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# Wood to Wheel: Process Improvement for the Production of Substituted Fuels from Renewable Biomass

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Venkata Prabhakar Soudham

venkata.soudham@chem.umu.se

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# The Problem: Our Society STOPS Without Liquid Fuels!

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# Biofuels production

- Ethanol ($C_2H_5OH$)
- Butanol ($C_4H_9OH$)

**First generation**

Ethanol fermentation:

Glucose ($C_6H_{12}O_6$) $\xrightarrow[\text{organisms}]{\text{Fermentation}}$ Bio-alcohols

Starch ($C_6H_{10}O_5$)$_n$ $\xrightarrow{\text{Enzymes}}$ Glucose $\xrightarrow[\text{organisms}]{\text{Fermentation}}$ Bio-alcohols

*Busslink - Stockholm*

E85 85% Ethanol

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

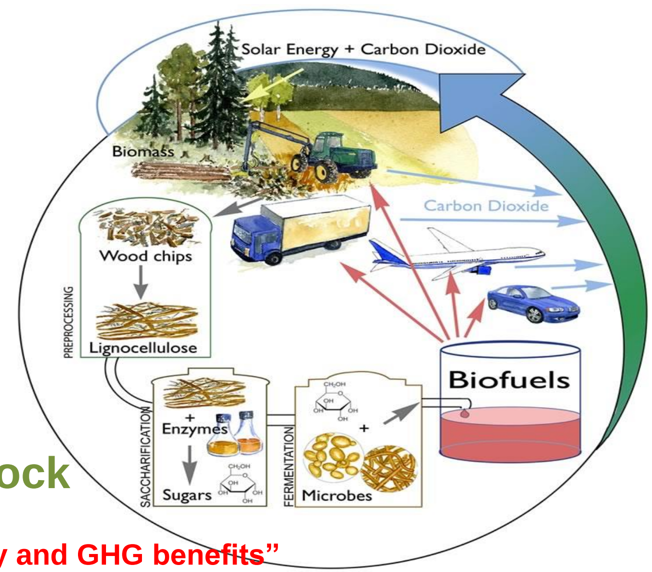
# Lignocellulosic materials

Forest residues

Agricultural residues

Municipal solid wastes

- Abundant
- Inexpensive
- Sustainable

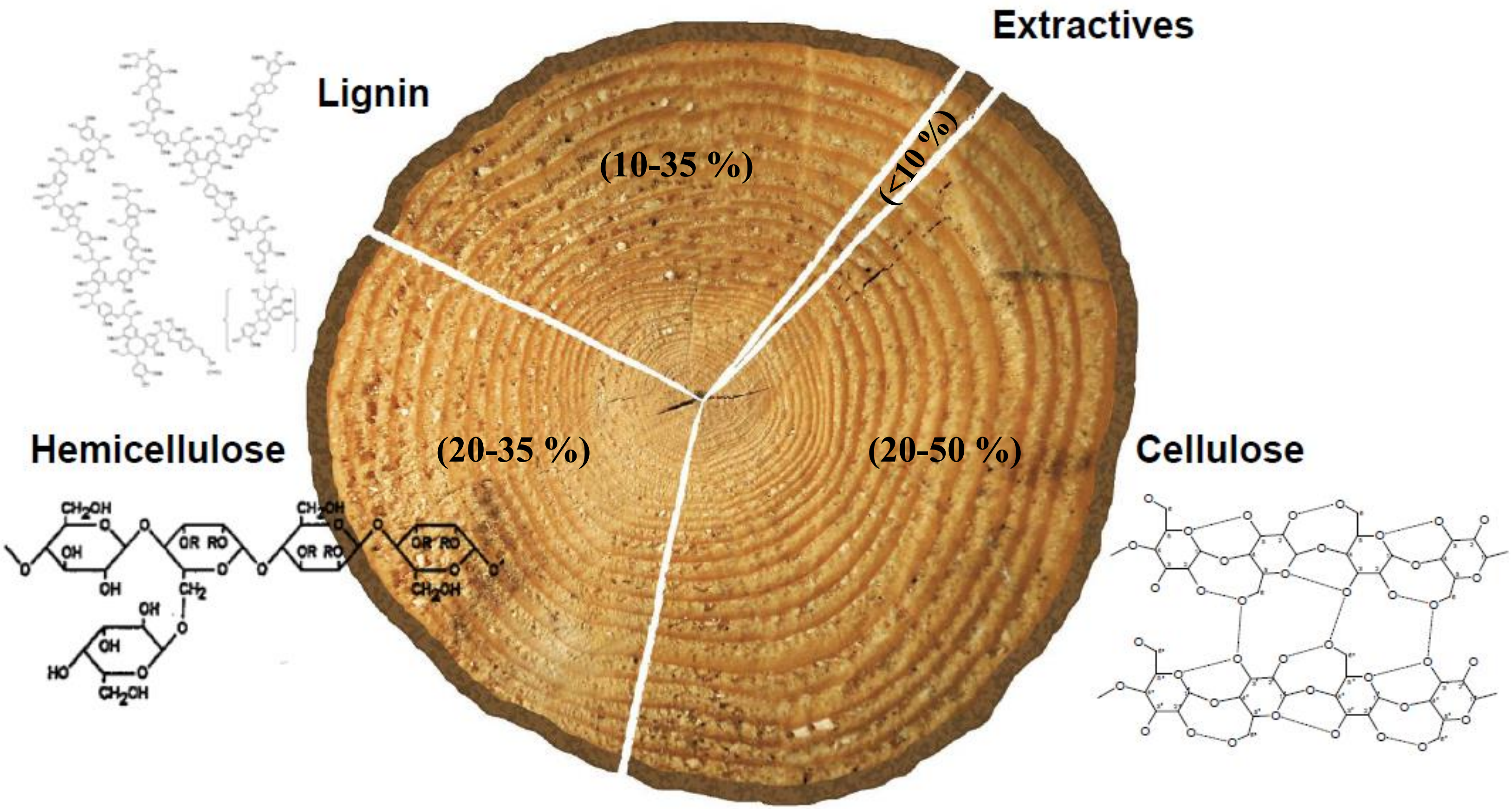



Source: www.bioimprove.se

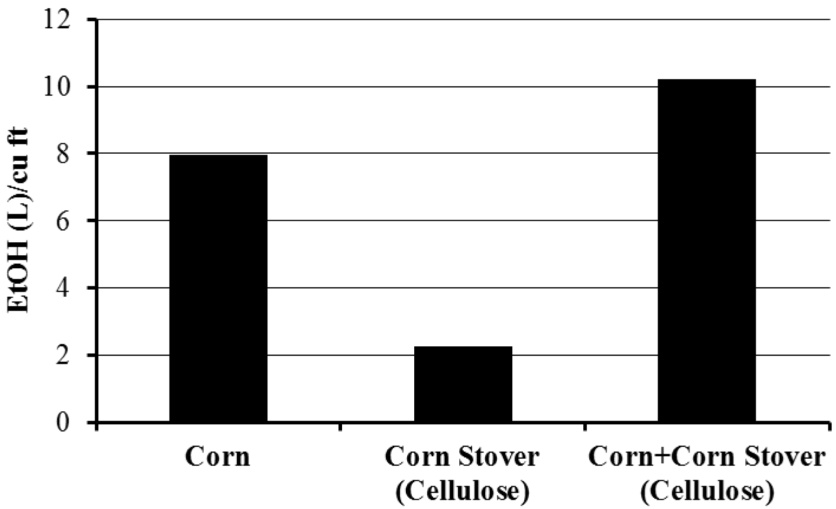
**Second generation feedstock**

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

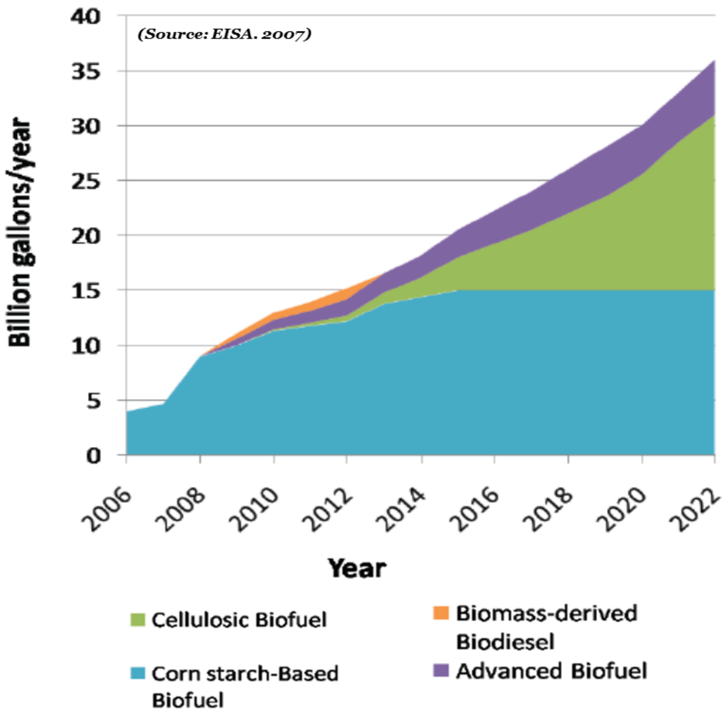
# Chemical Composition of Lignocellulose



