12th ECCRIA

The European Conference on Fuel and Energy Research and its Applications

AMBITION

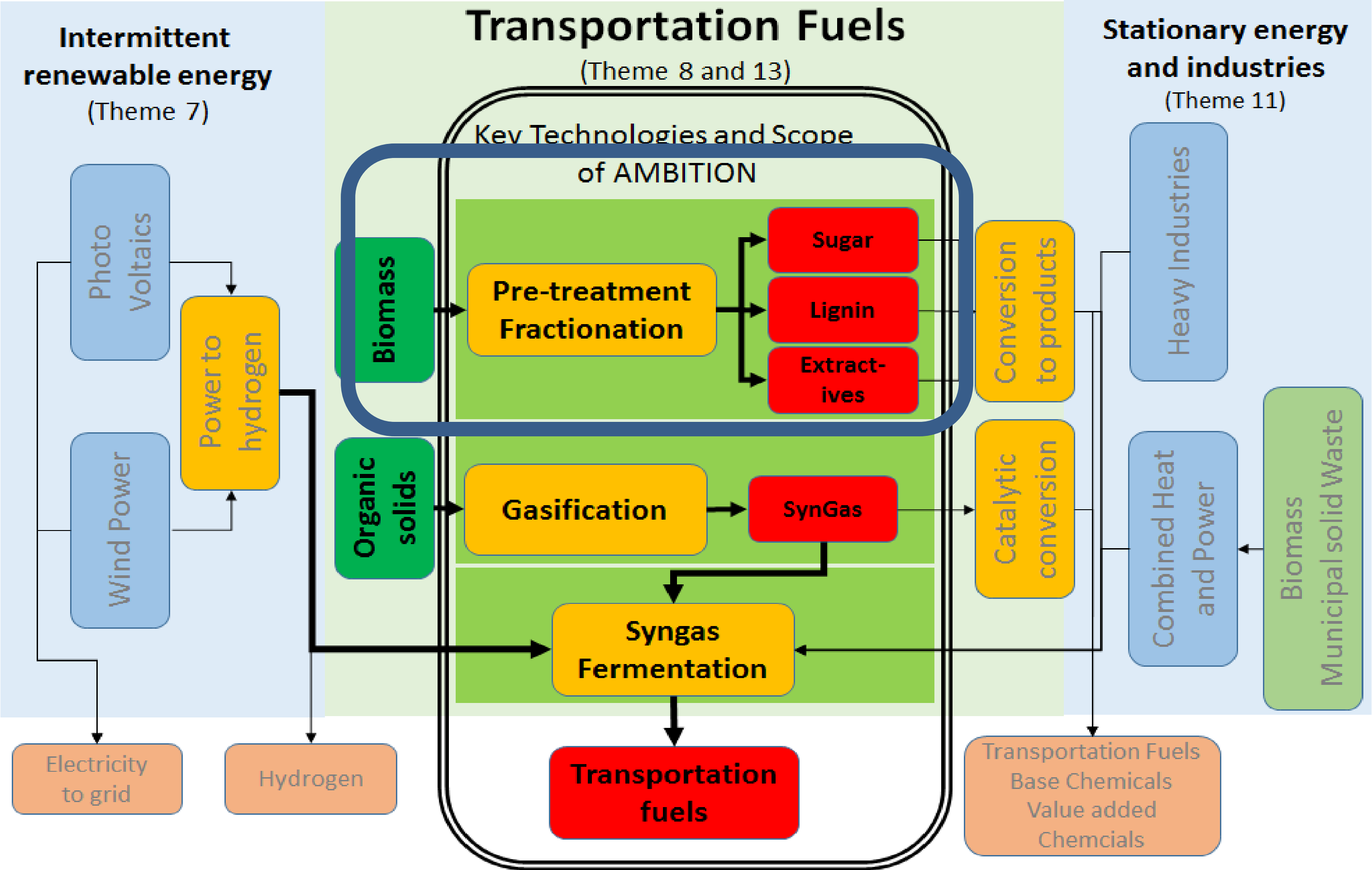
ADVANCED BIOFUEL PRODUCTION WITH ENERGY SYSTEM INTEGRATION

Recent Trends on Biomass Pretreatment

Francisco Gírio, LNEG

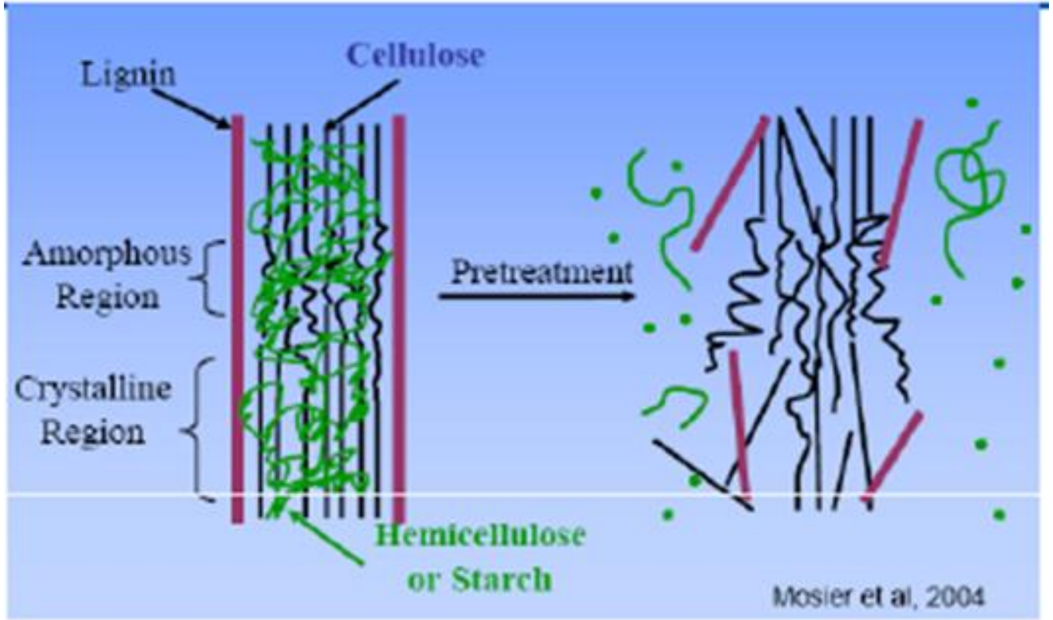
LNEG

EU AMBITION PROJECT



LC Biomass (heterogeneous) Chemical Structure

Feedstock Challenge: Lignocellulose biomass recalcitrance and heterogeneity is an issue!



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

