Biomass Fractionation Processes for the Biorefineries

Florbela Carvalheiro

SMIBIO Workshop

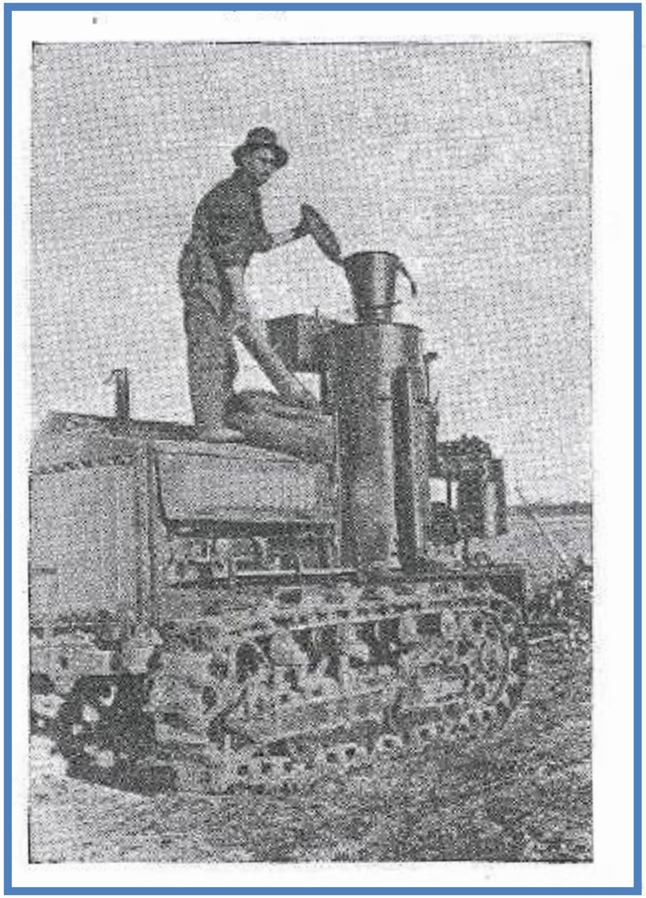
Small-scale Biorefineries for Rural Development in Latin America and Europe

November 23rd, 2016
Buenos Aires, Argentina

BIOREFINERY BACKGROUND

➢ Wood gas as fuel

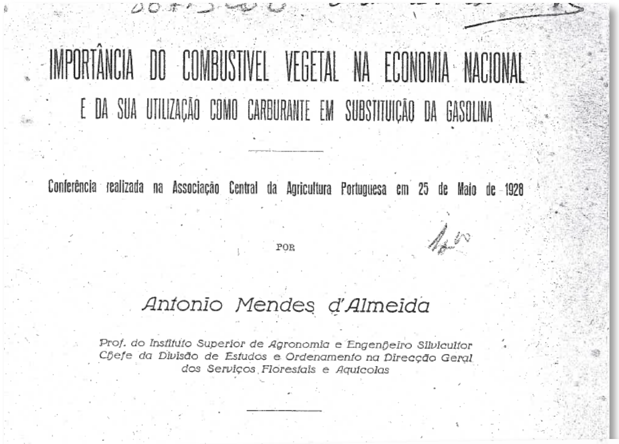
First farm tractor in **Portugal** working with charcoal (vineynard prunings), **Chamusca** (**1925**)



Prof Ruy Mayer

A. Mendes de Almeida (1928), Portugal

“Importance of vegetable fuel in the national economy and its use as fuel as gasoline substitute”



IMPORTÂNCIA DO COMBUSTIVEL VEGETAL NA ECONOMIA NACIONAL

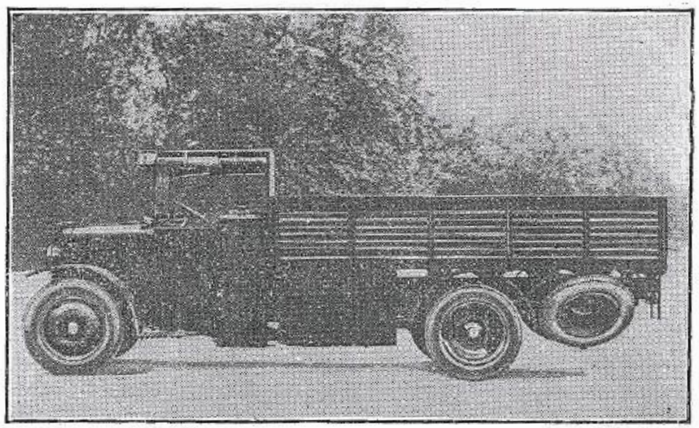
E DA SUA UTILIZAÇÃO COMO CARBURANTE EM SUBSTITUIÇÃO DA GASOLINA

Conferência realizada na Associação Central da Agricultura Portuguesa em 25 de Maio de 1928