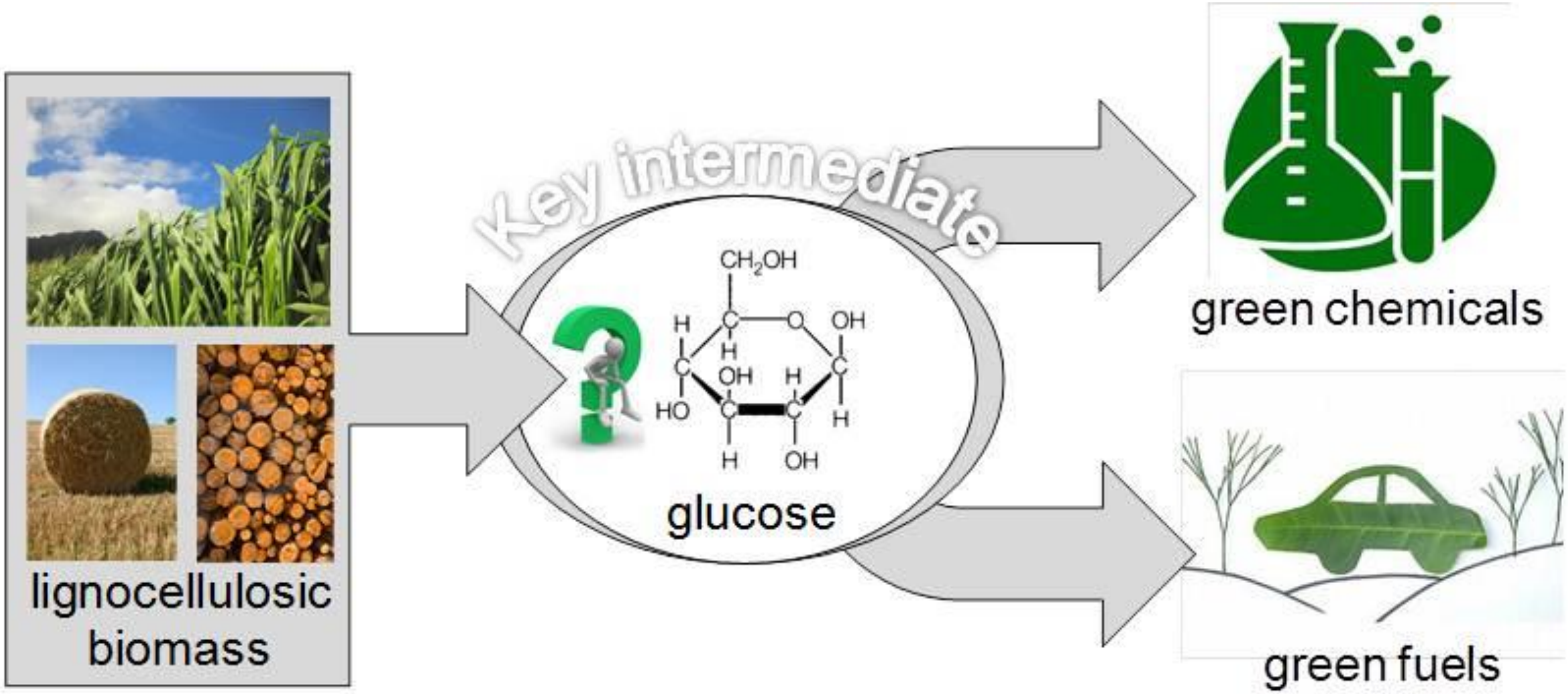
# First & Second Generation Biofuels




Corn Weighs more than Corn Stover



# Monomer Sugars?




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

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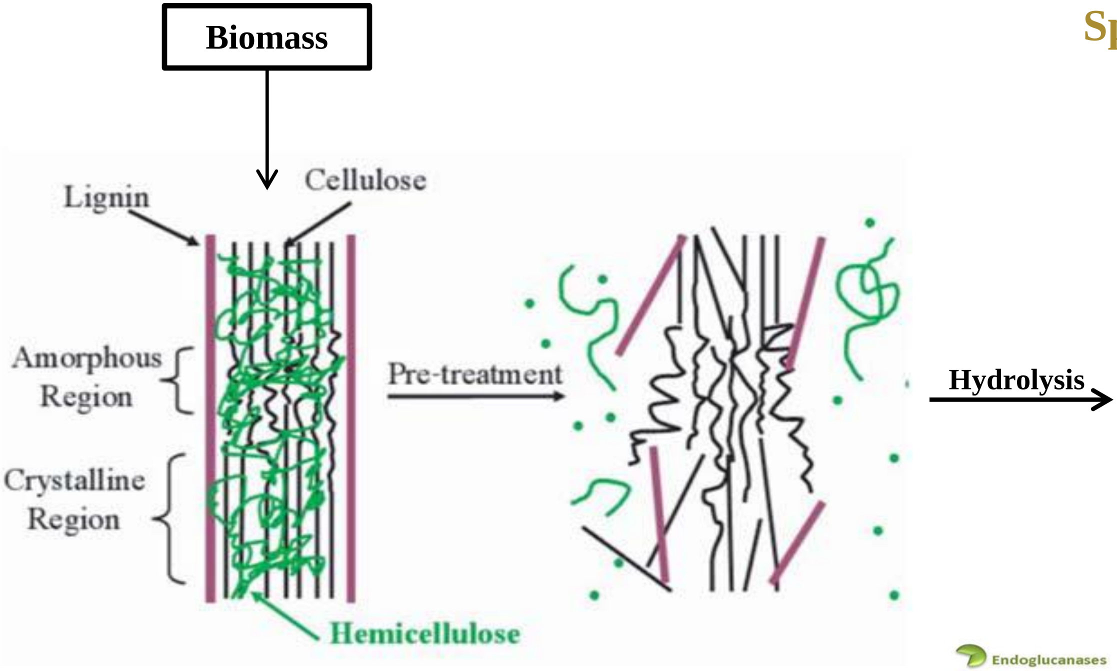
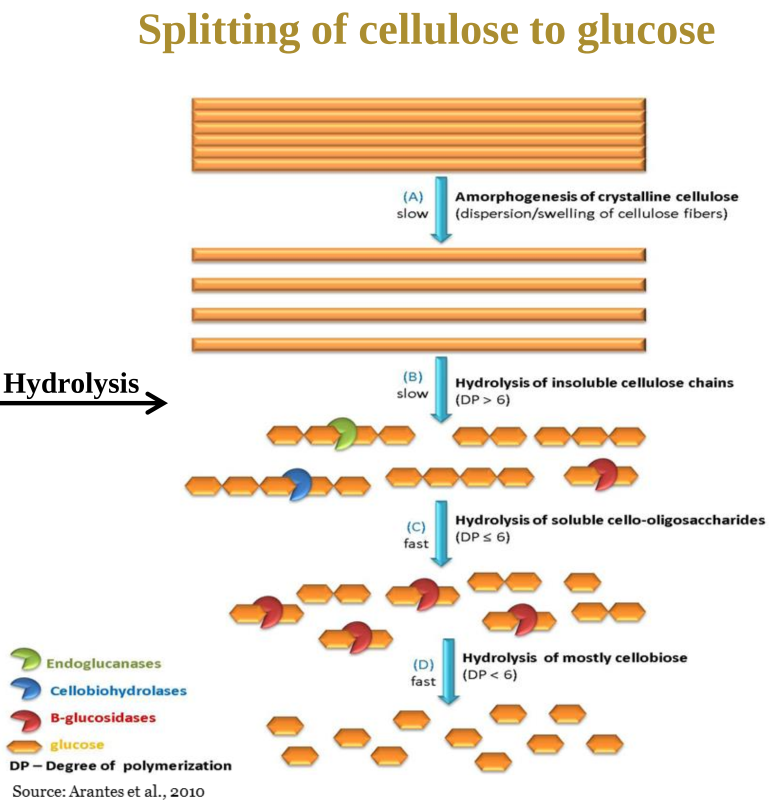
# Sugars extraction from biomass




Pretreatment goals:

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

**Severity factor: Log $R_o = t * e^{(T-Tr)/14.75}$** t: time (min), T: reaction temperature, Tr: reference temperature (100 C)