Main composition:
Cellulose, Hemicellulose , Lignin, Proteins, Pectins, Extractives, Ash

Biomass (Deconstruction) Pretreatments

Pretreatments → ***Essential to disrupt the complex structure of lignocellulosic biomass*** → **Hemicellulose solubilization +**
↑ Extraction of lignin
↓ Crystallinity of cellulose

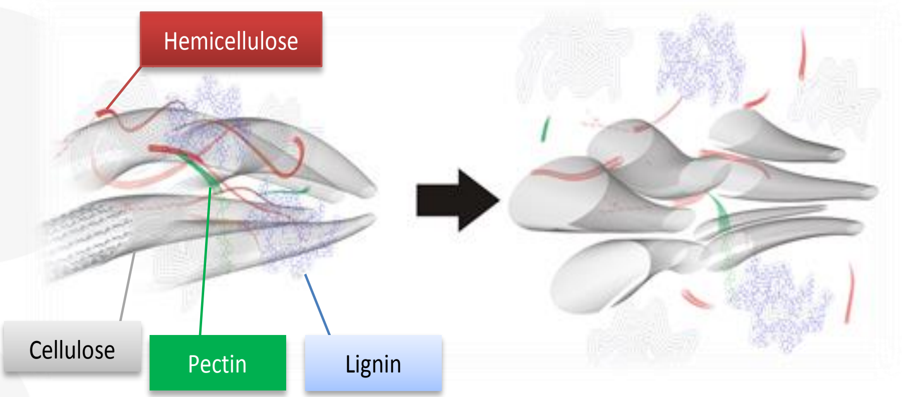
↓

↑ Surface area for enzyme binding and attack

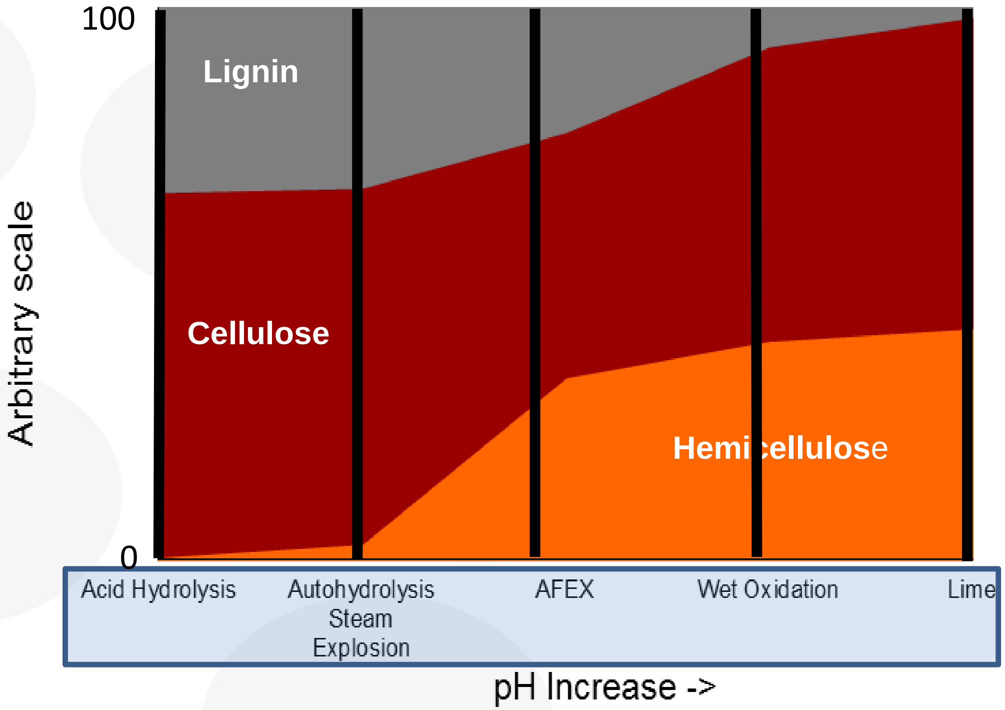
Examples of LC Biomass Pretreatment

Technologies:

- **Pulping (pulp&paper plants)**
- **Autohydrolysis (Hydrothermic)**
  (LHW/Steam Explosion)
- **Dilute acid hydrolysis**
- **Organosolv (acetone, ethanol)**
- **Alkaline (AFEX, etc)**

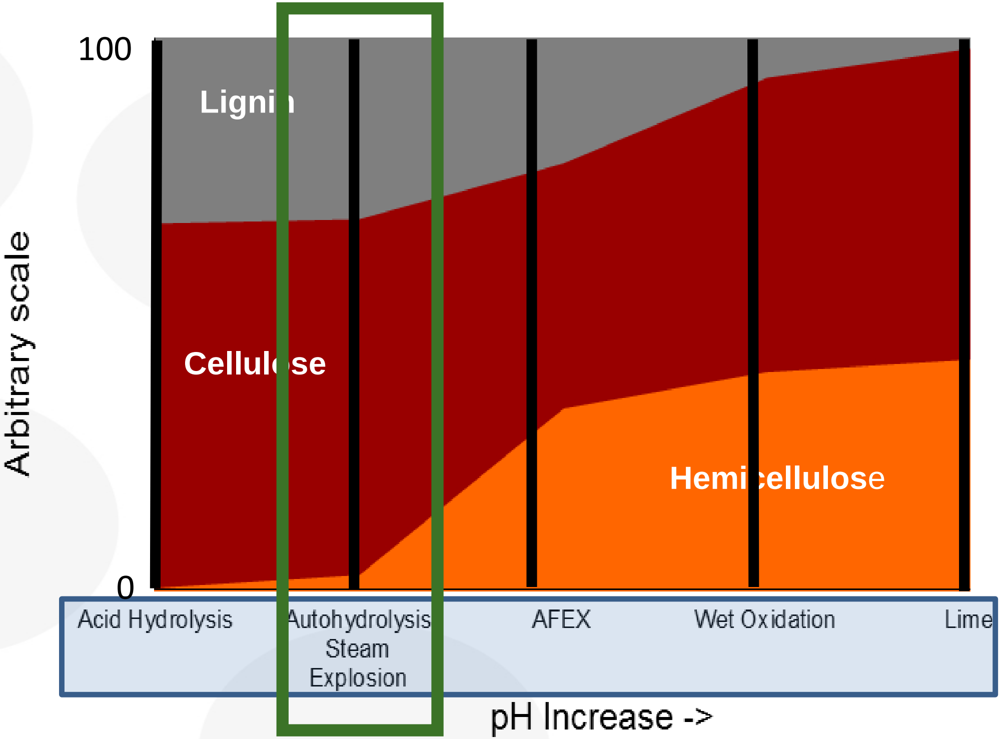


Biomass Composition after Pretreatment



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

Biomass Composition after Pretreatment



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

BetaRenewables (Proesa®)

Local: Crescentino (Italy)

270,000 ton/yr straw; 60 000 ton/year of ethanol , 13MWe generated from lignin. Production process: uncatalysed steam explosion (Proesa®), EH + Co-Fermentation C5+C6 sugars; since Oct 2013.

1st Commercial

Raízen

Local: Piracicaba – SP (Brazil)

sugar cane bagasse and straw; 32,000 ton/year Ethanol + electricity. Co-location with an existing 1G bioethanol plant from sugar cane. Production process: Iogen´s technology – acid-catalysed steam explosion, EH and Fermentation; since 2015.

1st Commercial

Clariant (SunLiquid®)

Local: Straubing - Munique (Germany)

Cereal straw, agricultural waste. 500 tons/year Ethanol + Lignin for CHP. Production process: uncatalyzed steam explosion, enzymatic hydrolysis and co-fermentation of C_5 and C_6 ; since 2012.

Demo

Hydrothermal pretreatments

Steam explosion (uncatalyzed)

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

Biomass Deconstruction LHW Facilities, Unit of Bioenergy at LNEG - Lisbon, Portugal

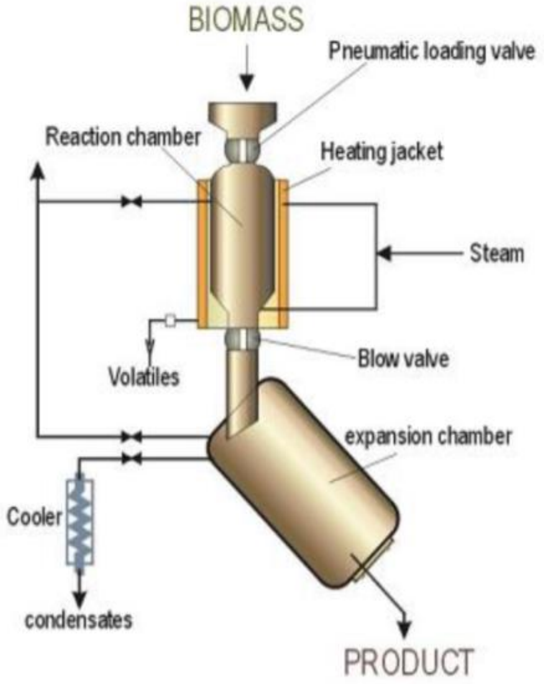


Figure 28: Steam explosion process (Isabella De Bari)