POR

Antonio Mendes d'Almeida

Prof. do Instituto Superior de Agronomia e Engenheiro Silvicultor
Chefe da Divisão de Estudos e Ordenamento na Direcção Geral
dos Serviços Florestais e Aquicolas



Camião a gasogenio «Panhard»

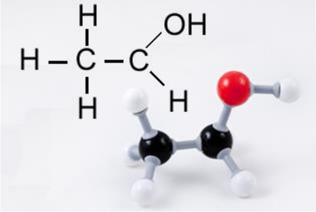
Photos: courtesy of H. Machado (ICNF)

BIOREFINERY BACKGROUND

➢ Ethanol

The first car moved by ethanol (Brazil, 1979)

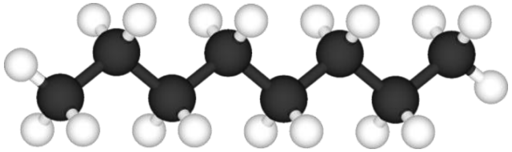
Fiat 147



BIOREFINERY

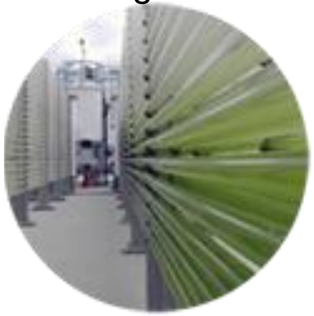
➢ Advanced biofuels

Aviation fuels with particular specifications



Lignocellulosic biomass

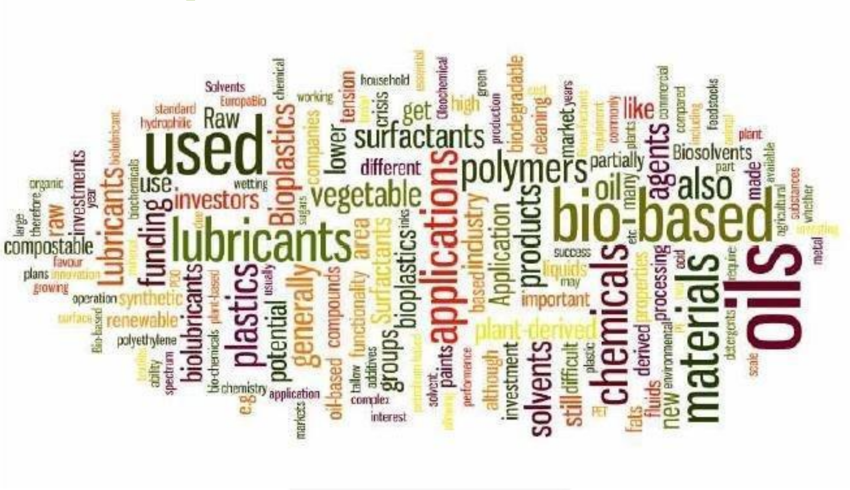
Algae



www.A4F.pt

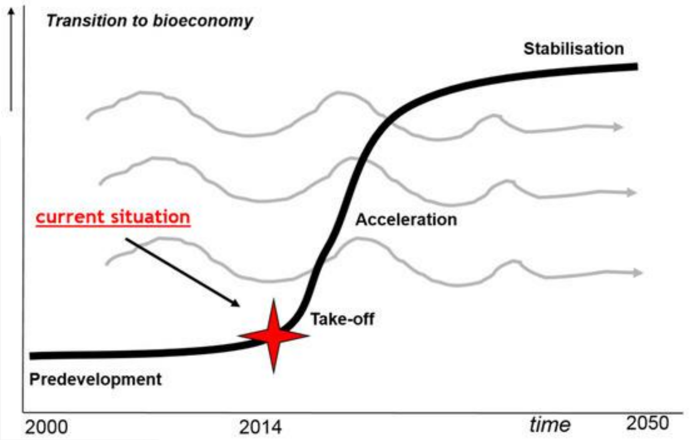
BIOREFINERY

➢ Bioproducts



Many other products from biomass

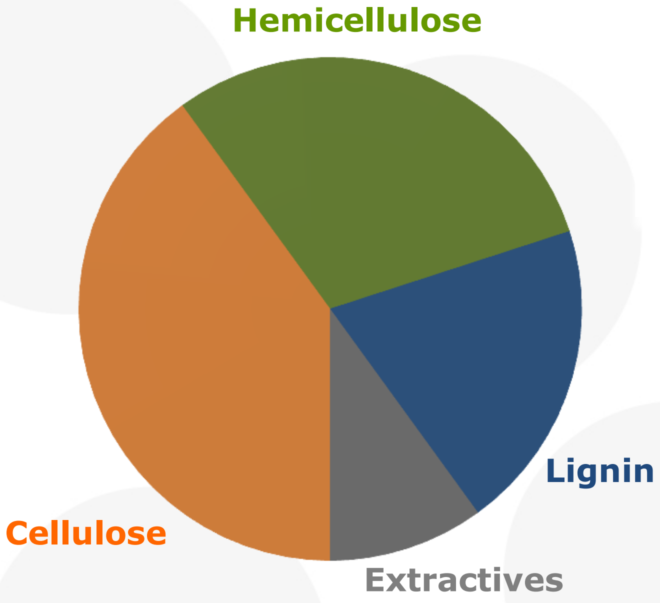
Bio-based economy

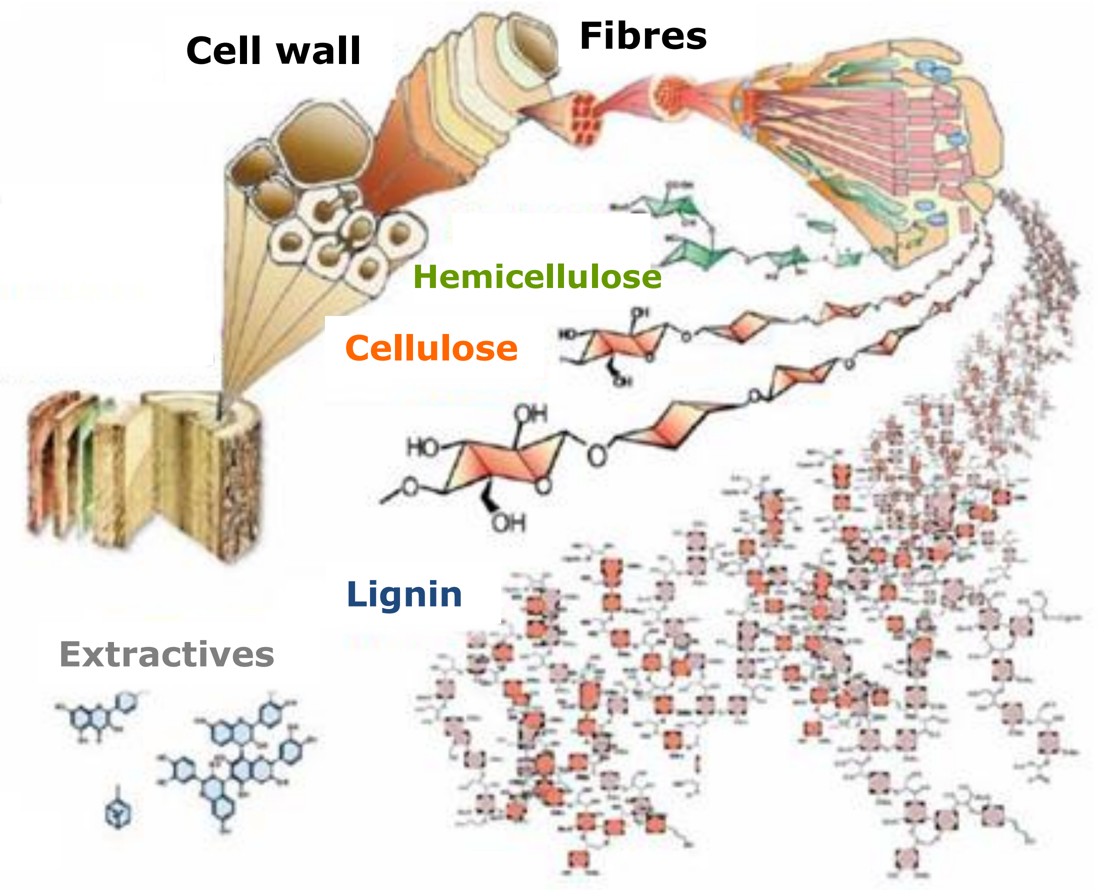


Prof. J. Routti, KE Finland WB workshop (2004)