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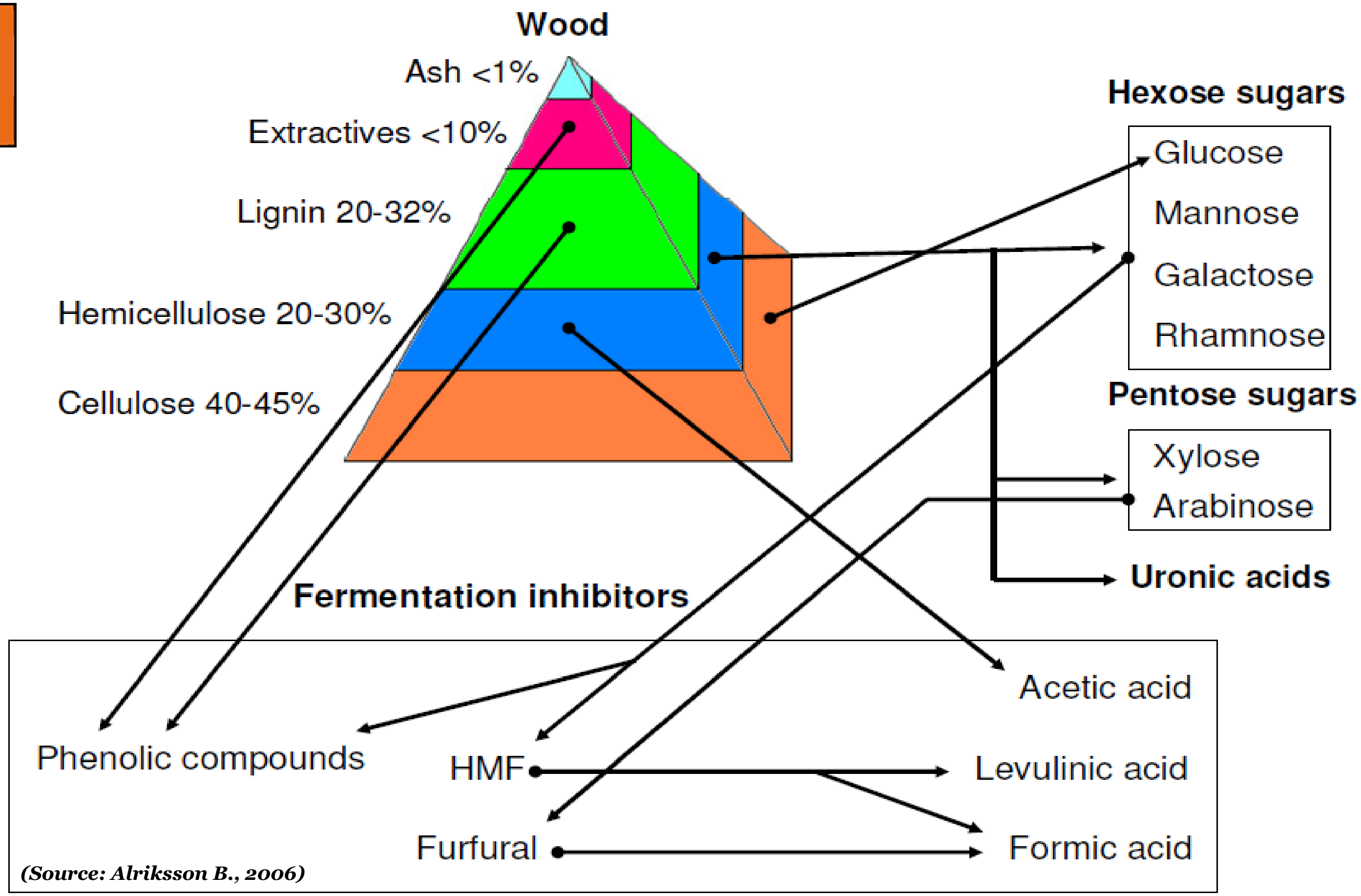
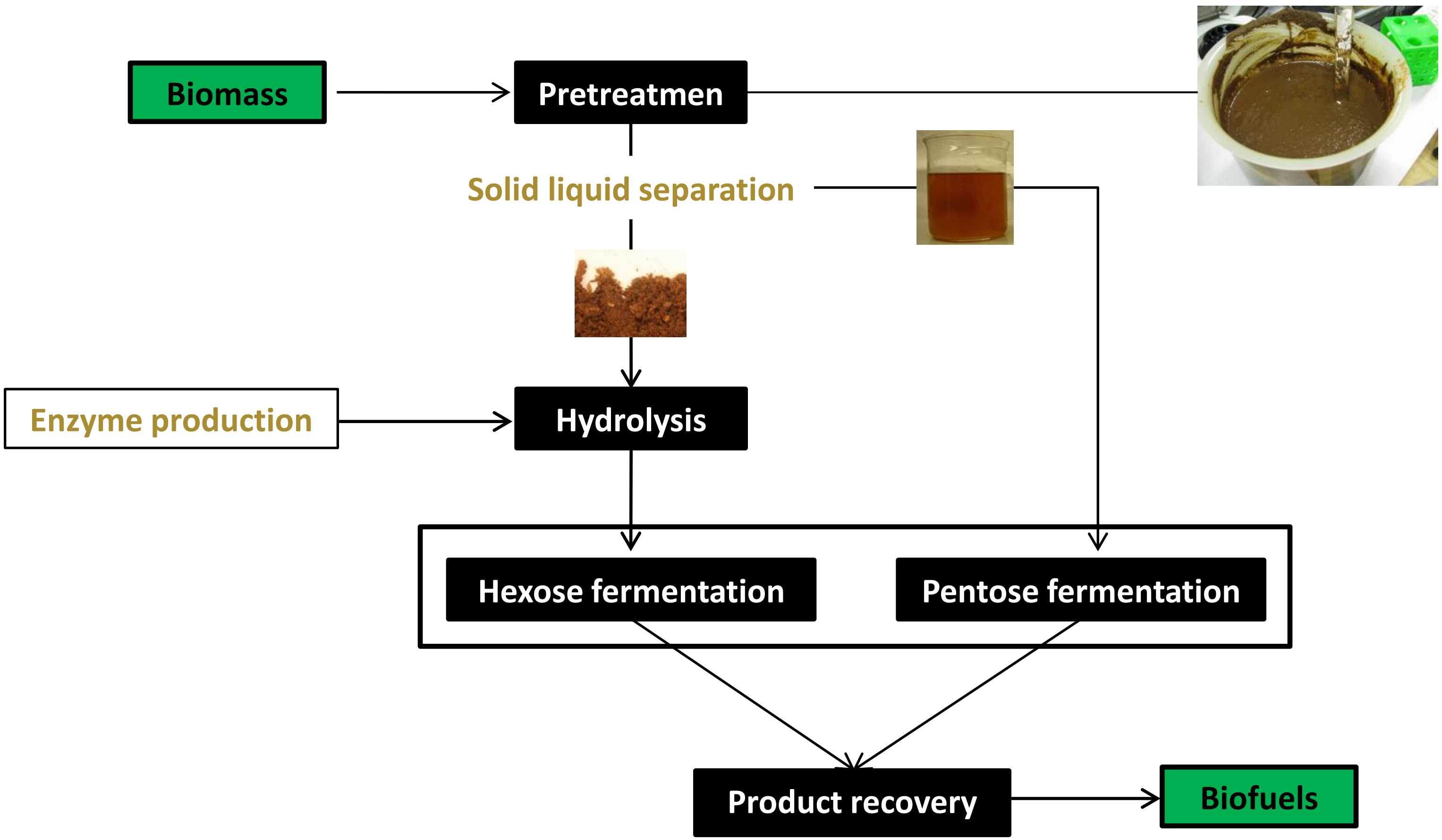
# Toxic Compounds from Pretreatment