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

Current status of Biomass Pretreatments

☐ **Insufficient (or no) separation of cellulose and lignin**

↓ Effectiveness of enzymatic cellulose hydrolysis

☐ **Formation of by-products that inhibit fermentation**

- Sugars → furans
- Lignin → phenolic compounds

☐ **Use of chemicals and energy-intensive**

☐ In general, **no clean technology (waste streams production)** (e.g. for dilute acid AFEX pretreatments)

☐ In general, **high costs of corrosion-resistant equipment** (e.g. for dilute acid pretreatment)

EU Project AMBITION – WP2: KPIs for Biomass Pretreatment

- **KPI 1:** Enhancement of lignocellulosic biomass fractionation reaching main separated streams with at least 80% purity each
- **KPI2:** Reduce up to 50% the amount of enzymes required to EH (of cellulose/hemicellulose) – reaching cellulose EH yield>90% and hemicellulose EH yield >95%
- **KPI3:** Decrease energy demand of pre-treatment by 25%

Reference Biomass Pretreatment: un-catalyzed steam explosion

The overall impact on sustainability and cost reduction for production of advanced ethanol:

- **Reduce GHG emissions** of “pretreatment + enzyme hydrolysis” steps of > **30%**
- **Increase** overall **energy efficiency** by 10-20%
- Should lower **overall production** cost (OPEX) of the biofuel by **20-30%**

EU Project AMBITION – WP2: Efficient low-temperature pre-treatment to generate valuable lignin and carbohydrates

Approach

Processes based on **non-hazardous catalysts and/or green solvents,** namely:

- **CATALYTIC IONIC LIQUIDS** (ILs) aqueous systems:

to drive the **direct conversion of hemicellulose** into sugars and to yield an easily digestible solid containing **low crystallinity cellulose** and upgradable **lignin.**

- **ORGANOSOLV PROCESSES:**

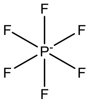
  - **Ketones**
  - **Furans**
  - **Higher Alcohols**
  - **Imidazole**
  - Ethanol (as base-case)

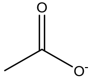
to **selectively remove and depolymerize lignin**, to **yield an easily digestible polysaccharide** containing solid and high quality lignin derived products

Novel Deconstruction Pretreatments

➢ Ionic Liquids

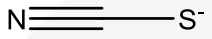
Anions

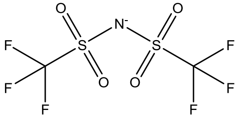

hexafluorophosphate


acetate

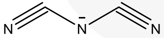
Cl^-
chloride

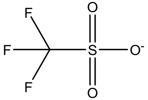
I^-
iodide

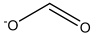

thiocyanate

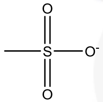

bis(trifluoromethanesulfonyl)amide

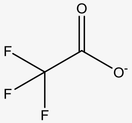
Br^-
bromide

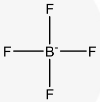

dicyanamide

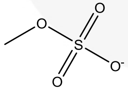

trifluoromethanesulfonate

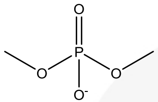

formate

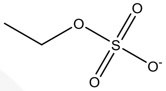

methanesulfonate


trifluoroacetate

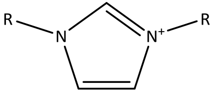

tetrafluoroborate

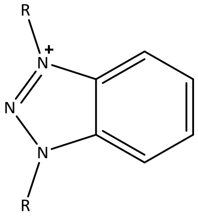

methylsulfate

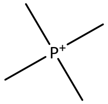

dimethylphosphate

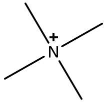

ethylsulfate

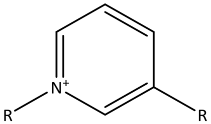
Cations

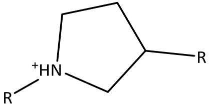

1-alkyl(1)-3-alkyl(2)-imidazolium


1-alkyl(1)-3-alkyl(2)-benzotriazolium


tetraalkylphosphonium


tetraalkylammonium


1-alkyl(1)-3-alkyl(2)-pyridinium


1-alkyl(1)-3-alkyl(2)-pyrrolidinium

Ionic Liquids – Chemical Reactivity

1) Alter the physicochemical properties of the biomass macromolecular components;
2) Extract a specific macromolecular fraction;
3) Perform different fractionation approaches after dissolution.

Advantages:

- ✓ ↓ Cellulose crystallinity;
- ✓ ↑ Extraction of lignin
- ✓ Less degradation of monosaccharides;
- ✓ Recyclability and reuse of ILs.