www.green4sea.com

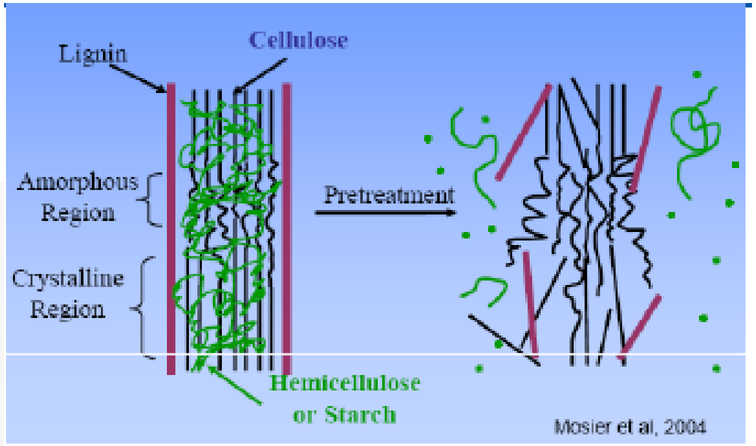
BIOMASS COMPOSITION





Per Hoffmann, Oskar Faix and Ralph Lehnen

BIOMASS PRETREATMENTS



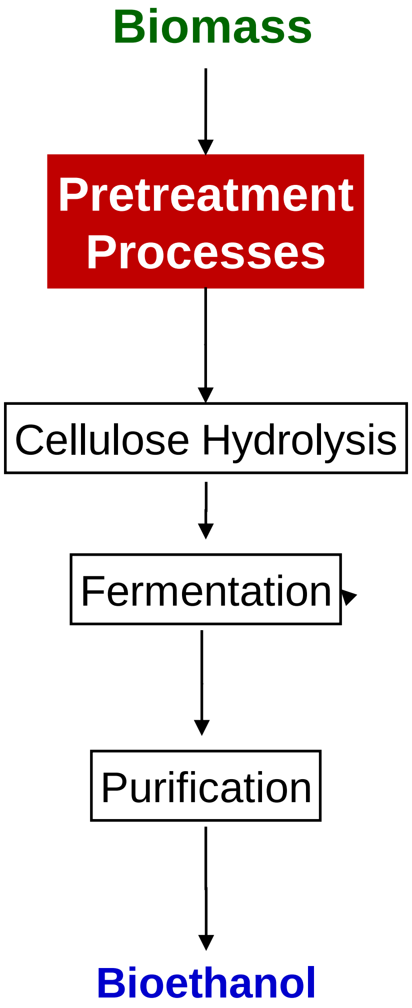
Mosier et al, 2004

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 products**
- 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**

PRETREATMENTS

Main pretreatment options

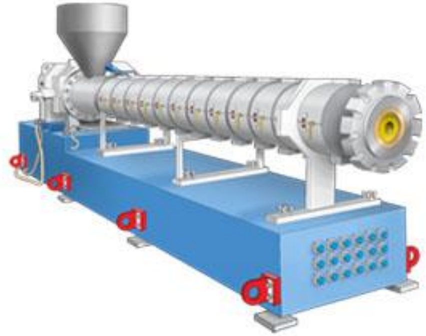
Physical	Chemical	Physico-chemical	Biological
Milling	**Acid processes**	**Autohydrolysis/ Liquid hot water**	Brown-, white- and soft-rot fungi
Grinding **Extrusion**	**Alkaline processes**	**Steam explosion**	
Ultrasound	Wet Oxidation	**Sub- and supercritical fluids**	
Irradiation (microwaves, ɣ-irradiation)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

*Alkali+Ionic liquids; Alkali+organic solvent; Alkali+steam explosion; Alkali+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**

CHEMICAL PROCESSES

➢Acid Hydrolysis

	Dilute acid	Concentrated acid
Type of acids	H_2SO_4, HCl, HNO_3, TFA, H_3PO_4, CH_3COOH (other carboxylic acids)	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**

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)

