Pretreatment & Enzymatic hydrolysis for production of substituted fuels from renewable biomass

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Industrial collaboration: Processum Biorefinery Initiative, MoRe Research and SEKAB E-Technology (Örnsköldvik)

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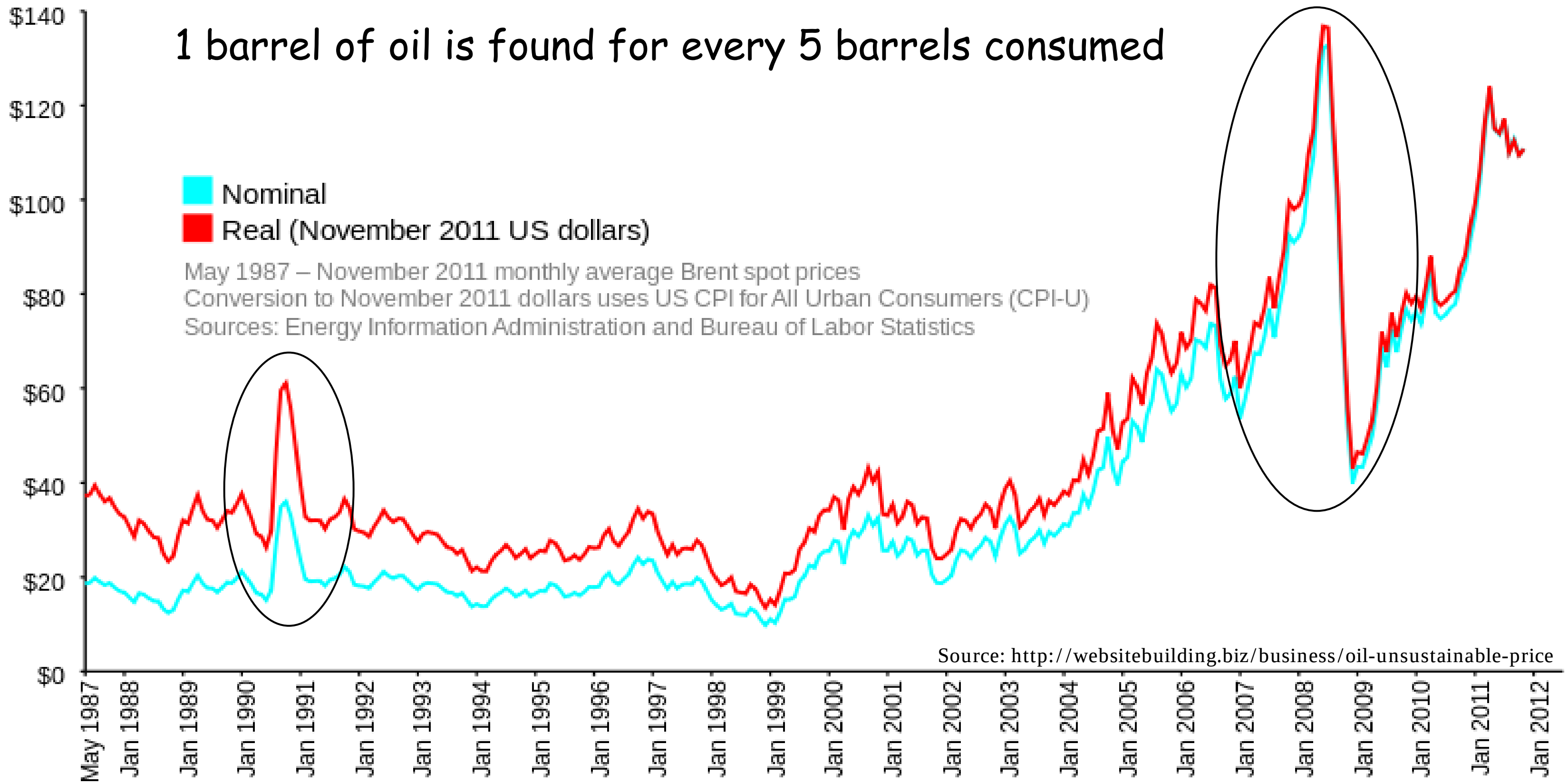
Peak Oil: The World's Greatest Challenge



Source: http://websitebuilding.biz/business/oil-unsustainable-price

The benefit of the present oil price hikes could be to focus attention on the possibility of a world less dependent on oil.

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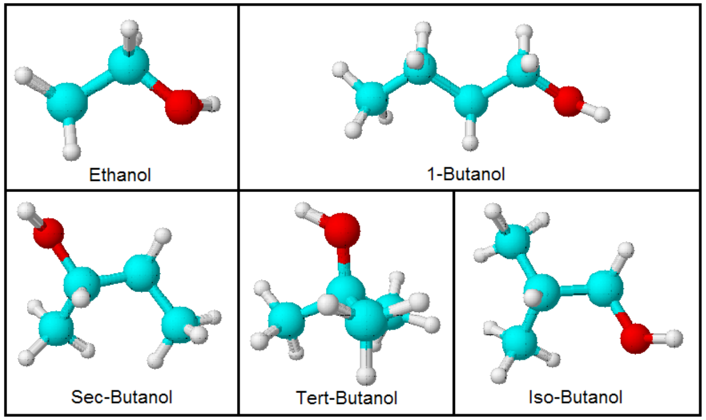
"Oil Will Be A Past Relic When Today's Babies Hit Fifty".

Source: www.conservativedailynews.com

Biofuels: a barrier for "sustainable fuel"

Source: Thomas Wallner (IBEX Seminar 2012)



	Gasoline	Ethanol	Butanol
Octane Number	86 – 94	112.5 – 114	87
LHV (MJ/Lit)	31.2 – 32.4	21.1 – 21.3	27.8
Heat of vaporization (MJ/kg)	0.36	0.92	0.43
Energy density (MJ/L))	32	19.6	29
Flash point (°C)	–	15	37
Solubility in waster	<0.1	Fully miscible	7
Boiling point	–	78°C	118°C
Density (kg/L)	0.74	0.79	0.81
Vapor Pressure (Bar)	0.480 – 1.034	0.159	0.023

Ethanol and Butanol contain oxygen and can both be used as oxygenates for gasoline.

- Can be blended with gasoline (e.g E5, E10, E25, E85..)

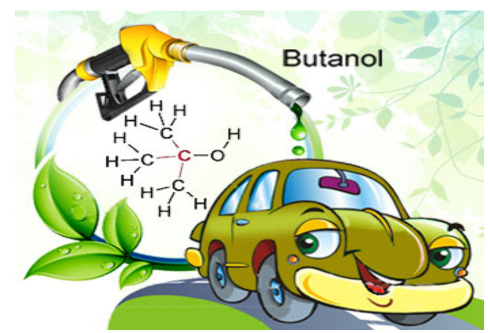
Butanol is better biofuel than ethanol

- More compatible with oil infrastructure
- Existing pipelines and filling stations can be used
- Can be blended with gasoline and with diesel

Busslink - Stockholm

E85 85% Ethanol

"Major oil companies show more interest in butanol than ethanol".



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Biofuels production

First generation

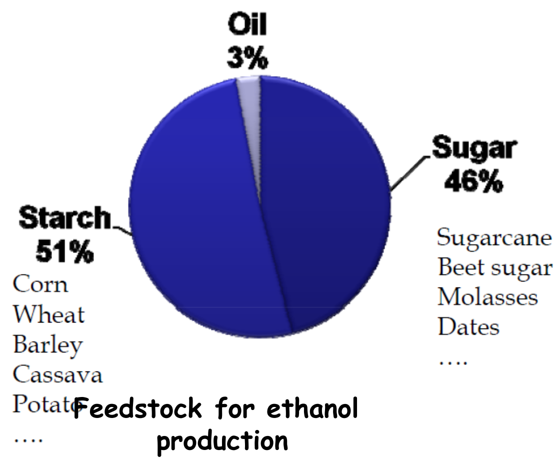
Ethanol from Fermentation:

$$\text{Sugar(s)} \xrightarrow{\text{Microorganisms}} \text{Ethanol} + \text{By-products}$$

$$\underset{\text{(starch)}}{(C_6H_{10}O_5)_n} + nH_20 \xrightarrow{\text{enzymes}} \underset{\text{(glucose)}}{nC_6H_{12}O_6}$$

$$\underset{\text{(glucose)}}{C_6H_{12}O_6} \xrightarrow{\text{yeast}} \underset{\text{(ethanol)}}{2CH_3CH_2OH} + 2CO_2 + \text{heat}$$

$$\underset{\text{Sugars (e.g. glucose)}}{C_6H_{12}O_6} \xrightarrow{\text{Microorganisms}} \underset{\text{(Butanol)}}{C_4H_9OH} + 2CO_2 + H_2O$$



Feedstock for ethanol production

Source: www.asiantrendsmonitoring.com

"...large increases in biofuels production is the main reason behind the steep rise in global food prices" -World Bank policy research working paper July 2008"

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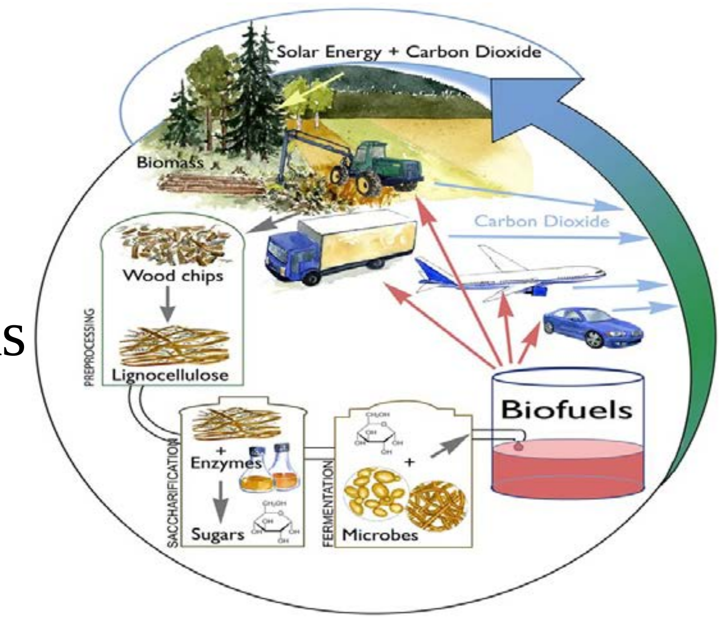
Lignocellulosic materials