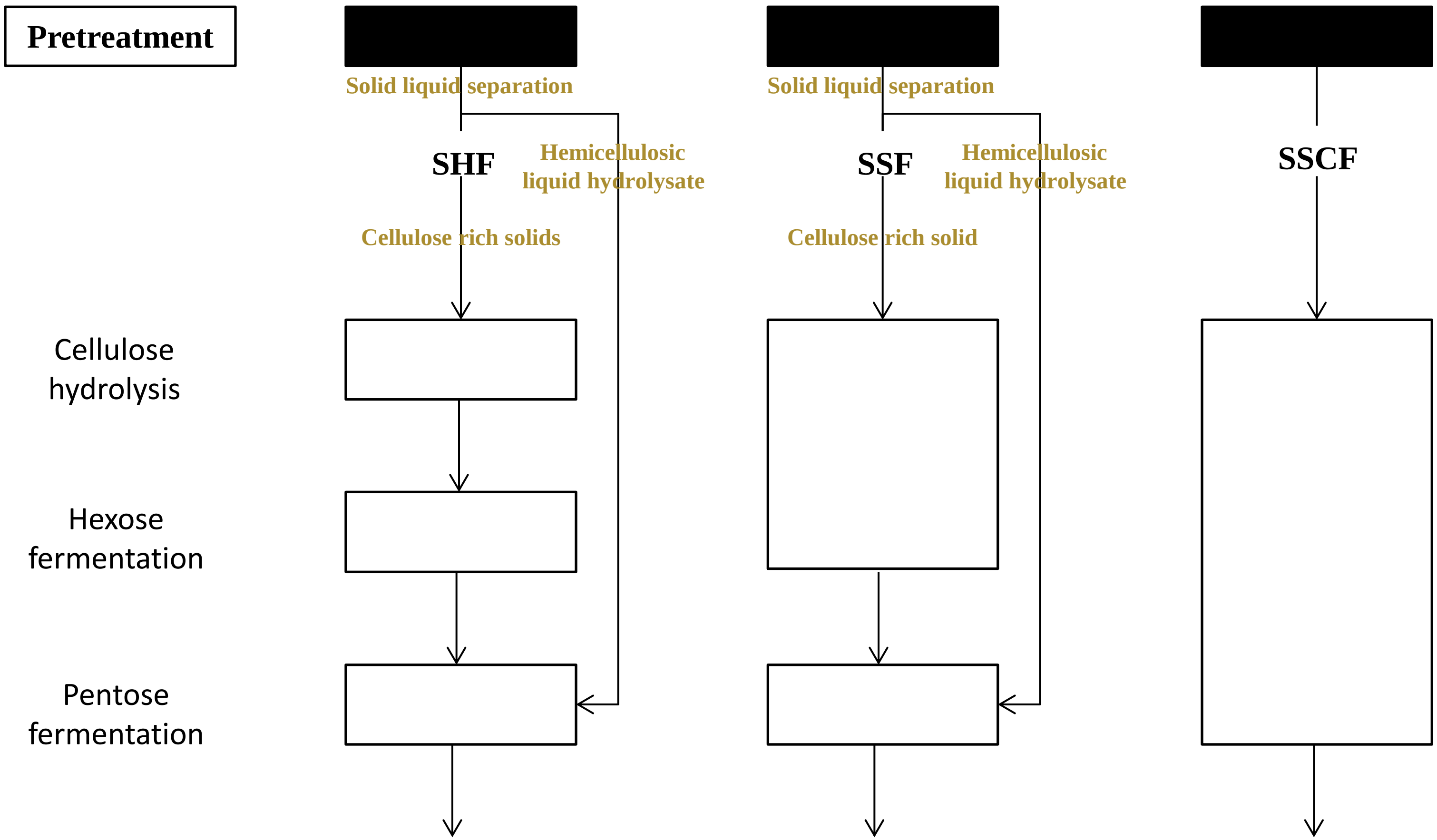

*(Source: Alriksson B., 2006)*

- **Sugars are inhibitory to the celluase enzymes**

# Bioconversion of lignocelluloses to biofules



# Featuring of Biomass Processing




SHF: Seperate Hydrolysis & Fermentation; SSF: Simultanious Saccharification & Fermentation
SSCF: Simultanious Saccharification & Co-Fermentation

# Critical Areas of Research

- **Evaluation of lignocellulose recalcitrance: Screening of transgenic Aspens**

- **Application of different solvents for the biomass pre-treatment**
  - Existing: $\mathbf{H_2SO_4}$, $\mathbf{SO_2}$, and $\mathbf{CH_3COOH}$ etc..
  - Green solvents: Ionic Liquids (IL's):

    1-allyl-3-methylimidazolium formate **[Amim](HCO2)**

    1,8-diazabicyclo-[5.4.0]-undec-7-ene (**DBU**), mono-ethanol amine (**MEA**), $\mathbf{SO_2}$ / $\mathbf{CO_2}$

- **Investigation of strategies to lighten the toxicity of lignocellulose hydrolysates using**

  1. Fenton's reagent: **Fe(+2)** and $\mathbf{H_2O_2}$
  2. Reducing agents:

     Sodium sulphite **($Na_2SO_3$)**,
     Sodium dithionite **($Na_2S_2O_4$)**,
     Dithiothreitol (**DTT: $C_4H_{10}O_2S_2$**)
  3. Alkali: **NaOH, $Ca(OH)_2$, $NH_4(OH)$**

# Screening of Transgenic Aspens

BIO IMPROVE
www.bioimprove.se

– **210 plants (14 constructs, 3 lines each)**

Selected on basis of growth characteristics (height, width) and lignin content.

– Investigation of factors that govern the recalcitrance of lignocelluloses up on their conversion to valuable products

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# Strategy for screening

BIOIMPROVE

Harvesting, cutting, lyophilization, milling, sieving

Acid pretreatment targeting hemicellulose

Steam pretreatment

No pretreatment

IL pretreatment

pretreatment targeting Lignin

Steam pretreatment

Separation of liquid and solid fraction

Wash of solid fraction

Enzymatic hydrolysis

Rapid analysis of glucose in liquid fraction

Detailed analysis of liquid fractions

Detailed analysis of solid fractions

Analysis of wood composition

– Protocols were developed for an optimal investigation

A battery of pretreatment techniques that together give more information than is obtained with only one pretretment technique.