CHEMICAL PROCESSES

➢ Acid Hydrolysis

Weyland BioEthanol

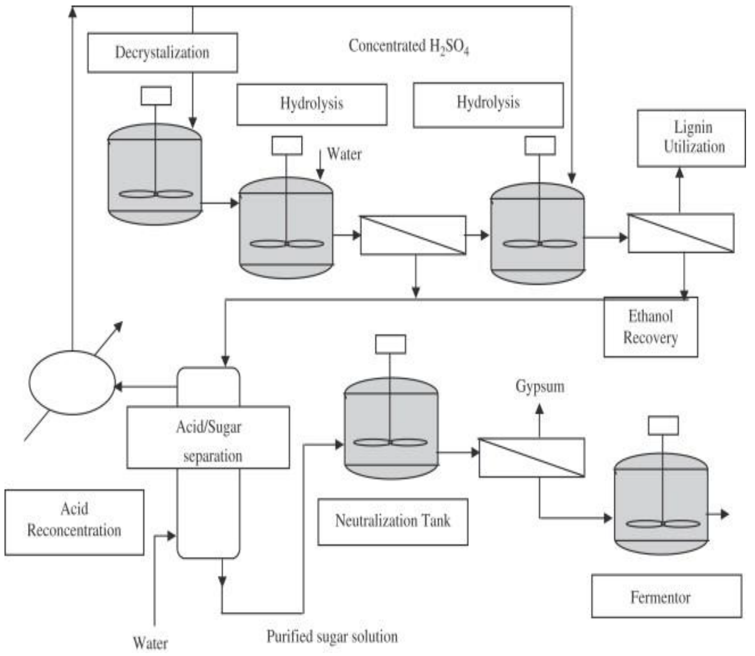
Pretreatment: concentrated acid process

Feedstock: Wood and agriculture wastes

Technology demonstrated for sugarcane bagasse, corn stover, corn cobs, rice straw, hardwoods, softwoods, wood wastes and paper wastes

Products: ethanol and lignin

Acid recycling



Pilot plant Norway

CHEMICAL PROCESSES

Alkaline processes

- **Hydroxides**: NaOH, $Ca(OH)_2$, KOH (lime)
- **Ammonia**: Soaking in Aqueous Ammonia (SAA), Ammonia Recycling Process (**ARP**) and Ammonia Fibre Explosion (**AFEX**)

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

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

** Difficult to separate from hemicellulose

CHEMICAL PROCESSES

➢ Alkaline processes

DEINOVE
The deinococcus way

Paris, France

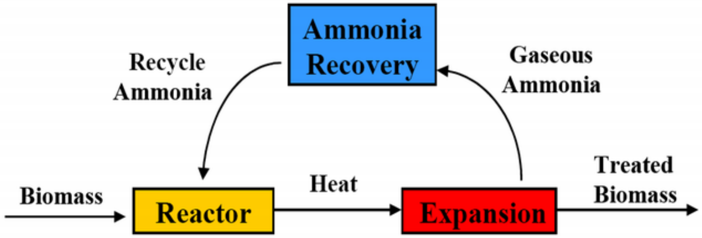
Pretreatment: AFEX

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 processes

- Water/**organic solvents** (acetone, ethanol, methanol, butanol, benzene)
- Organic solvent can be used in combination with a catalyst (e.g., **acids**)

Alcell, Acetocell, Formacell, Acetosolv, Formosolv, Milox

- Temperature: room - 200ºC (150-200ºC)
- Solubilisation of **lignin** and hydrolysis of hemicelluloses

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

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

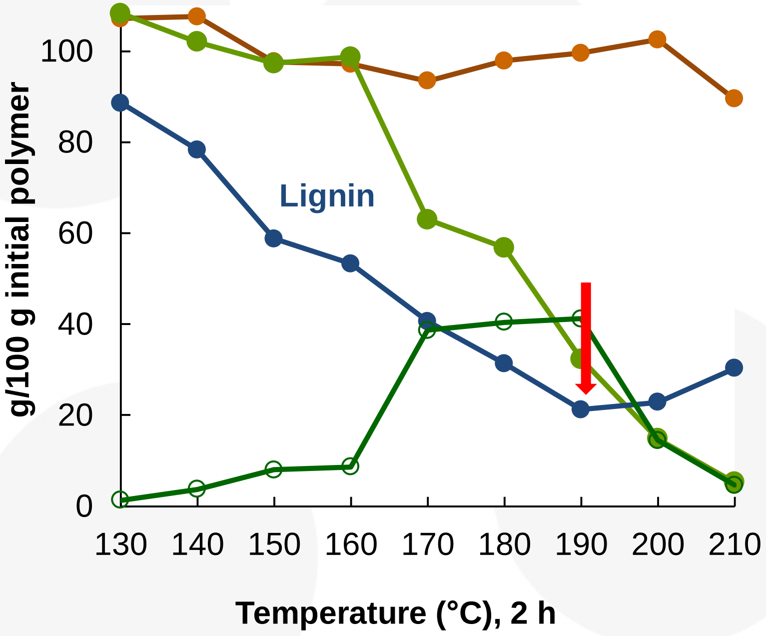
✓**Production of high quality lignin (value added applications)**