Forest residues

Agricultural residues

Municipal solid wastes

- Abundant
- Inexpensive
- Sustainable and potential feed stocks



Source: www.bioimprove.se

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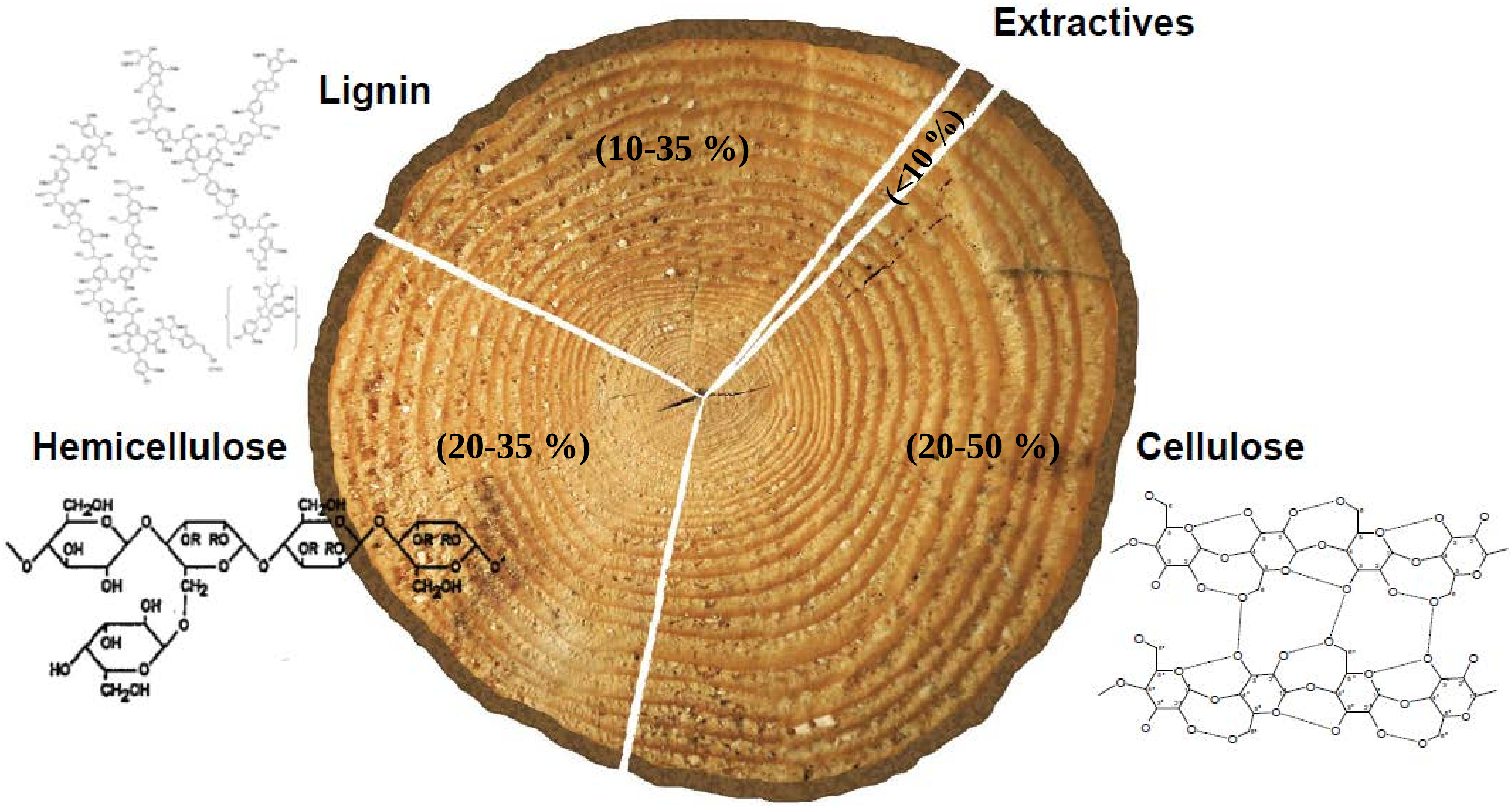
Chemical composition of Lignocellulose



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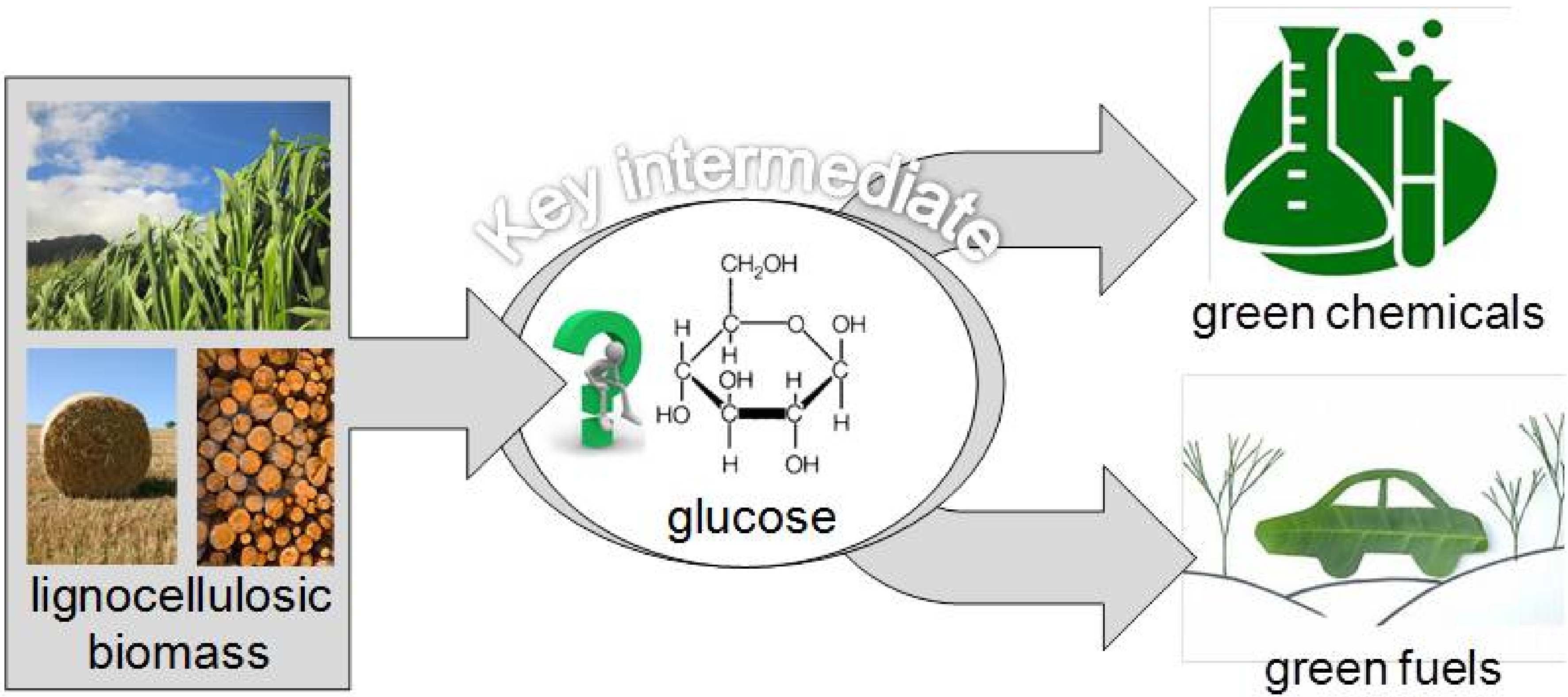
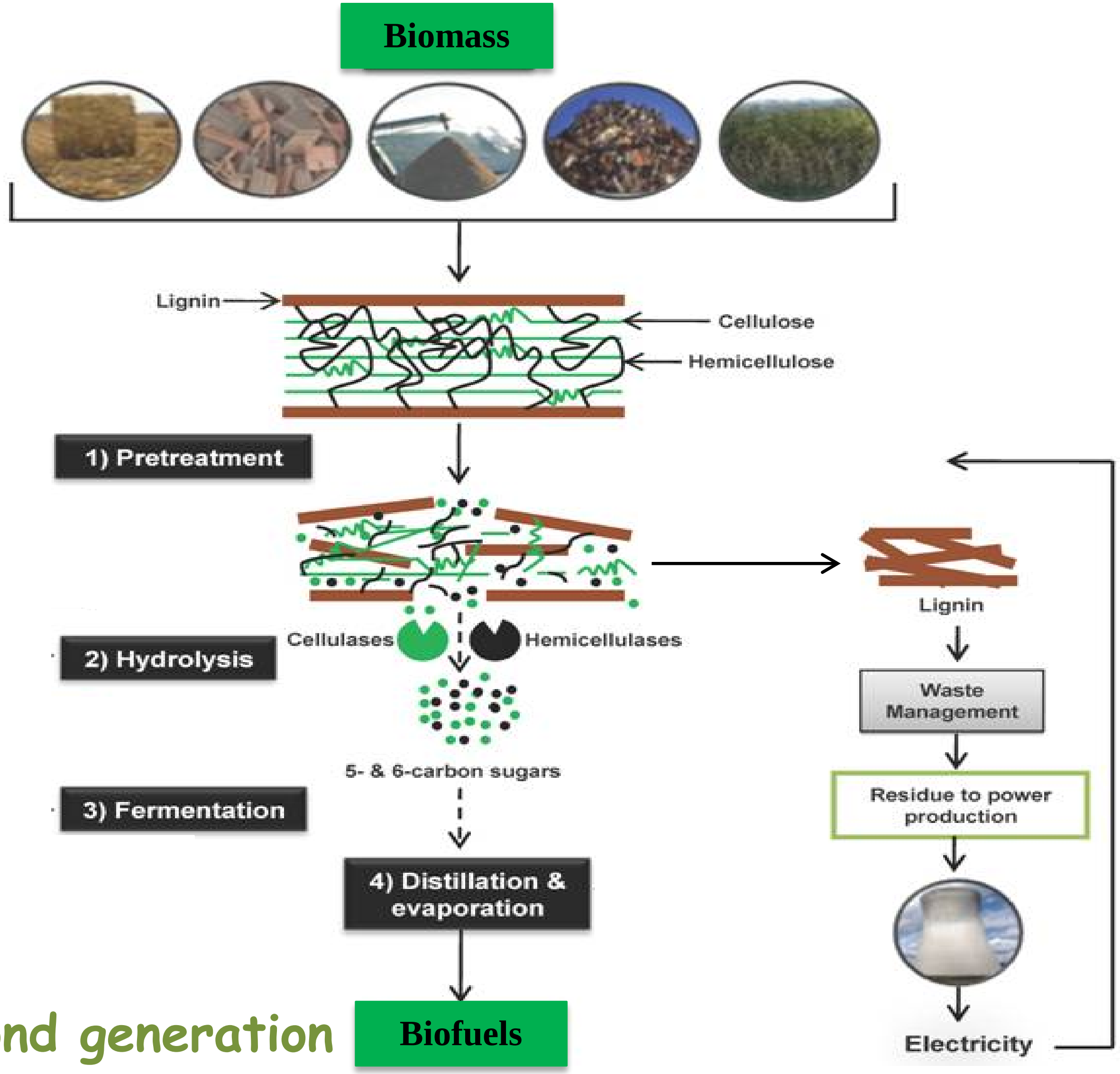
Monomer sugars