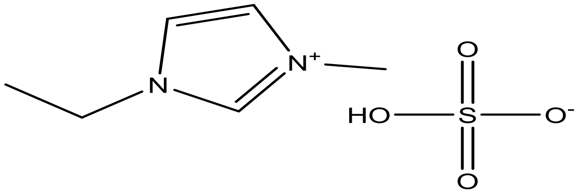
A. M. da Costa Lopes, K. João, A. R. C. Morais, E. Bogel-Lukasik and R. Bogel-Lukasik, *Sustain. Chem. Process.*, 2013, **1:3**

General properties

- ❖ High polarity
- ❖ Negligible volatility
- ❖ Thermal stability
- ❖ High conductivity
- ❖ Large electrochemical window

Ionic liquid-based biomass pretreatment

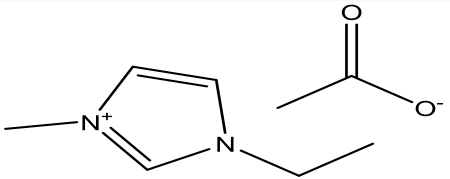
1 Hydrogen-bond acidic ionic liquid process



1-ethyl-3-methylimidazolium hydrogensulfate
([emim][HSO$_4$])

- **Solvent and catalyst**
- **Hydrolysis** of macromolecules
- **Conversion** of monosaccharides
- **Fractionation** approach

2 Hydrogen-bond basic ionic liquid process



1-ethyl-3-methylimidazolium acetate
[emim][OAc]

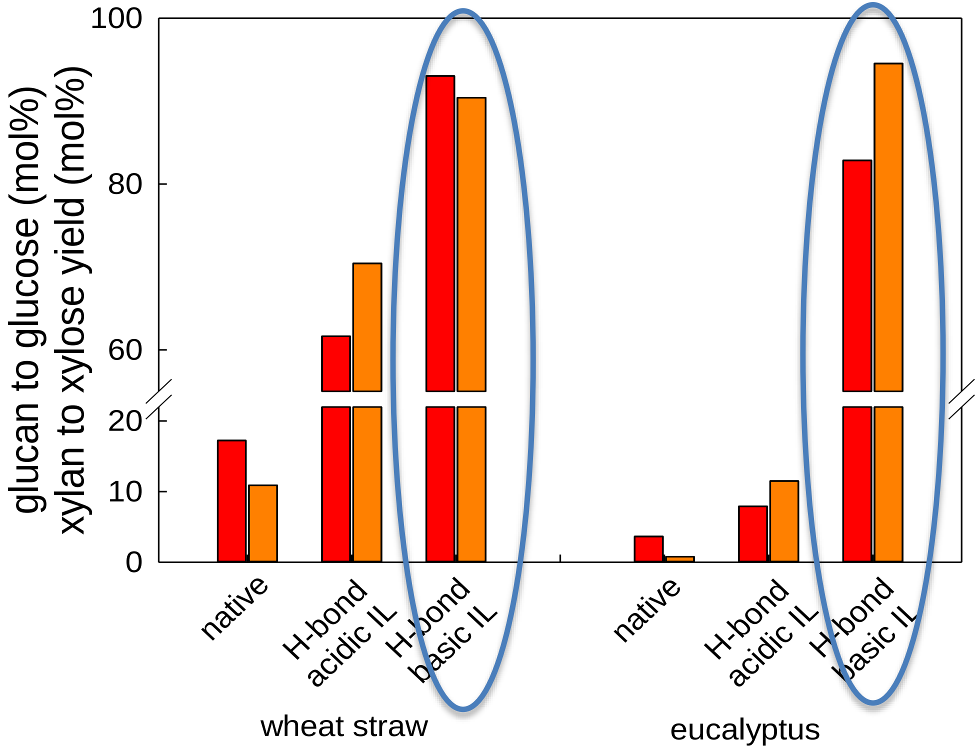
- **Good solvent**
- **Extraction** of macromolecules
- **Fractionation** approach

Wheat straw
Eucalyptus residues

Comparison of H-bond acidic & basic ionic liquids on WS & Eucalyptus

Biomass pre-treated at 140 ^{o}C

Enzymatic hydrolysis



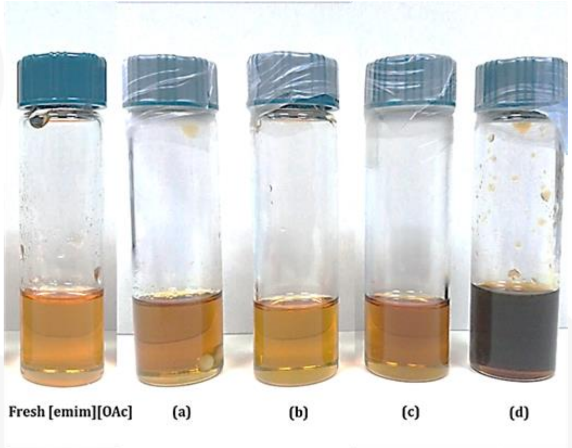
Glucose, xylose

CTec2® (10% w/w cellulose); 50 °C; 72h; 180 rpm; 5% (w/v) solids; 0.02% (w/v) sodium azide

CE analysis of recovered [emim][CH_3COO]

- **Ionic Liquid Recovery with co-extraction of Phenolics compounds**

Ionic liquid recovery (up to 96 %, w/w)



Colour of the fresh [emim][OAc] and recovered ILs after the wheat straw pre-treatment at different temperatures: **(a)** 80° C; **(b)** 100° C; **(C)** 120° C and **(d)** 140° C.