ORGANOSOLV

Ethanol/water

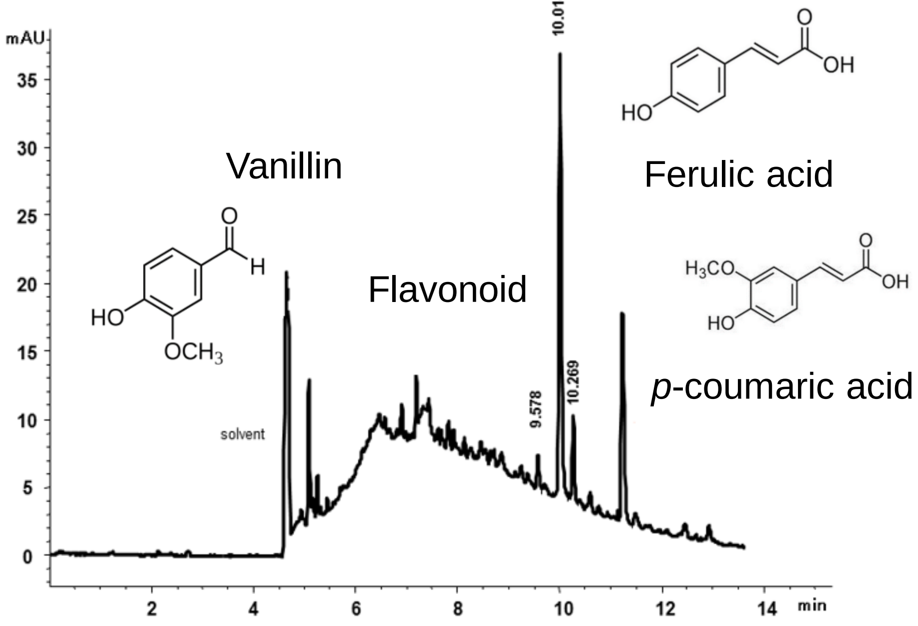
Corn cobs, rice straw

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

CHEMICAL PROCESSES

Demo plant

Toulouse, France

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

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

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, …

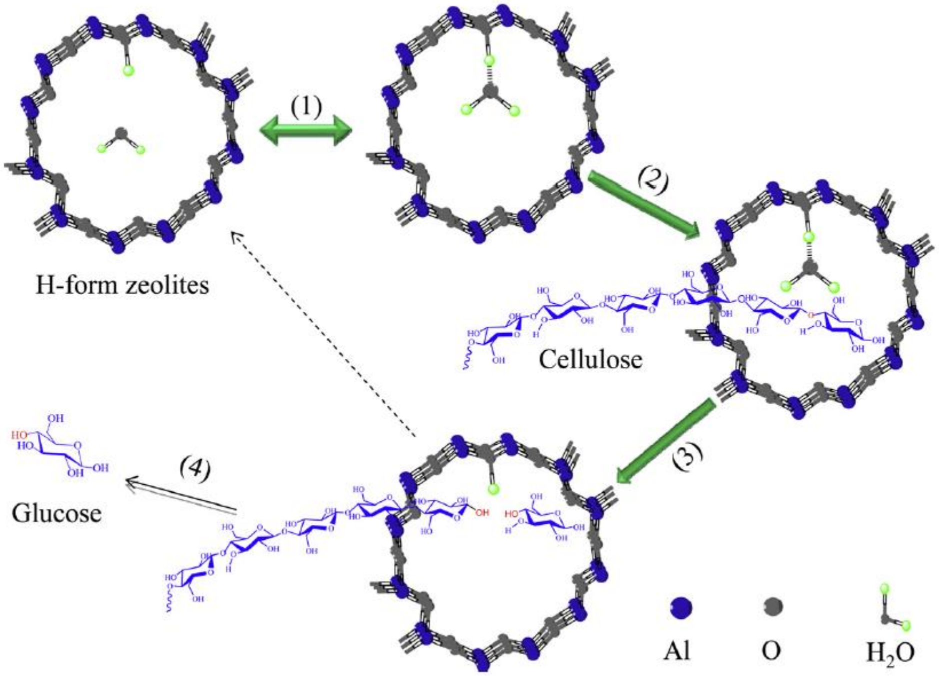
Kim and Lee (2005) Biores Technol. 96: 2007-2013

- **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



s 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

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

✘ **Solid-solid interaction required (mass transfer limitations, pore diameters, …) may limit accessibility**