Source: http://www.catchbio.com/results/catalytic_hydrolysis_of_cellulose

Cellulosic fules production



Second generation

"Cellulosic fuels can achieve much greater energy and GHG benefits"

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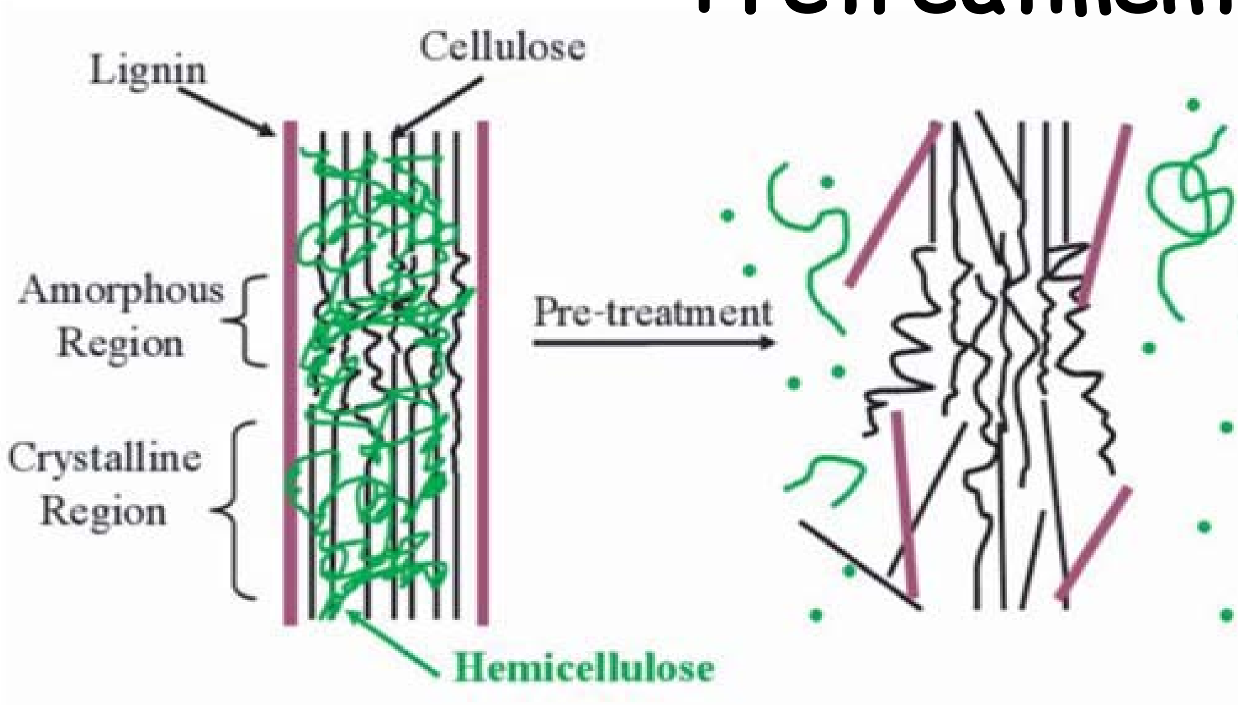
Pretreatment



Goals:

– Opening crystalline structure of Lignocellulose
– Hydrolysis of hemicelluloses
– Enhance the enzymatic hydrolysis

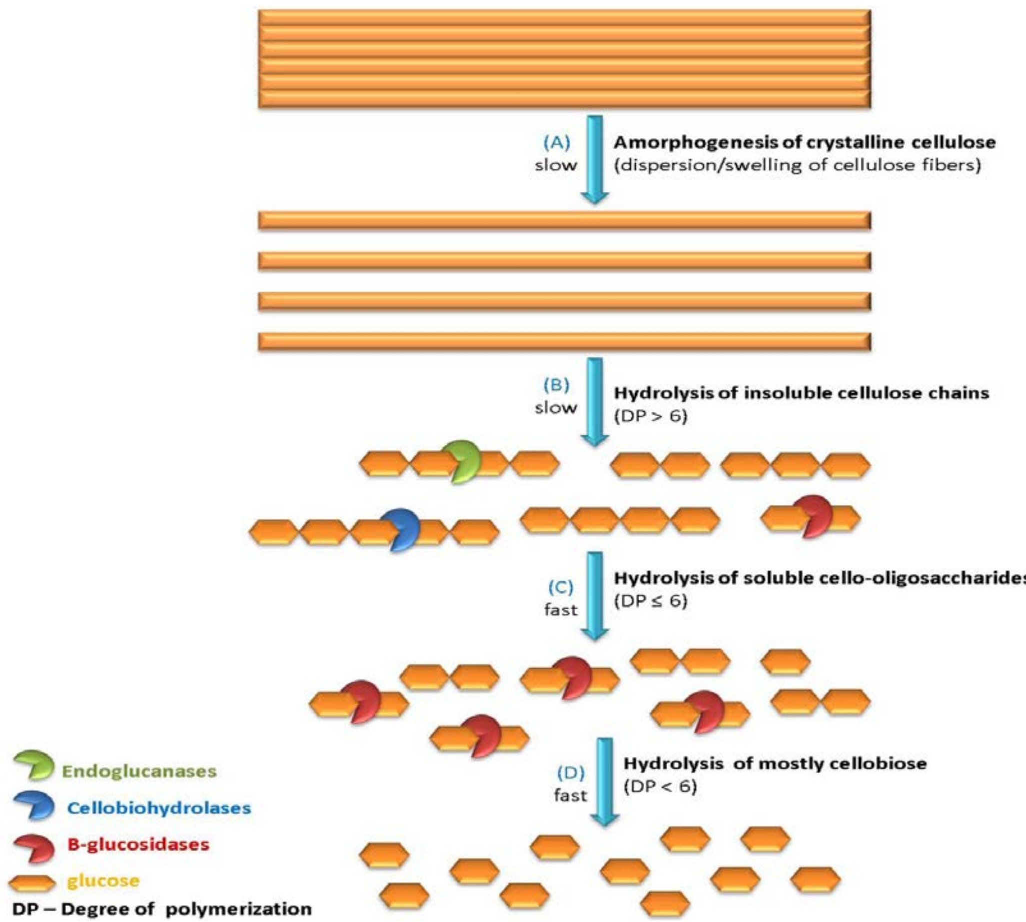
IL's: Novel alternative green solvents for the pretreatment of lignocelluloses.

Physical methods	Physical-chemical Methods	Chemical Methods	Biological methods
➢ Mechanical Pre-treatment. ➢ Heat treatment ➢ Microwave irradiation	➢ Steam explosion. ➢ Liquid hot water (LHW). ➢ Ammonia fiber explosion (AFEX). ➢ CO2 explosion.	➢ Ozonolysis. ➢ Dilute-acid hydrolysis. ➢ Concentrated-acid hydrolysis. ➢ Alkaline hydrolysis. ➢ Oxidative delignification. ➢ Wet oxidation. ➢ Organosolv process. ➢ Dissolution in IL's	➢ Fungal pretreatment.