Solid Phase Extraction

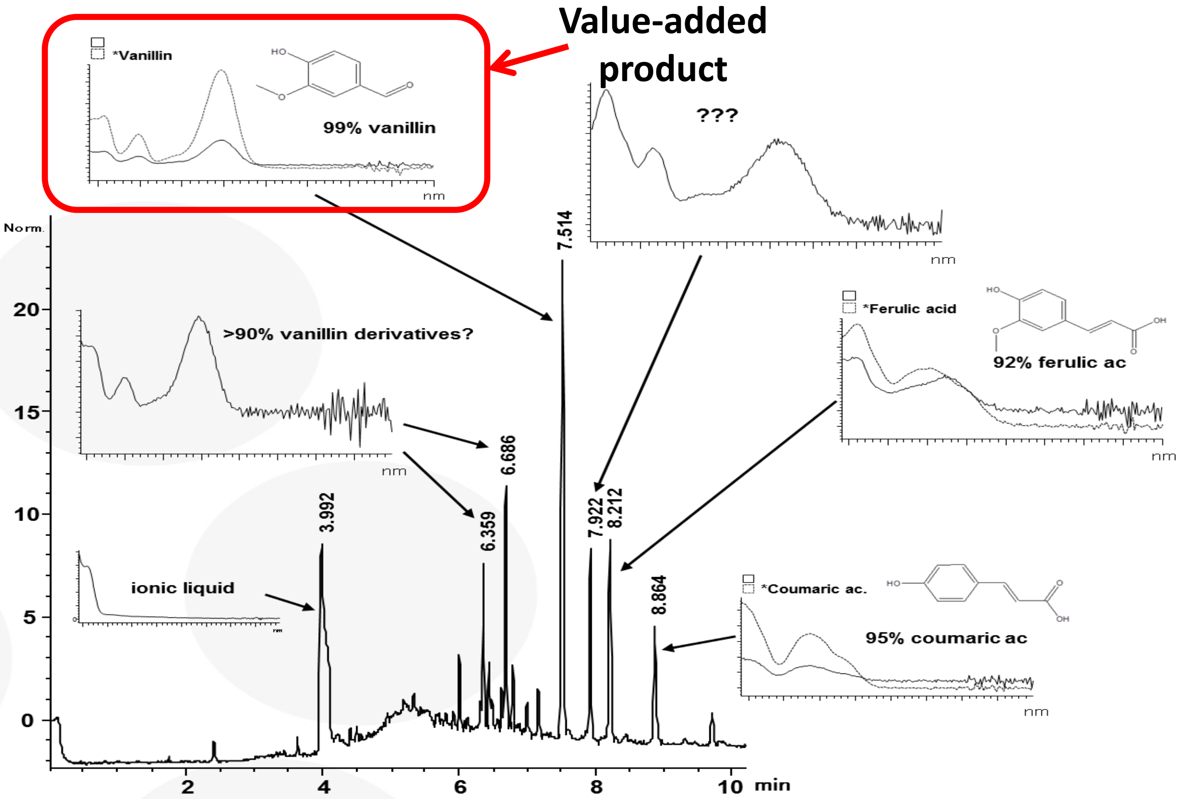
(SPE)

Capillary Electrophoresis

(CE)

S. P. Magalhães da Silva, A. M. da Costa Lopes, L. B. Roseiro and R. Bogel-Lukasik, *RSC Adv.*, 2013, **3**, 16040.

CE analysis of recovered [emim][CH_3COO]



Electropherogram recorded at 320 nm showing the phenolic profile of the recovered IL after pre-treatment at 100° C during 18h.

S. P. Magalhães da Silva, A. M. da Costa Lopes, L. B. Roseiro and R. Bogel-Lukasik, *RSC Adv.*, 2013, **3**, 16040.

Ionic liquid-based biomass pre-treatment (status at the end of 1st year AMBITION project)

		[emim][HSO_4]		[emim][OAc]	
KPI		**Wheat straw**	**Eucalyptus**	**Wheat straw**	**Eucalyptus**
Purity>80%	**Pre-treated solid**	**61.9%***	**68.9%***	-----------	-----------
	Liquid	> 90%		-----------	-----------
	Cellulose-rich	-----------	-----------	**81.6%**	**77.1%**
	Hemicellulose-rich	-----------	-----------	**80.8%**	**
	Lignin-rich	-----------	-----------	***	
Cellulose>90% Hemicellulose>95%	**Cellulose yield (glucan to glucose)**	**59.3%**	**7.9%**	**91.2%**	**82.9%**
	Hemicellulose yield (xylan to xylose)	**70.7%**	**11.5%**	**96.9%**	**94.6%**
Low Energy requirements by 25% decrease at least (*reference: steam explosion*)	**Temperature**	Reduction by >35% in comparison to baseline method (140 °C vs. 210 °C)			

*can be increased, e.g. by delignification; ** due to low amount recovered was not chemically characterized