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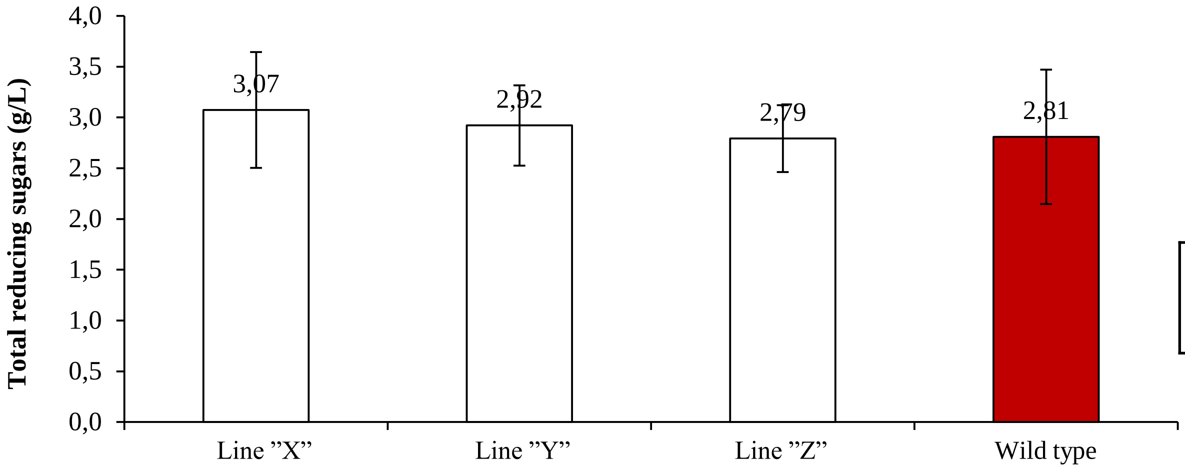
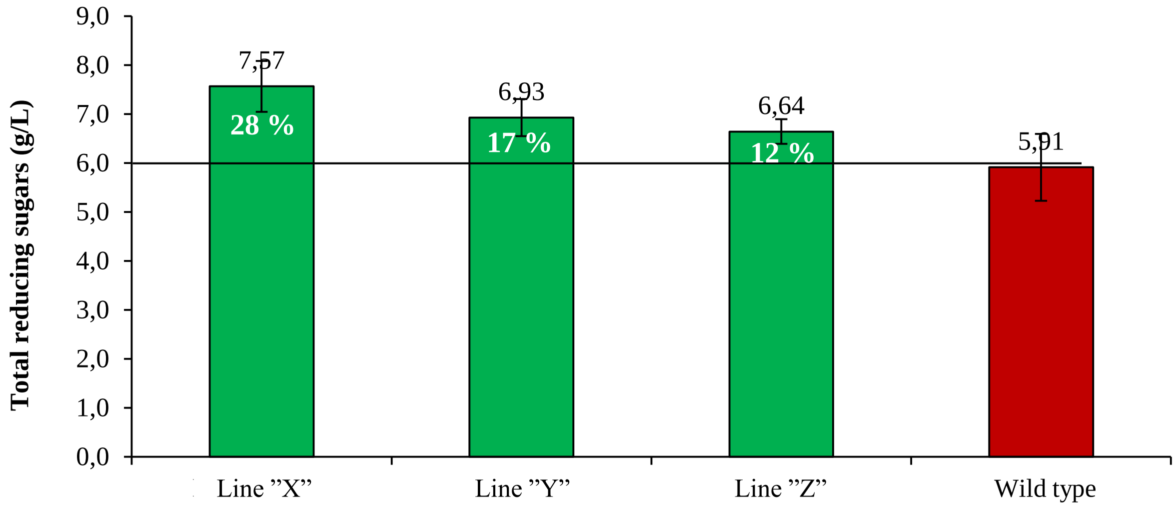
## No pretreatment




**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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# Evaluation of different solvents for the pre-treatment of lignocelluloses

1. A comparision study of $SO_2$ and $H_2SO_4$ pretreatments of chipped Norwegian spruce performed at biorefinery demo plant (Örnsköldsvik, SWEDEN)

2. Fractionation of forestry wood using $CH_3COOH$

3. Pre-treatment of different lignocelluloses (e.g. Birch, Pine, Spruce, Sugar cane bagasse, and Reed canary grass) using IL solvents: [Amim]($HCO_2$), DBU-MEA-$SO_2$, and DBU-MEA-$CO_2$

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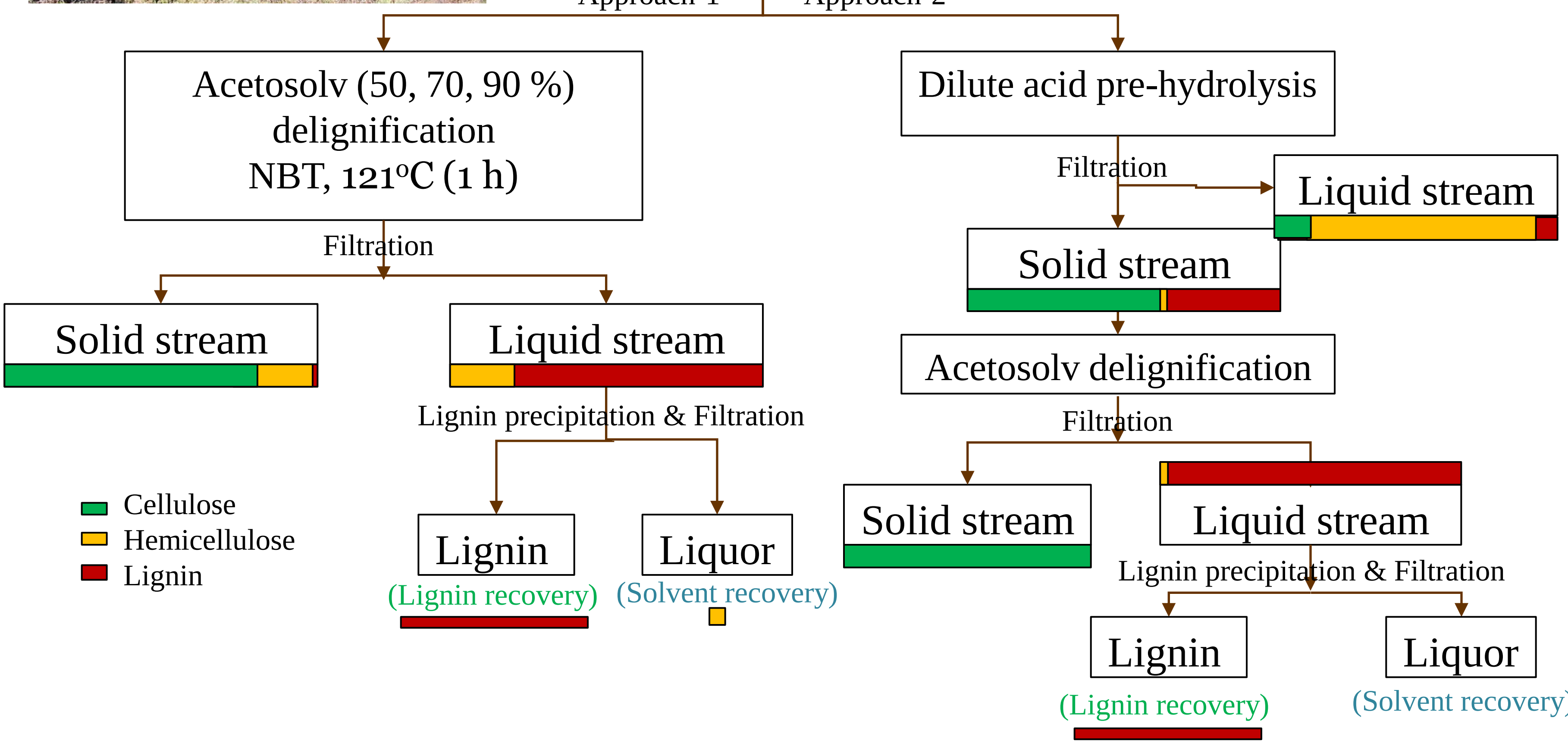
# 2. Fractionation of Marabou wood with Acetic acid

