.*, 2013, **61**, 7874.

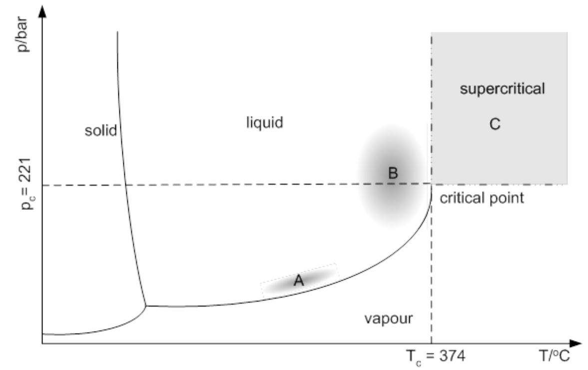
Images: courtesy of R. Lukasik

PHYSICO-CHEMICAL PROCESSES

➢ Hydrothermal processes

- Liquid hot water (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



Gírio, F.M., Fonseca, C., Carvalheiro, F., Duarte, L.C., Marques, S., Bogel-Lukasic, R. (2010) *Biores. Technol.*, **101**, 4775-4800.

PHYSICO-CHEMICAL PROCESSES

➢ Hydrothermal

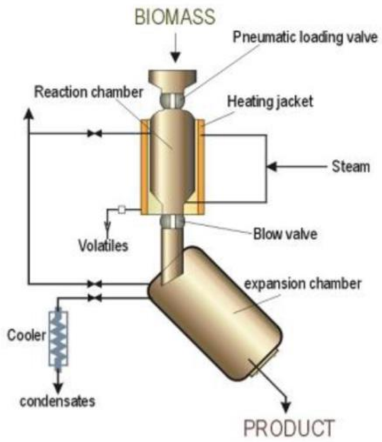
Autohydrolysis/liquid hot water

- Biomass mixed with water and heated to a defined temperature (150-230ºC, minutes-hours)

LNEG, UB, Biomass Deconstruction Laboratory

Steam explosion

- Saturated steam (< 240ºC, seconds-minutes)
- Biomass is wetted by steam (high pressure) and exploded (pressure within the reactor is rapidly released)
- Disaggregation of lignocellulosic matrix, breaking down inter- and intra-molecular linkages (forces resulting from decompression), ultrastructure modification



Adpt. "Lignocellulosic ethanol" (2013), D. Chiaramonti, A. Giovannini, R. Janssen, R. Mergner, WIP Renewable Energies

PHYSICO-CHEMICAL PROCESSES

➢ Hydrothermal

	LHW (Autohydrolysis)	Steam explosion*
Temperature	High	High
Solid concentration	**Low**	**Low-high**
Hemicellulose removal	**High**	**High**
Hemicellulose recovery	High	Medium/low
Lignin removal	Minor	Minor**
Cellulose removal	Minor	Minor
Enzymatic digestibility	High	(Very) High
Inhibitors formation	Low	Low/medium
Energy requirements	Low	Low***
Corrosion problems	Minor	Minor
Waste generation	Low	Low
Other	**Hemicelluloses as oligomers**	Chemicals catalysts required (softwoods)
Proven at pilot scale	Yes	Yes

*impregnation of material with acid catalyst (H_2SO_4, SO_2), CO_2 (CO_2 explosion), alkali (ammonia, AFEX) is also possible
**alteration of lignin structure
***in part due the energy savings for grinding, milling

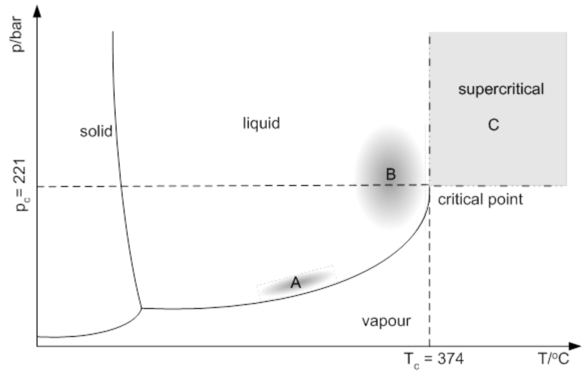
NOVEL PHYSICO-CHEMICAL PROCESSES

➢ Supercritical fluids (ScF)