Hydrolysis

Splitting of cellulose to glucose by

- Concentrated acid hydrolysis
  at room Temp. by e.g.
  - » 72% H_2SO_4
  - » 42% HCl
- Dilute acid hydrolysis
  - » e.g. 0.5% H_2SO_4 at 200-220°C (ca 20-25 bar), 5-10 min
- Cellulases enzymes
  at ca 45°C and 24-72 hours



Source: Arantes et al., 2010

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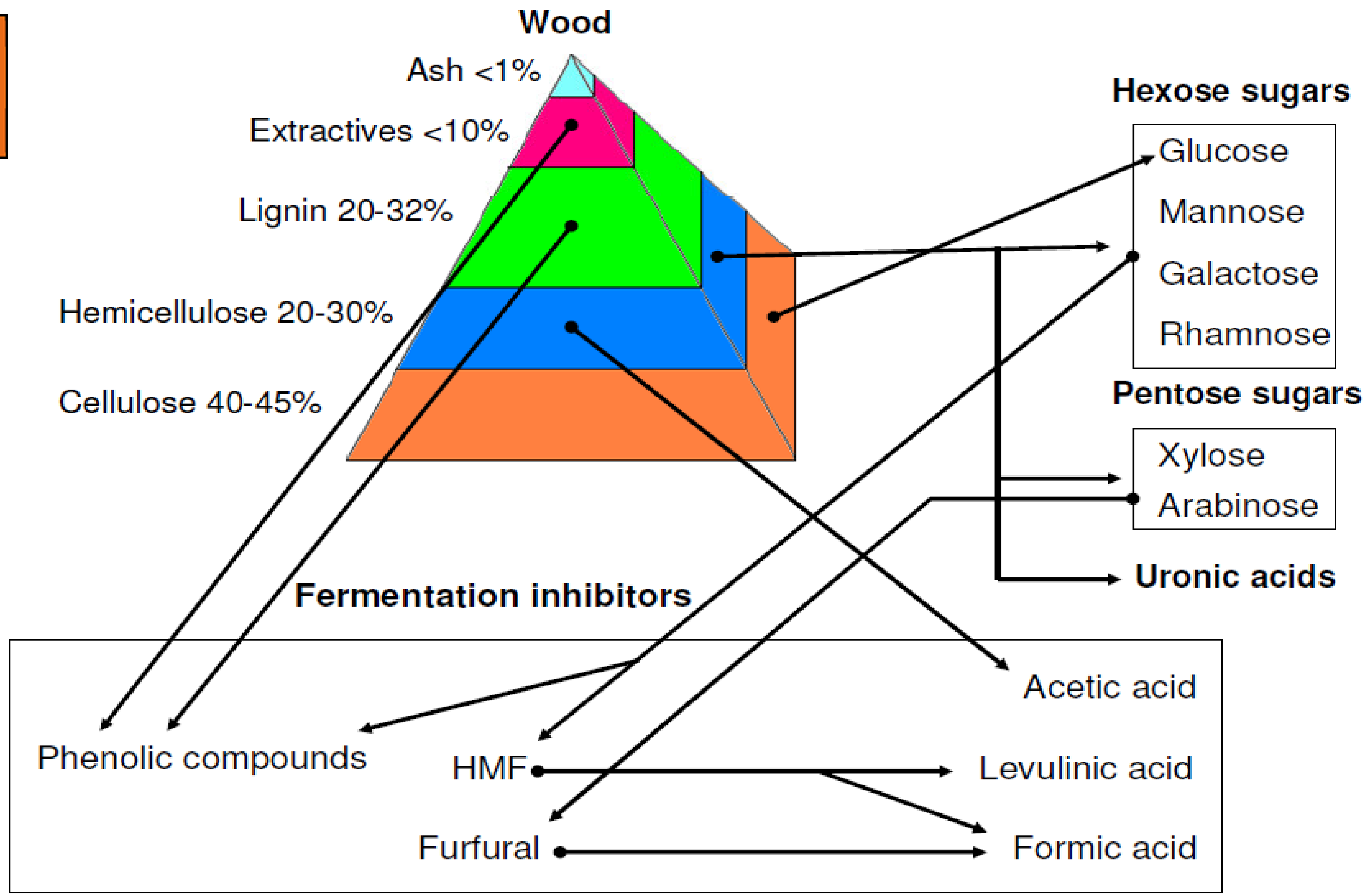
Toxic compounds from Pretreatment



(Source: Alriksson B., 2006)

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Work flow

- Identifying biomass with good bio-processing properties
- Evaluating the existing and new solvents for pretreatment of biomass. *(soudham et al., 2011a) (soudham et al., 2013)*
- Investigations to improve hydrolysis efficiency. *(soudham et al., 2011b).*

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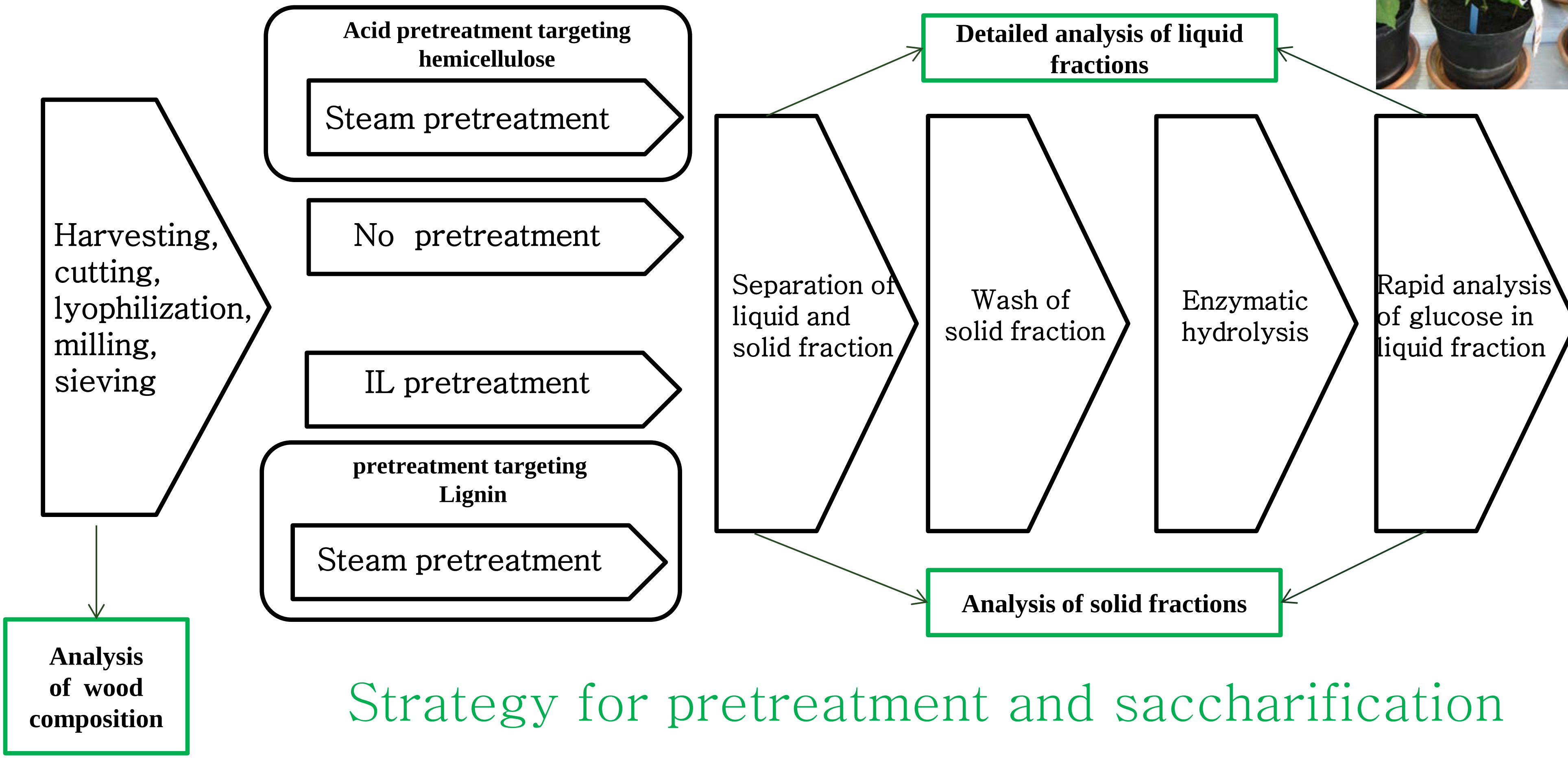
Identifying biomass

screening of transgenic aspens



Strategy for pretreatment and saccharification

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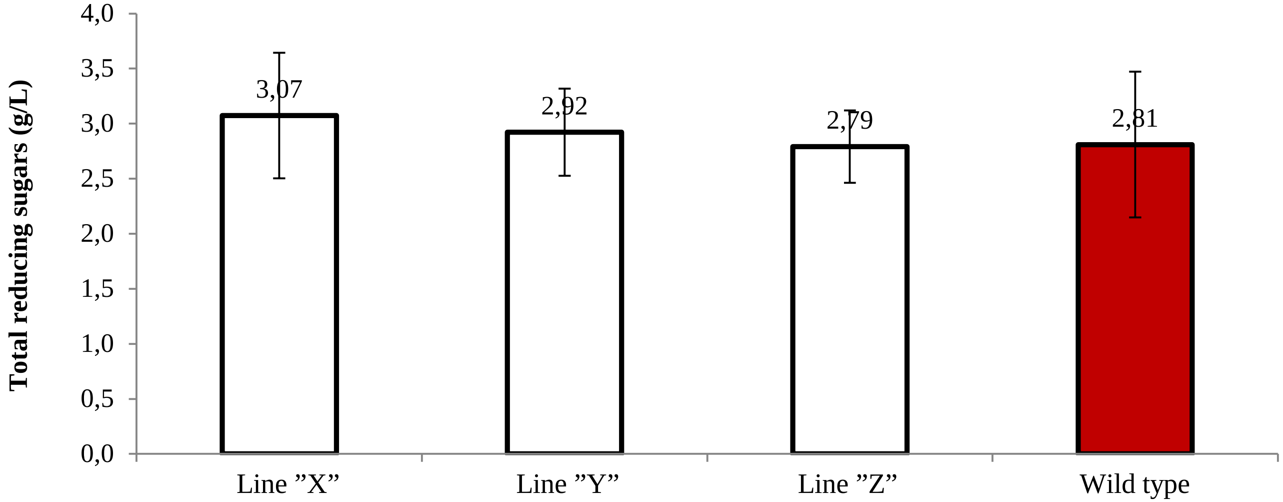
BIOIMPROVE