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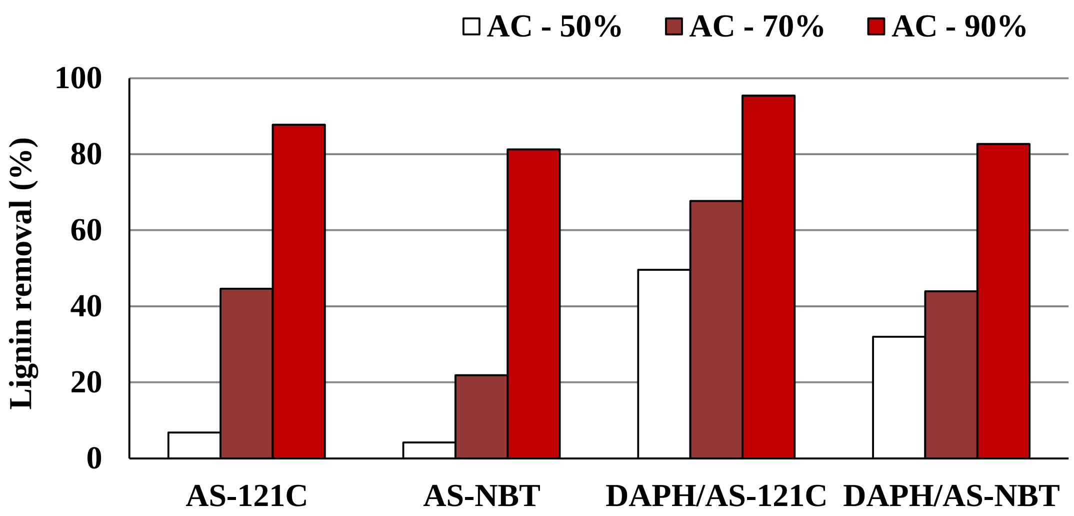
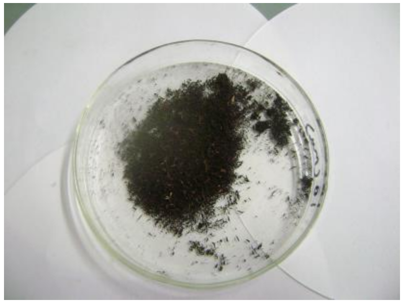
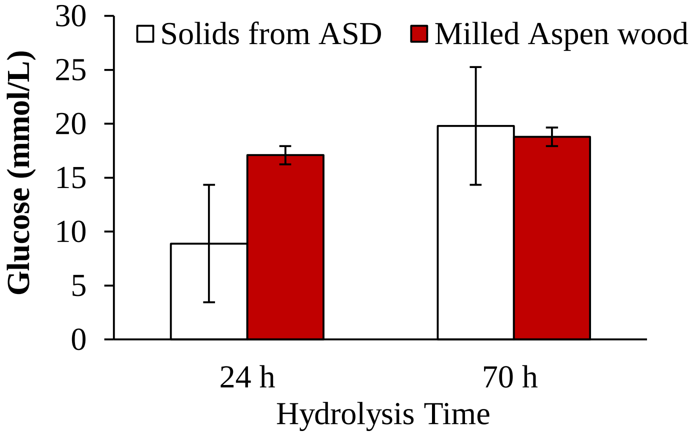
# Lignin removal and recovery



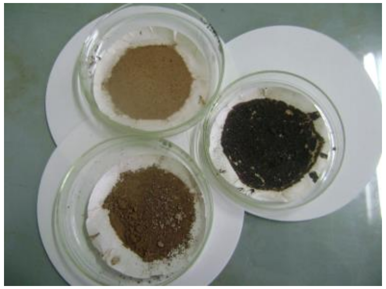

**Pulp after delignification**



**Enzymatic hydrolysis of transgenic aspens after AS delignification**




AS – 121C



AS – NBT


Recovered lignin

# 3. Pre-treatment of Lignocelluloses using various Ionic Liquid Solvents


Biorefinery demo plant <www.sekab.com> (Örnsköldsvik, SWEDEN)

Agriculture residues

Microcrystalline cellulose

Wood chips

Solvation of cellulosic material in ionic liquid.

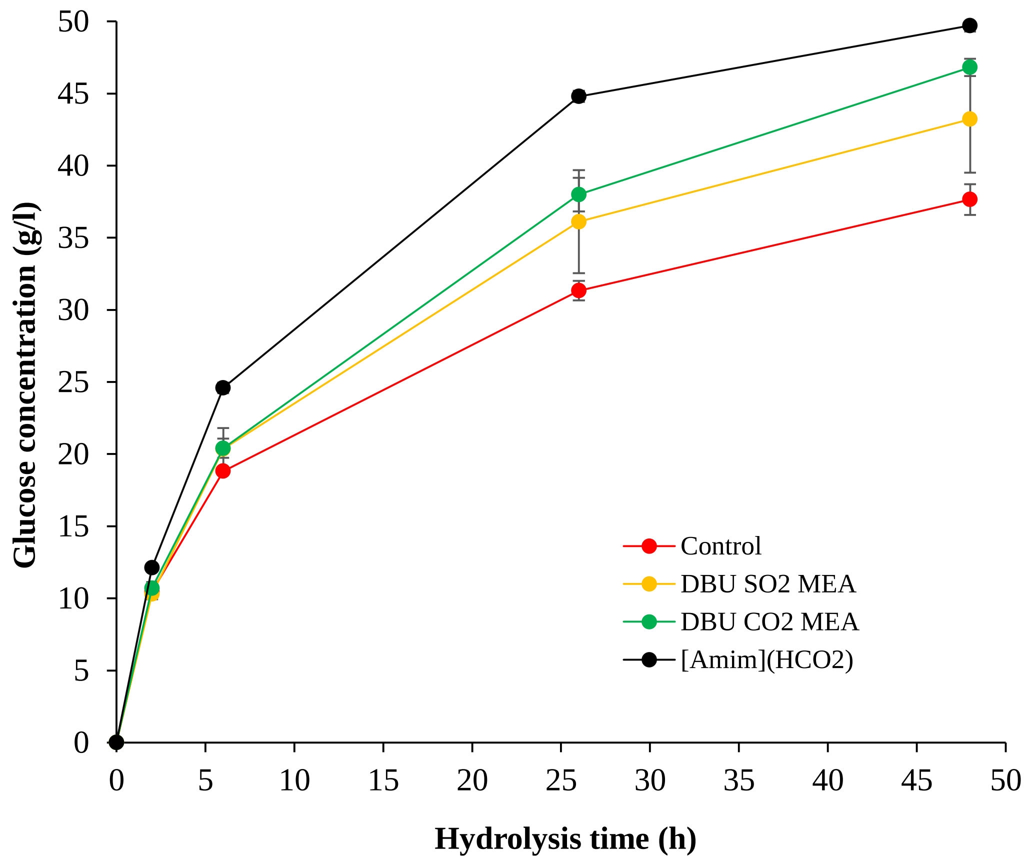
# Cellulose dissolution in various IL-solvents