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

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 stover sillage	Corn stover	Wheat straw	Wheat straw
Temperature (ºC)	150	150	180	140	120
Concentration (mM)	50	50	100	100	200
Salt (mg/100 g feedstock)	45	45	90	10	20
pH	n.r.	3.6	3.64	n.r.	1.73
Time (min)	10	12.7	20	20	120
Xylose yield	**91.8**	**93.4**	**89.6**	**89.0**	**20.6**
Xylose yield (oligomers)	8.9	8.9	n.r.	n.r.	n.r.
Furfural yield					**62**
	Sun et. (2011)	Sun et. (2011a)	Zhao et al. (2010)	Liu et al. (2009)	Marcotullio et al. (2010)

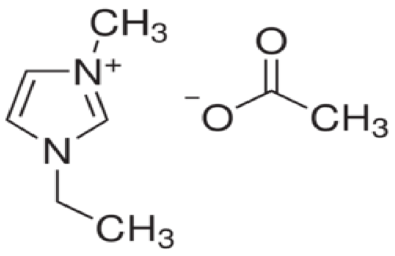
NOVEL CHEMICAL PROCESSES

➢ 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 (?)

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

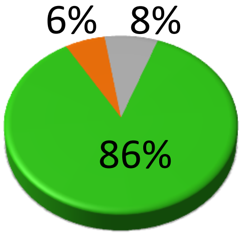
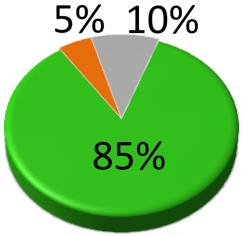
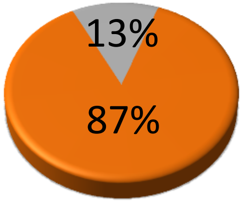
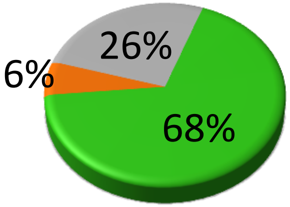
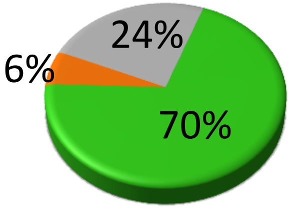
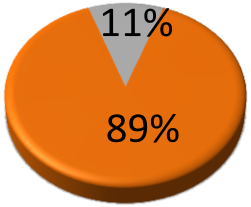
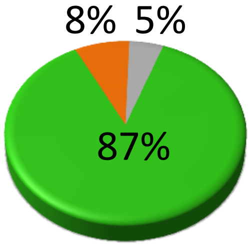
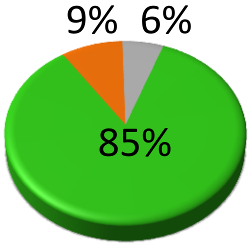
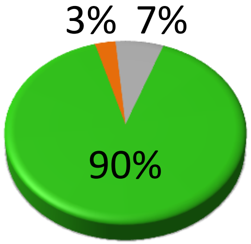
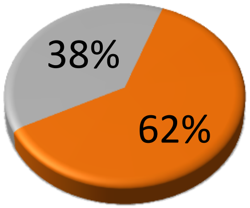
- **Imidazolium ILs** dissolve up to 25% of cellulose (**Rogers et al., 2002**), breaking the extensive hydrogen bonding network
- **Chlorine ILs**; (Cl- strong proton acceptor in the interaction between IL and hydroxyl groups of the carbohydrate). High melting point/viscosity
- Newly **designed ILs** (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)

NOVEL CHEMICAL PROCESSES

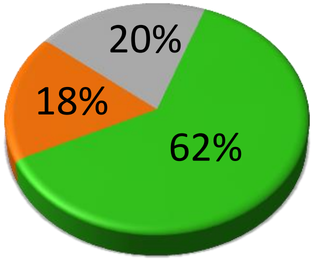
➢ IONIC LIQUIDS (ILS)

- ✘ 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

ILs	Cellulose	Hemicellulose	Lignin
[emim][CH_3COO]			
[bmim][SCN]			
[bmim][$N(CN)_2$]			NQ
[bmim][HSO_4]		NQ	

Wheat straw



🟩 **Carbohydrates**

🟧 **Lignin**

⬜ **Others**

NQ Not quantified

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.