www.bioimprove.se

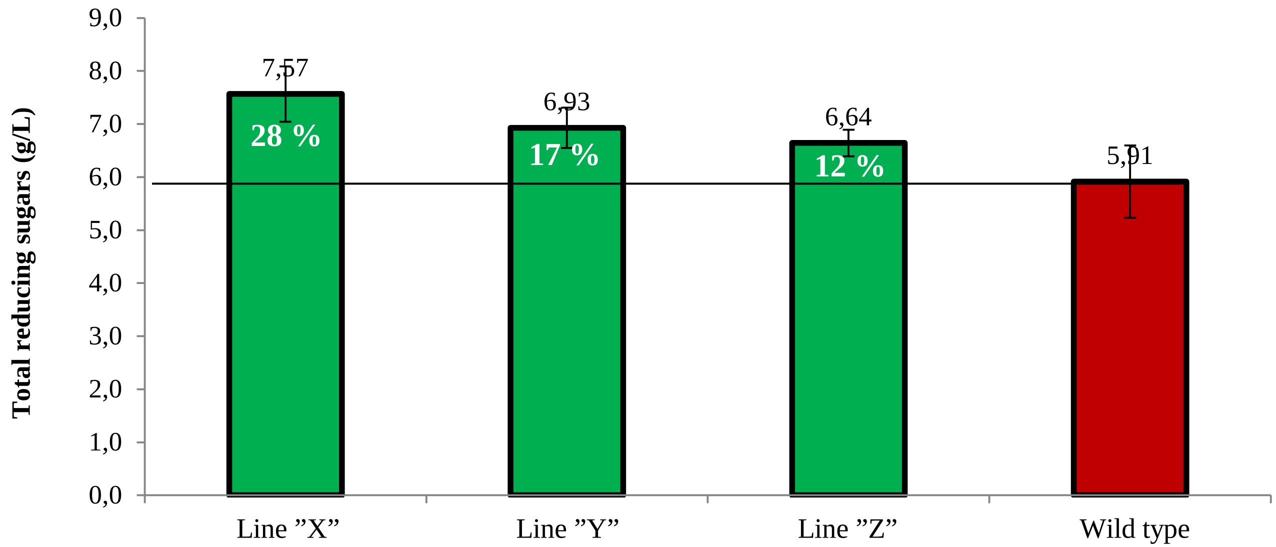
No pretreatment



T-Test: P Critical = 0.05

Line ”X”	**0,52**
Line ”Y”	**0,76**
Line ”Z”	**0,96**

Steam pretreatment with acid catalyst



T-Test: P Critical = 0.05

Line ”X”	**<0,01**
Line ”Y”	**<0,01**
Line ”Z”	**<0,01**

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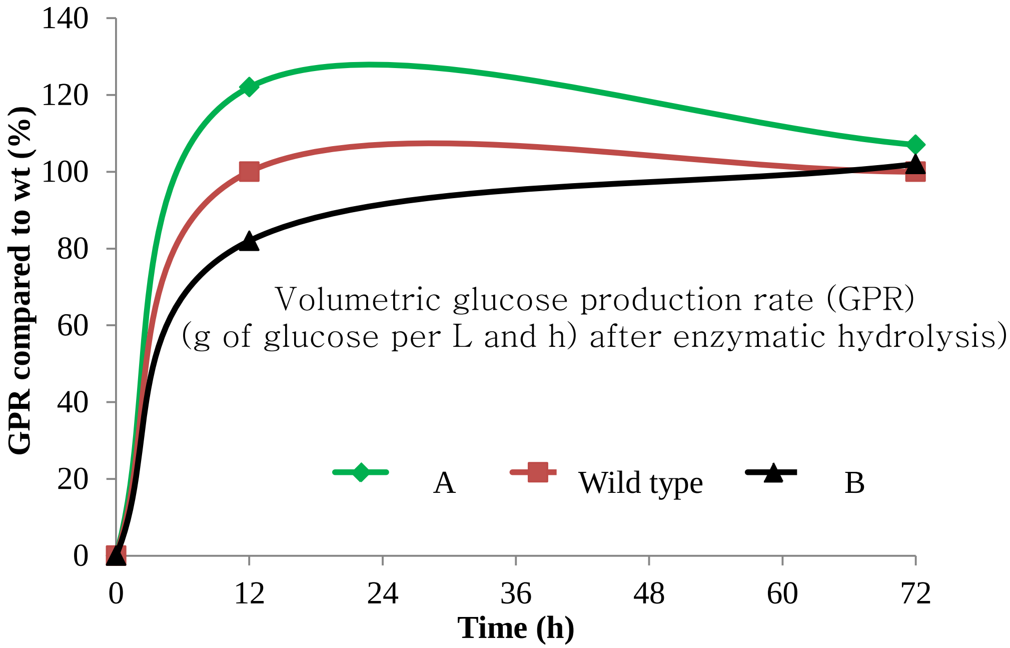


Dissolution in green solvents:

IL's such as

- [emim][OAc]
- [emim][Me2PO4]

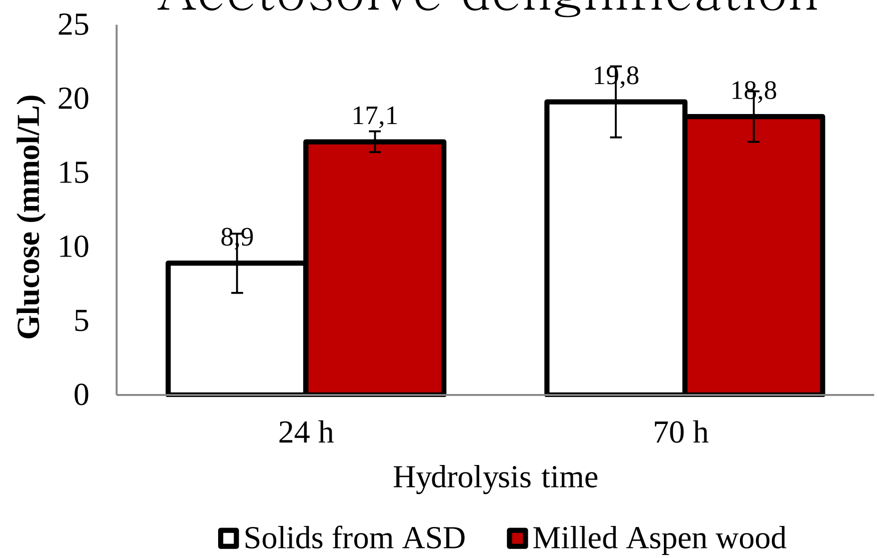
(Not studied)

Delignification stratagy:

Steam pretreatment with organic solvents

- Acetosolve delignification (ASD) (Acetic acid, HCl)
- Ethanol

Acetosolve delignification



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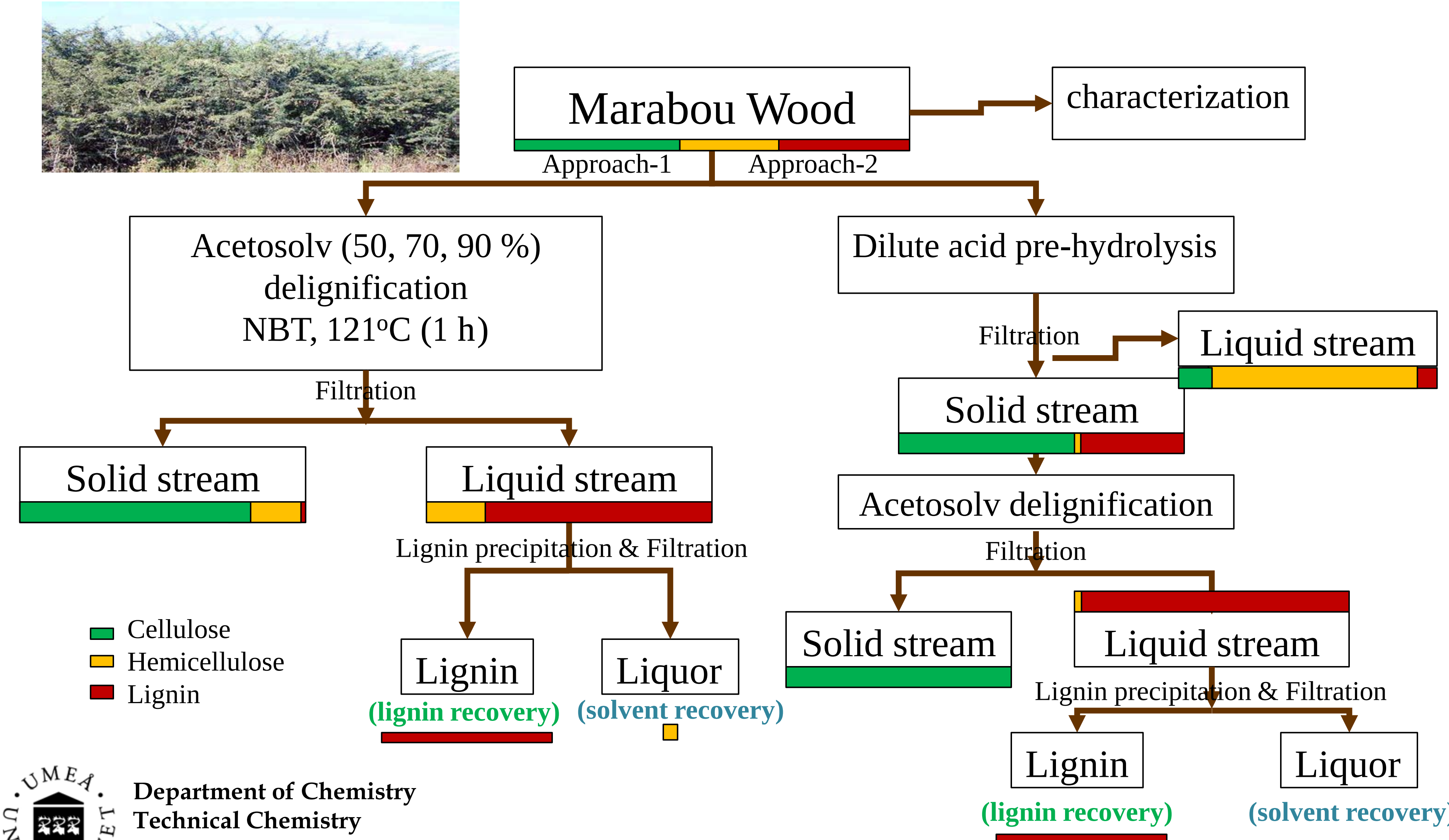
Fractionation of Marabou wood