- **ScF** is a compound above its T_c and p_c

  Water (T_c=374.0°C, p_c=221.0 bar)

  CO_2 (T_c=31.0°C, p_c=73.8 bar)



- **Sc water**

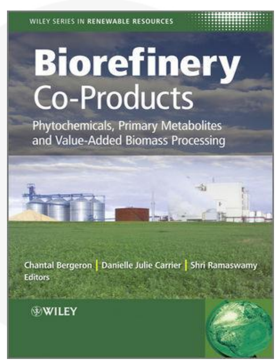
  Hemicellulose can be completely separated and **digestibility** of **cellulose** significantly increased (220ºC, K_w=6.34*10^{-12}, pH =5.5)

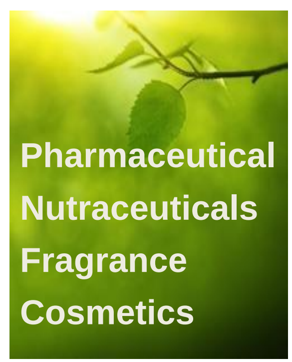
- **Sc CO_2**

  Significantly increase the **digestibility of cellulose** (any significant change in microscopic morphology of LMC). Yield can be enhanced by addition of organic acids (and with Sc CO_2 the addition of acids is lower)

NOVEL PHYSICO-CHEMICAL PROCESSES

- ✘ **Capital cost**
- ✘ **a wide range of improvements to be achieved before SF will be implemented in larger scale**
- ✓ **Can be particularly interesting for extraction of (very) high value products**





PHYSICO-CHEMICAL

➢ Hydrothermal processes

BETARENEWABLES biochemtex

Commercial

Crescentino, Italy

Feedstocks: *Arundo donax*, wheat straw and rice straw

Pretreatment: Proesa^{TM} technology, uncatalysed steam explosion

Products: Ethanol and lignin (for energy)

<u>Envisage</u>

Biofuels: Ethanol, Bio-Jet, Butanol

Biochemicals: Fatty Alcohols 1,4 Butanediol, Farnasene, Acrylic Acid, Succinic Acid, Others

Lignin derivatives: Phenols, Xylene, Terephthalic Acid

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PHYSICO-CHEMICAL

➢ Hydrothermal processes

Inbicon DONG energy

Demo plant

Kalundborg, Denmark *www.inbicon.com*

CLARIANT

Demo plant

Straubing,Germany *www.sunliquid.com*

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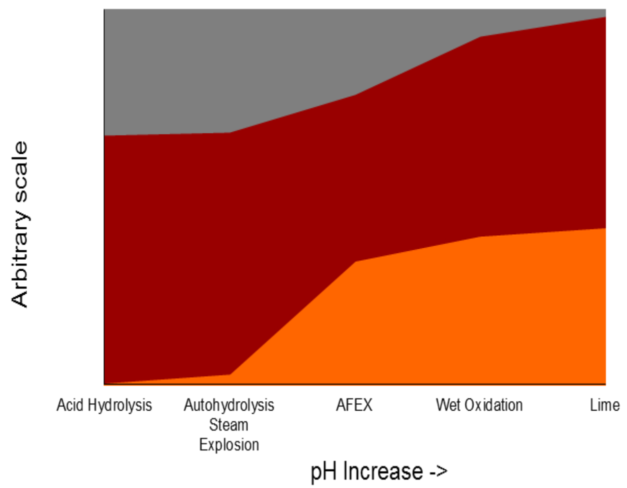
CONCLUSIONS

- 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 is advantageous



Carvalheiro, F., Duarte, L.C., Gírio, F. M. (2008). J. Scientific & Ind. Res., 67, 849-864.

- ***Novel processes,*** ***e.g.***, **the ones based on ILs, can also be effective, as they may be able to convey the two goals in a single process**

CONCLUSIONS

What do we except from a pretreatment?

- **Consolidated (bio)processing**
- **One-pot but multireaction processes**
- **Selective**
- **Low levels of (non-harzard) catalysts**
- **Low energy demanding**
- **Low cost**

We are on the way … but some progresses are still needed

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