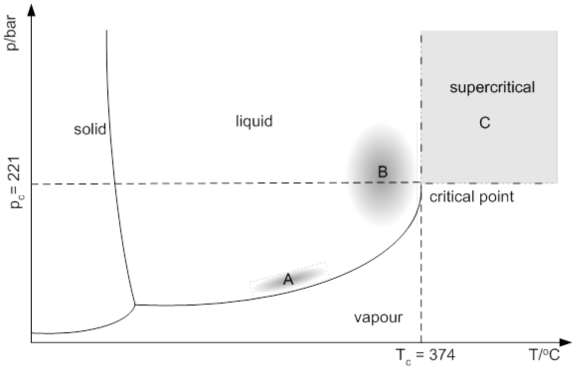
Images: courtesy of R. Lukasik

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

Hydrothermal processes

	LHW (Autohydrolysis)	Steam explosion*
Temperature	High	High
Solid concentration (LSR)	**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

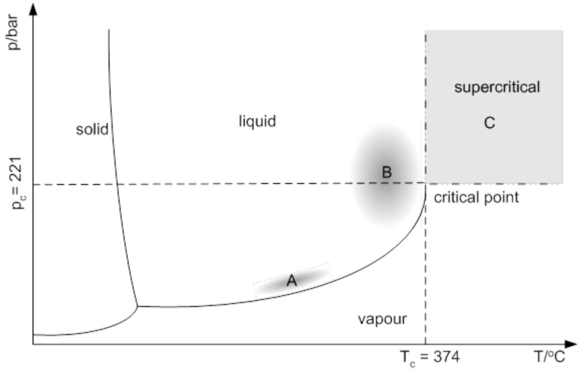
NOVEL PHYSICO-CHEMICAL PROCESSES

➢ 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**

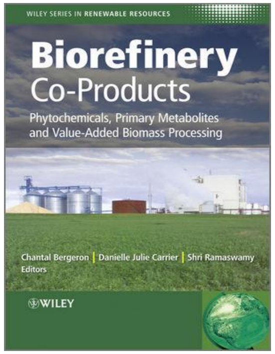
  Hemicellulose can be completely separated and **digestibility** of **cellulose** significantly increased (220ºC, K_w=6.34*10^{-12}, pH =5.5)

- **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 CHEMICAL PROCESSES

- ✗ **Capital cost**
- ✗ **a wide range of improvements to be achieved before SF will be implemented in larger scale**
- ✓ **The use of sub or supercritical fluids is beneficial for hemicellulose recovery**
- ✓ **Can be particularly interesting for extraction of (very) high value products**



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PHYSICO-CHEMICAL

➢ Hydrothermal processes

Demo plant


Courtesy of DONG Energy A/S

Kalundborg, Denmark www.inbicon.com

Feedstocks: wheat straw (mainly), sugarcane bagasse

Pretreatment: hydrothermal treatment using steam

Products:

Bioethanol (C6 fermentation), phase 1; C6+C5 fermentation (40-45% higher ethanol yield), phase 2

Lignin pellets

Biogas: from vinasse, C5 molasses,

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)

Biofuels: Ethanol, Bio-Jet, Butanol

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

Lignin derivatives: Phenols, Xylene, Terephthalic Acid

LNEG

PHYSICO-CHEMICAL

➢ Hydrothermal processes

CLARIANT

Demo

Straubing,Germany

www.sunliquid.com

Feedstocks*:* cereal straw and agriculture waste

Pretreatment: ‘mechanical and thermal pre-treatment’; steam

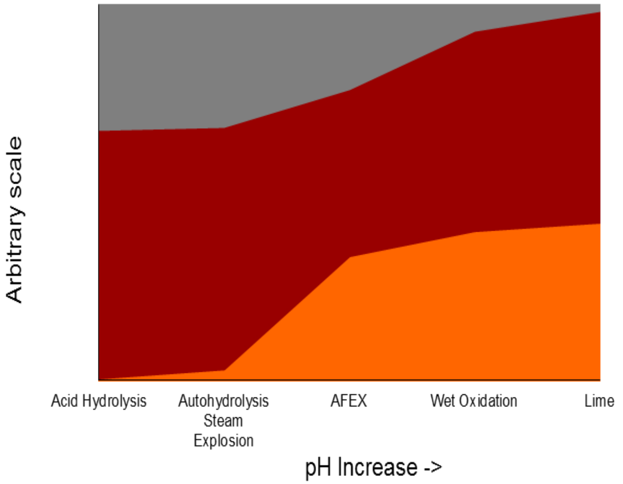
Product: Ethanol

Co-fermentation of C5 and C6; integrated enzyme production

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 may be advantageous



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

- *Novel processes* for example 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

LNEG
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www.lneg.pt

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