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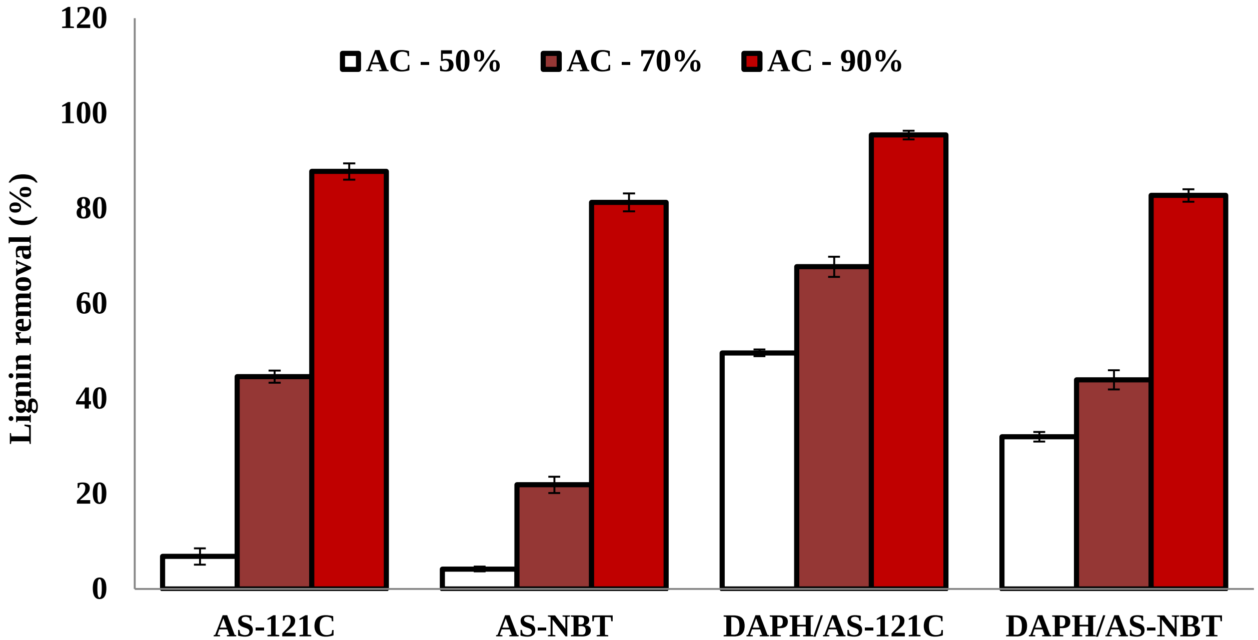
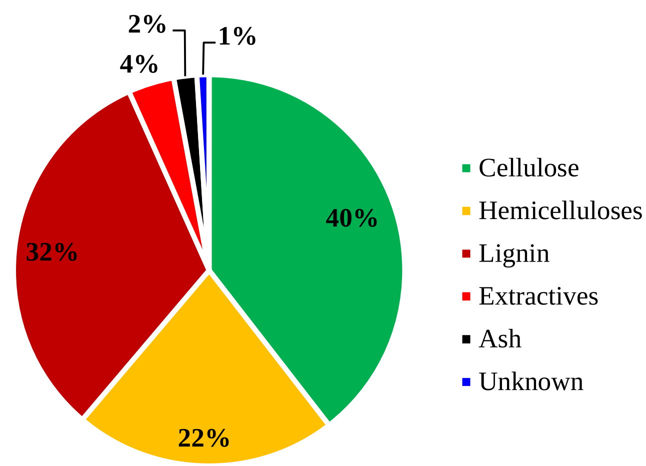
Lignin removal and recovery



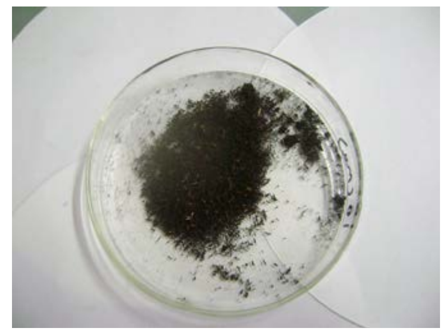
Chemical composition of Marabou wood



AS – 121C

AS – NBT

Recovered lignin



Pulp after delignification

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For. Stud. China, 2011, 13(1): 64–70
DOI 10.1007/s11632-011-0106-x

RESEARCH ARTICLE

Acetosolv delignification of marabou (*Dichrostachys cinerea*) wood with and without acid prehydrolysis

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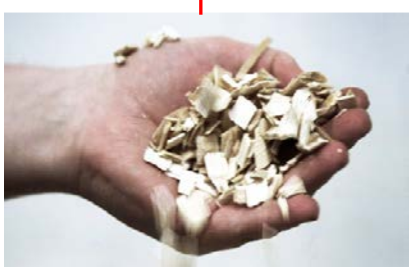
[3] Department of Biotechnology, Lorena School of Engineering, University of São Paulo, Lorena 12602-810, Brazil

Enzymatic hydrolysis of softwood and agricultural residues after treatment with ionic liquid (1-allyl-3-methylimidazolium formate)

Thermochemical pretreatment of sugarcane bagasse and Norwegian spruce was performed in the Örnsköldsvik demo plant in Sweden (<www.sekab.com>).

Sugarcane bagasse

Microcrystalline cellulose



Spruce wood

Solvation of cellulosic material in ionic liquid. The figure shows 5% (w/w) cellulose dissolved in [AMIM][Fo].

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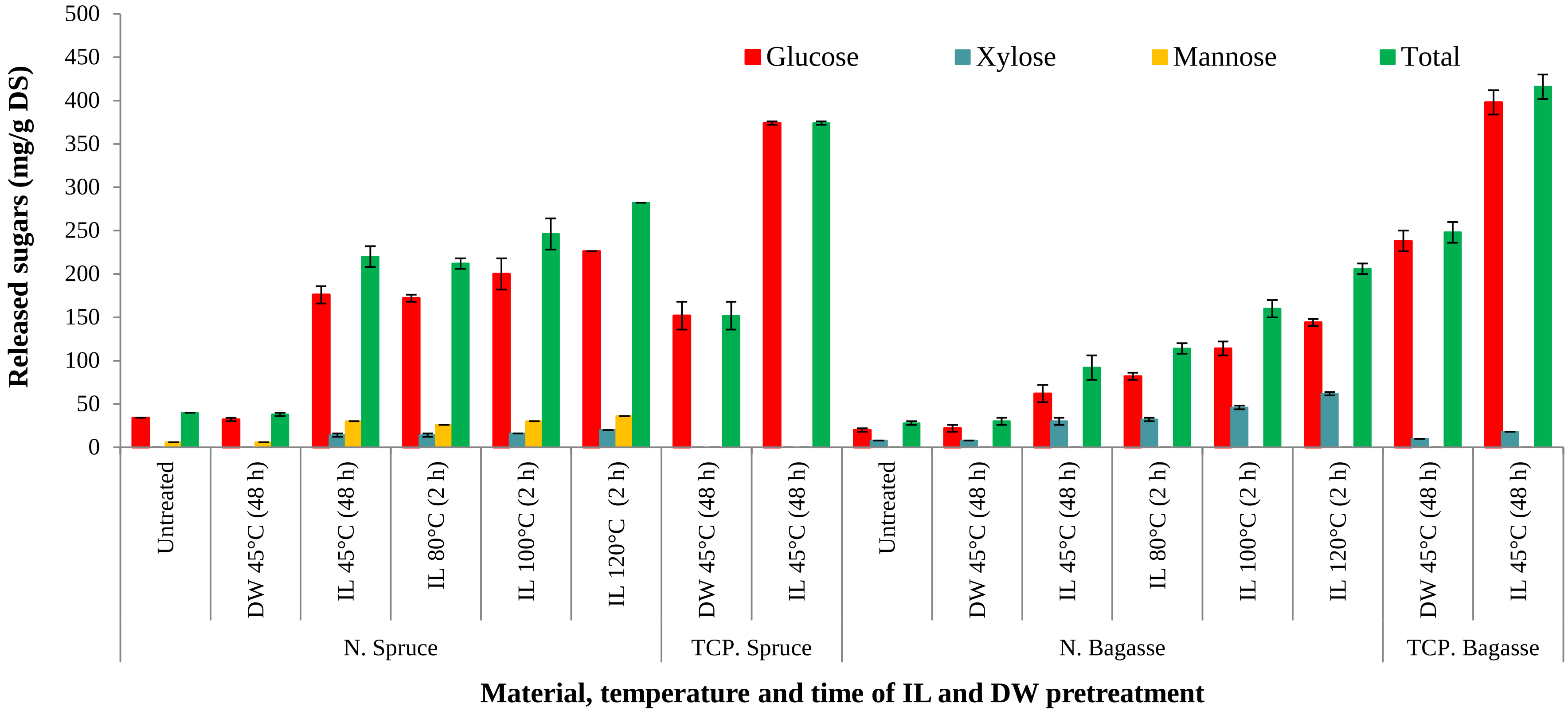
Enzymatic hydrolysis of Norway spruce and sugarcane bagasse after treatment with Ionic Liquid



Monomer sugars obtained after enzymatic hydrolysis (72 h at 45 ºC) of native (N) and thermo – chemically pretreated (TCP) spruce and sugarcane bagasse. The cellulosic substrates were treatment with [AMIM]Fo ionic liquid (IL) or deionized water (DW).