*** unknown precise purity but it is high purity lignin, free from polysaccharides as determined by FTIR analysis

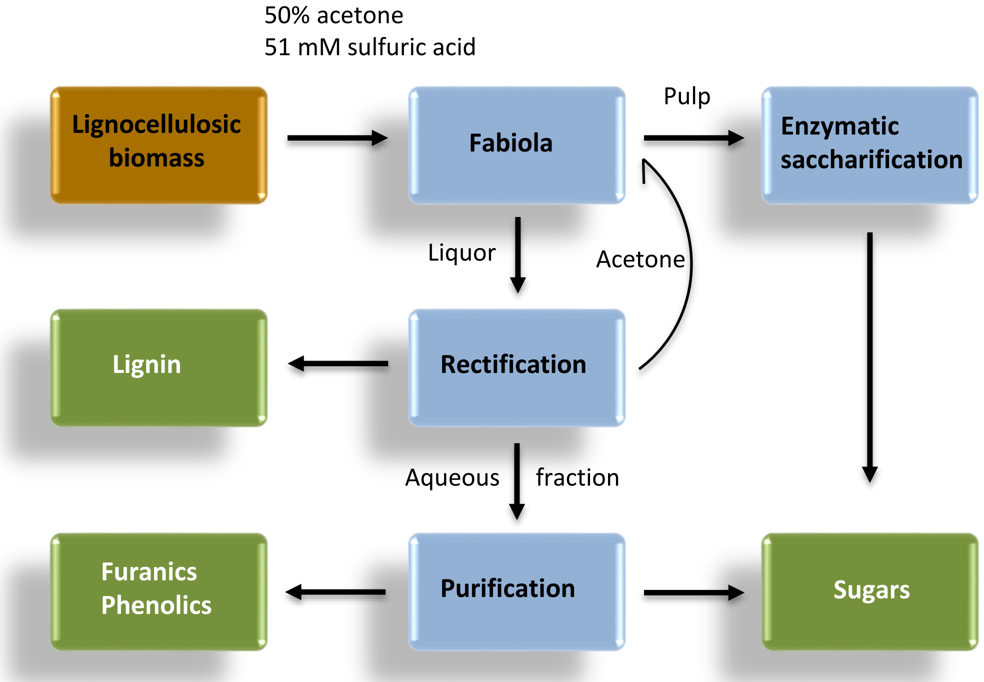
Organosolv based biomass pre-treatment

Target: Selective lignin extraction using low-temperature organosolv processes, based on the use og:

- **ketones**,
- **higher alcohols**,
- **imidazole**, **furans**
- **other alternative solvents**

in order to recover **high quality lignin (**for added-value applications) & **sugar streams** e.g. for subsequent fermentation or catalytic hydroprocessing.

Fabiola Process: mild acetone organosolv fractionation



50% acetone
51 mM sulfuric acid

Lignocellulosic biomass

Fabiola

Pulp

Enzymatic saccharification

Liquor

Acetone

Lignin

Rectification

Aqueous fraction

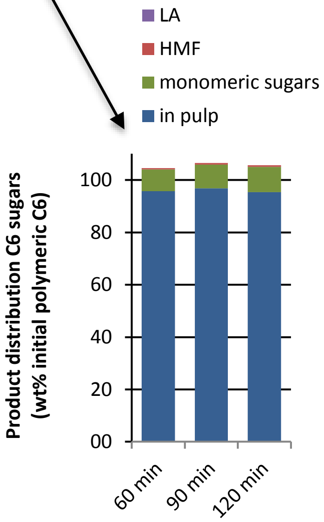
Furanics Phenolics

Purification

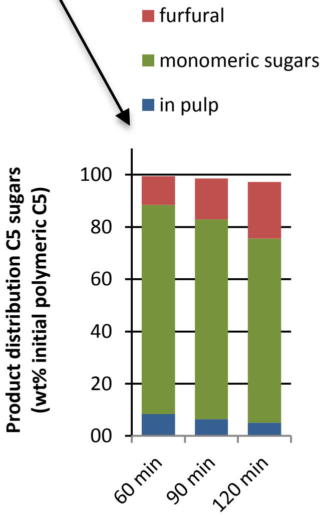
Sugars

Fabiola Process: mild acetone organosolv fractionation

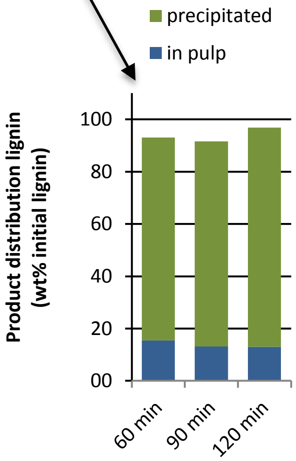
Cellulose: Remains in the pulp: 89% glucose yield after EH



Hemicellulose: 80% yield monomeric sugars



Lignin: 85% delignification



ECN

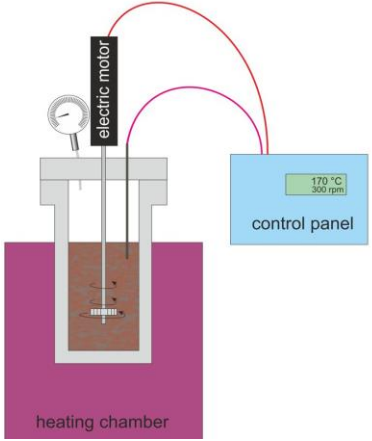
Efficient fractionation of eucalyptus already achieved at 140ºC (60 min, 51 mM sulfuric acid)