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Research Article SCI

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Enzymatic hydrolysis of Norway spruce and sugarcane bagasse after treatment with 1-allyl-3-methylimidazolium formate

Venkata Prabhakar Soudham,[a] John Gräsvik,[a] Björn Alriksson,[b] Jyri-Pekka Mikkola[a,c] and Leif J. Jönsson[a,*]

Investigations to improve the enzymatic hydrolysis of toxic lignocellulose hydrolyzates

- In-situ detoxification of toxic lignocellulose hydrolyzates with the addition of a reducing agent sodium sulfite, dithionite, or dithiothreitol. (*Soudham et al., 2011b*)

- Chemical conditioning of inhibitory lignocellulose hydrolyzates with the solvents "X" or "Y".

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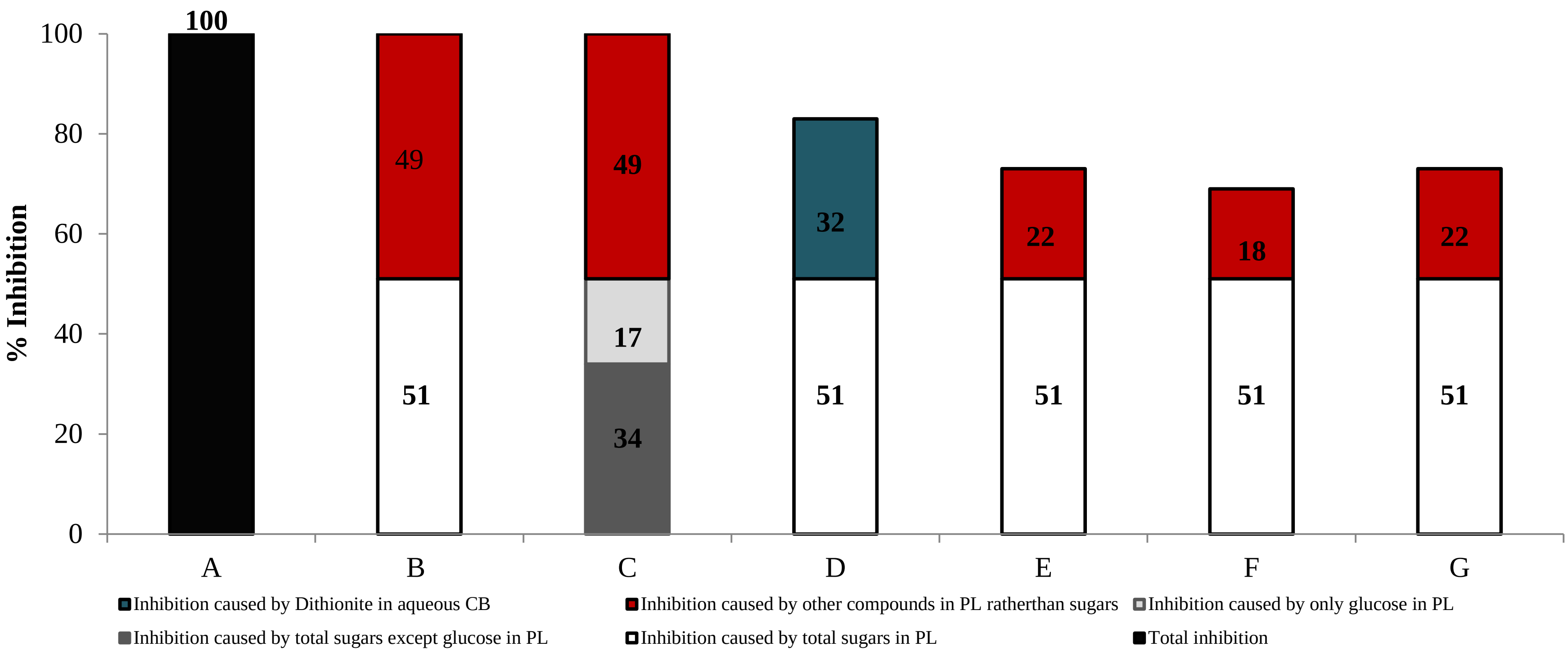
Inhibition of enzymatic hydrolysis by pretreatment liquid



Composition of total inhibition Caused by the (A) PL, (B) sugars and other compounds in PL, (C) glucose, rest of the sugars and other compounds in PL, (D) total sugars and 15mM Dithionite in CB, and Composition of inhibition after conditioning PL with (E) 15mM DTT (F) 15mM Sodium sulfite, (G) 15mM Dithionite.

***Inhibition was calculated based on glucose production during the 96 h enzymatic hydrolysis**
PL: Pretreatment Liquid   CB: Aqueous citrate buffer

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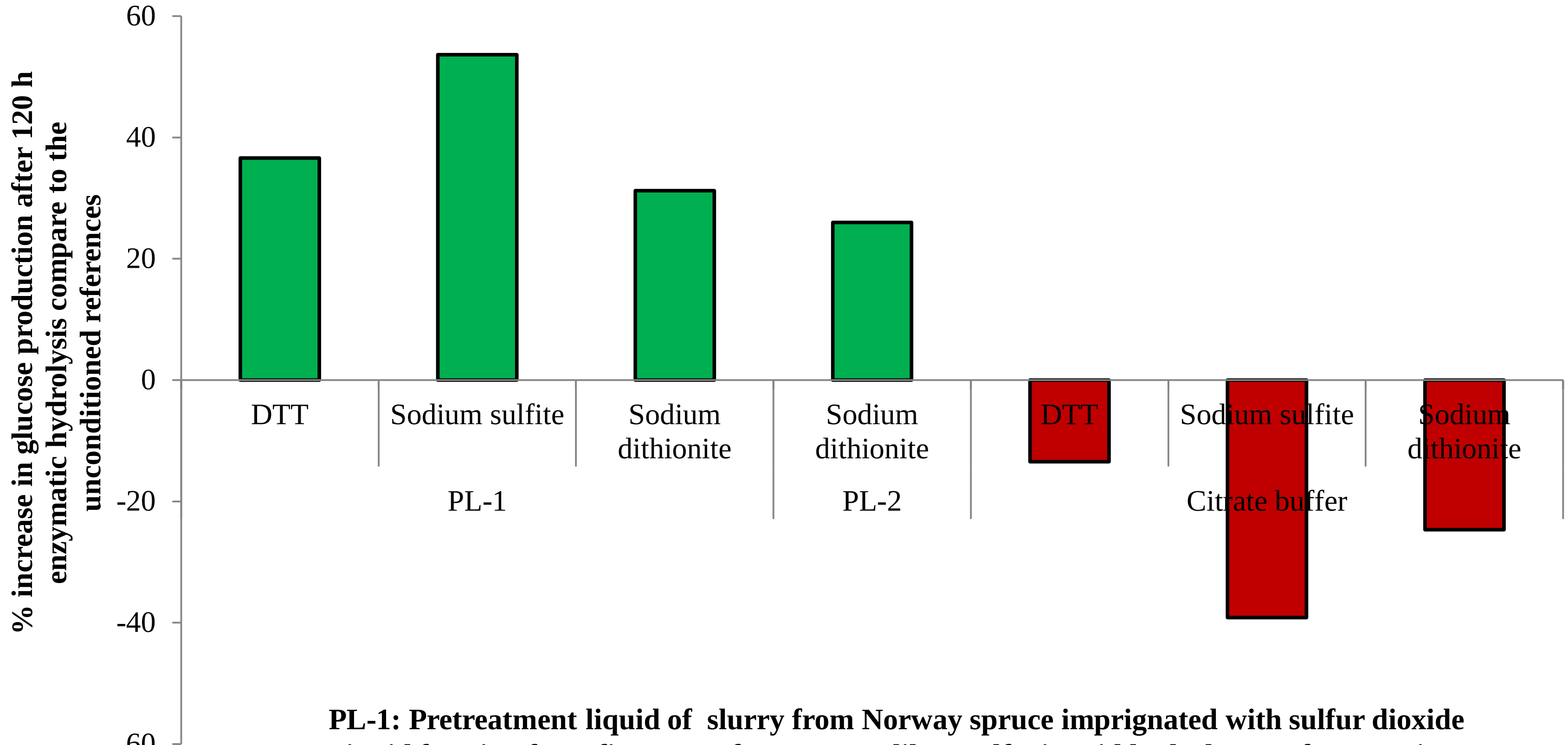
Reducing agents improve enzymatic hydrolysis of cellulosic substrates



PL-1: Pretreatment liquid of slurry from Norway spruce imprignated with sulfur dioxide
PL-2: Liquid fraction from first step of a two-step dilute sulfuric acid hydrolysate of Norwegian spruce

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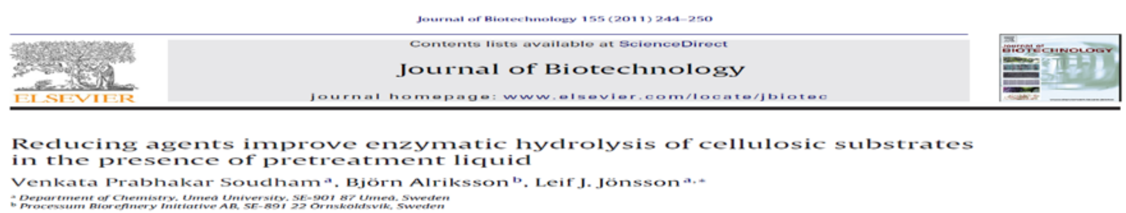

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journal homepage: www.elsevier.com/locate/jbiotec

Reducing agents improve enzymatic hydrolysis of cellulosic substrates in the presence of pretreatment liquid

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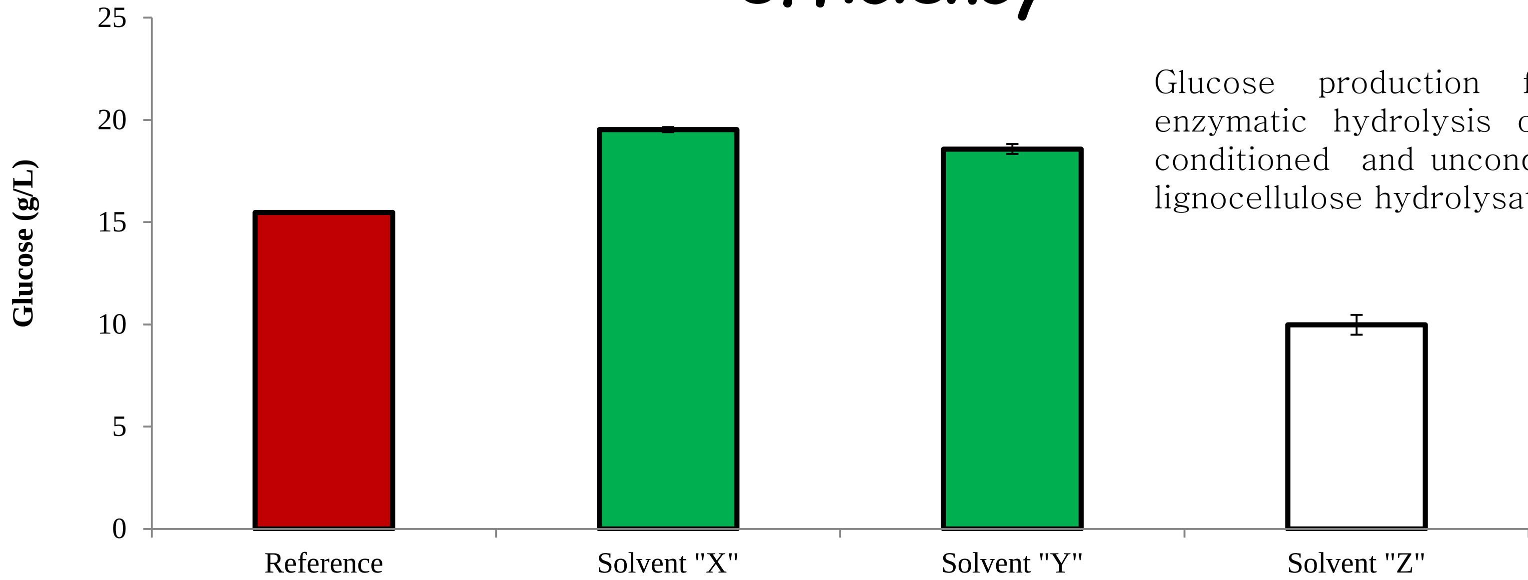
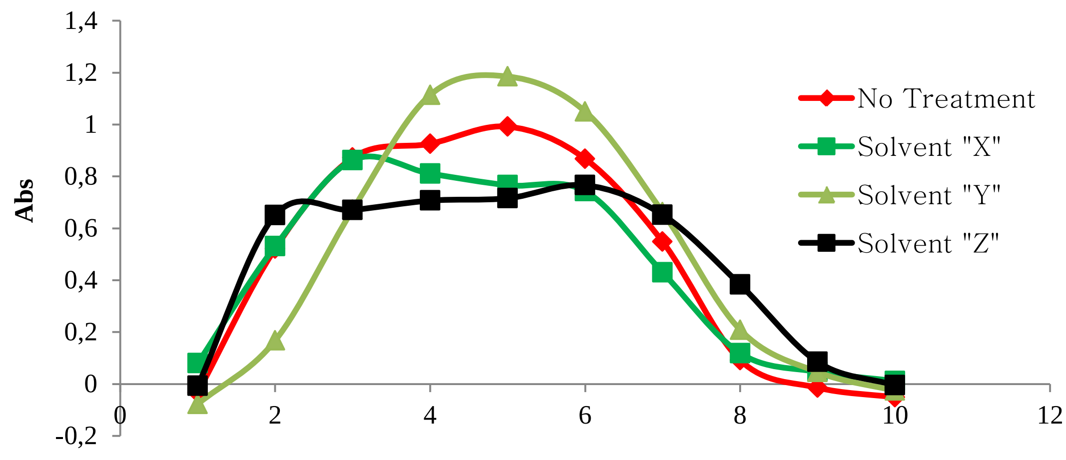
[b] Processum Biorefinery Initiative AB, SE-891 22 Örnsköldsvik, Sweden

Conditioning of inhibitory ligocellulose hydrolyzate with chemical solvents was improved saccharification efficiency



Glucose production from 72 h enzymatic hydrolysis of chemically conditioned and unconditioned toxic lignocellulose hydrolysate.

GPC analyses of the conditioned and unconditioned pretreatment liquids of lignocellulose hydrolysate.



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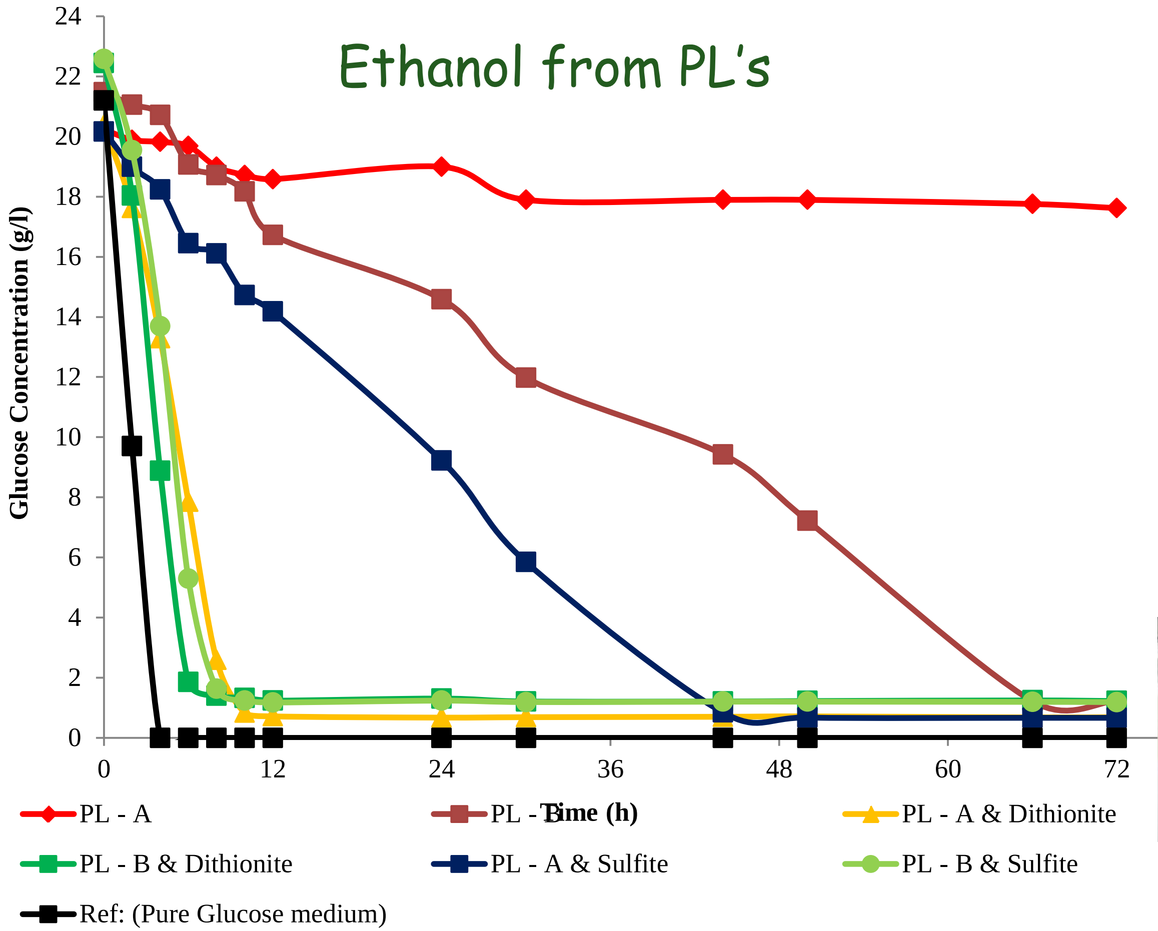
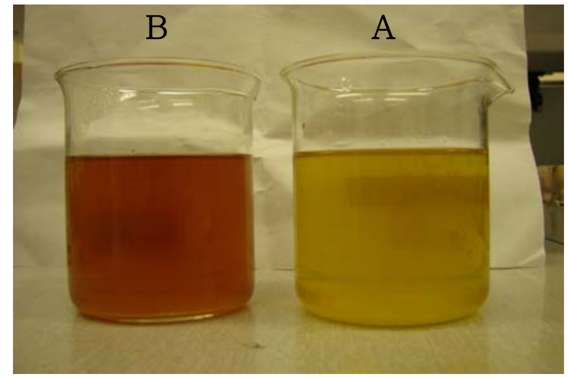
Comparison of classical thermo-chemical pretreatment (TCP) techniques (pilot scale) with the catalysts “A” and “B”





Total Phenols

PL – A: 2,2 (g/l); PL – B: 5,4 (g/l)

Slurry of ”A”

Slurry of ”B”

suspended solids (16.9%)
pH: 1.6–1.7

*PL – Pretreatment liquid

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Conclusion

- About 210 transgenic aspens were screened with a battery of pretreatment techniques.

- Acetosolv delignification efficiently removed >90% of lignin from forestry wood. But, the enzymatic hydrolysis of acetosolv pulps was very poor.

- Dissolution of both forestry wood and agricultural residues in IL (1-allyl-3-methylimidazolium formate) was very effective even under very mild conditions.
- IL's as solvents for screening of transgenic plants could be a useful novel approach.

- Chemical treatment of toxic lignocellulose hydrolysates improved the hydrolysis efficiency up to 57%.

- Furthermore, not all, only few, specific phenolic compounds could be inhibitory in the bioconversion of biomass to biofuels.

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➢The Biorefinery of the Future (www.bioraffinaderi.se)

➢SEKAB E-Technology AB.

Thank you

"…Any type of bio-fuel helps substantially reduce fossil energy and petroleum usage, and there by also reduces GHG emissions".

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