Similar results for ethanol organosolv are only obtained using T >180ºC

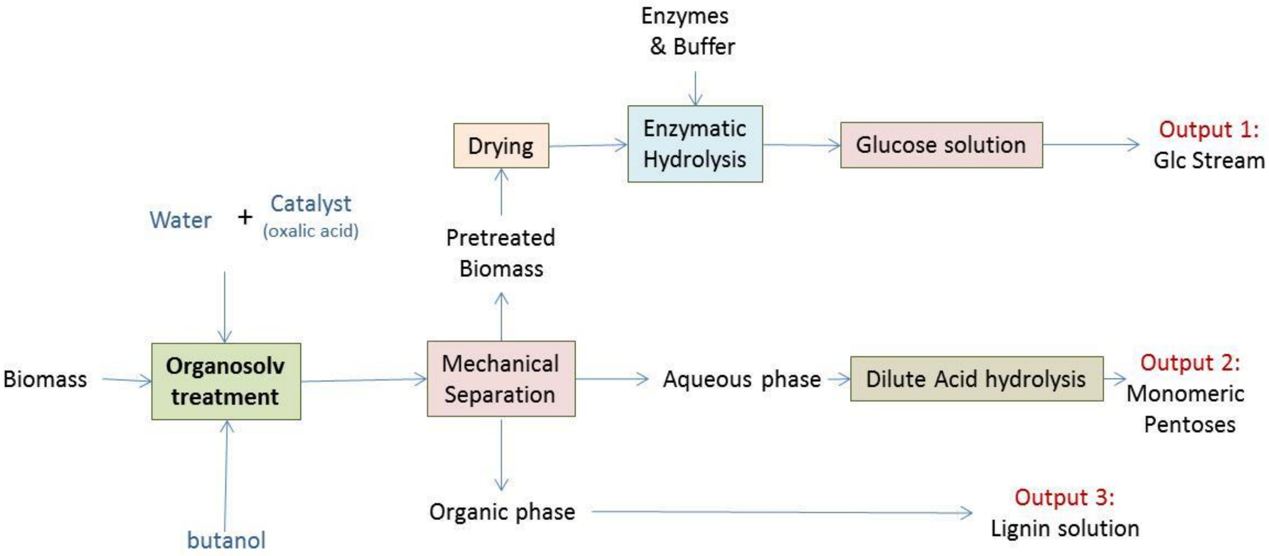
Issue: Industrial scale-up

AMBITION

ENEA Triphasic Organosolv



Biomass:water:butanol = 1:10:10


Enzymes & Buffer

Drying

Enzymatic Hydrolysis

Glucose solution

Output 1:
Glc Stream

Water + Catalyst (oxalic acid)

Pretreated Biomass

Biomass

Organosolv treatment

Mechanical Separation

Aqueous phase

Dilute Acid hydrolysis

Output 2:
Monomeric Pentoses

butanol

Organic phase

Output 3:
Lignin solution

ENEA Triphasic Organosolv

Experimental Design

Wheat straw:

- **Temperature**, ºC, in the range **140-180**;
- **Time**, minutes, in the range **30-90**;
- **Catalyst** (**oxalic acid**), as wt% respect the dry biomass, in the range of **0-10**

Eucalyptus wood:

- **Temperature**, ° C, in the range **140-180**;
- **Catalyst** (**oxalic acid**), as wt% respect the dry biomass, in the range of **0-10**
- **Time,** minutes, **60 (constant)**

Study Type:	Response Surface
Design Type:	Box-Behnken
Runs:	15 (3 center points)
Design Model:	Quadratic

Study Type:	Response Surface
Design Type:	Central Composite
Runs:	10 (2 center points)
Design Model:	Quadratic

ENEA Triphasic Organosolv

		[BUTANOL]	
KPI	**Parameter**	**Wheat straw**	**Eucalyptus**
Purity>80%	**Cellulose-rich fraction**	**59.0%***	**75.9%***
	Hemicellulose-rich fraction	**58.1%**	**55.1%**
	Lignin-rich fraction	**46.7%**	**61%**
Cellulose>90% Hemicellulose>95%	**Cellulose yield (glucan to glucose)**	**94%**	**79.5%**
	Hemicellulose yield (xylan to xylose)**	**88.5%**	**94%**
Low Energy requirements by 25% decrease at least (*reference: steam explosion*)	**Temperature**	**Reduction to 175ºC**	**Reduction to 170ºC**

*glucan content in the solid phase

**xylan in the pretreated solid

*** possible reduction by using other solvents (2-MTHF)

General conclusions

All biomass pretreatment options under development are steadily **reaching** or **moving towards** the required targets

- Purity; Saccharification yields; Energy requirements
- Op. conditions seem to support the pretreatments of feedstock mixtures, with minimum loss of efficiency for:
  - ❖ **ILs ([emim][OAc])**;
  - ❖ Organosolv: **Butanol-** and **Acetone**-based

LNEG team

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Luís Duarte
Luísa Roseiro
Belina Ribeiro
Susana Marques
Céu Penedo
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Kay Dahmen

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