DBU $SO_2$ MEAS

1-allyl-3-methylimidazolium formate ([Amim](HCO2)

DBU $CO_2$ MEAS

Microcrystalline cellulose



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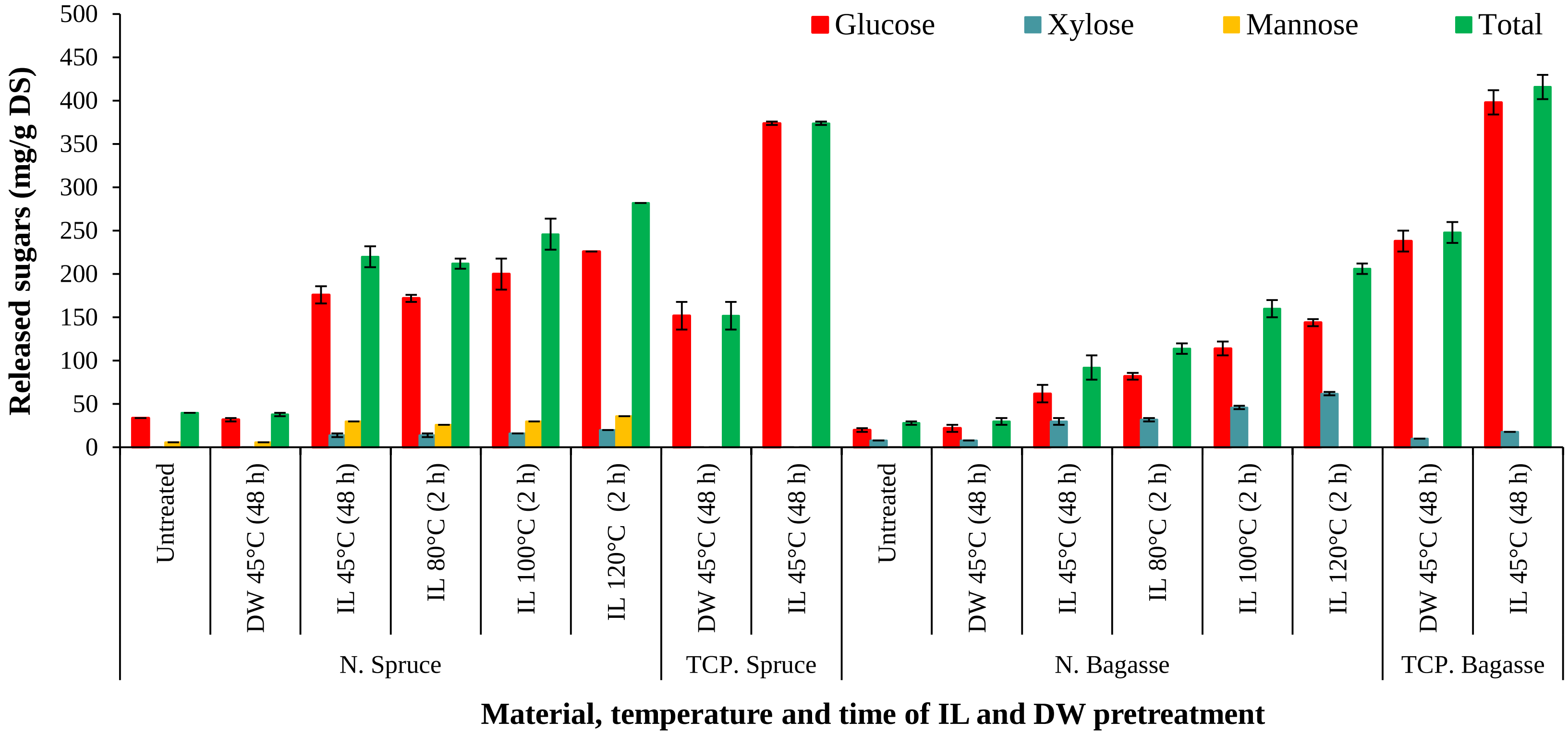
# Enzymatic Hydrolysis of Norway Spruce wood & Sugar Cane Bagasse after treatment with [Amim]($HCO_2$) IL




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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# Addresing the problems associated with acid pretreated lignocellulose hydrolysates

1. Fenton's reagent: **Fe(+2)** and **$H_2O_2$**

2. Reducing agents:
   - Sodium sulphite (**$Na_2SO_3$**),
   - Sodium dithionite (**$Na_2S_2O_4$**),
   - Dithiothreitol (DTT: **$C_4H_{10}O_2S_2$**)

3. Alkali: **NaOH**, **$Ca(OH)_2$**, **$NH_4(OH)$**

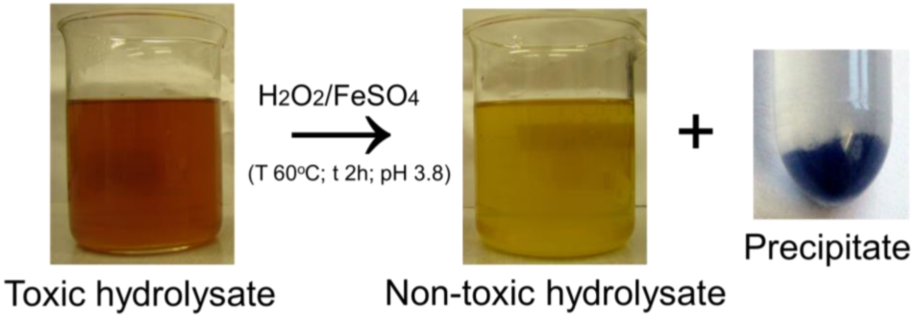
# 1. Detoxificaion with Fenton's reagent i.e $H_2O_2$ and $FeSO_4$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-}$$

$${}^{\bullet}OH + RH \rightarrow H_2O + {}^{\bullet}R,\ RH = \text{Organic compound}$$

$${}^{\bullet}R + O_2 \rightarrow {}^{\bullet}ROO \rightarrow \text{Degradation products}$$

- **A widely used technology in waste water treatment**
- **Considered as environmentally friendly**



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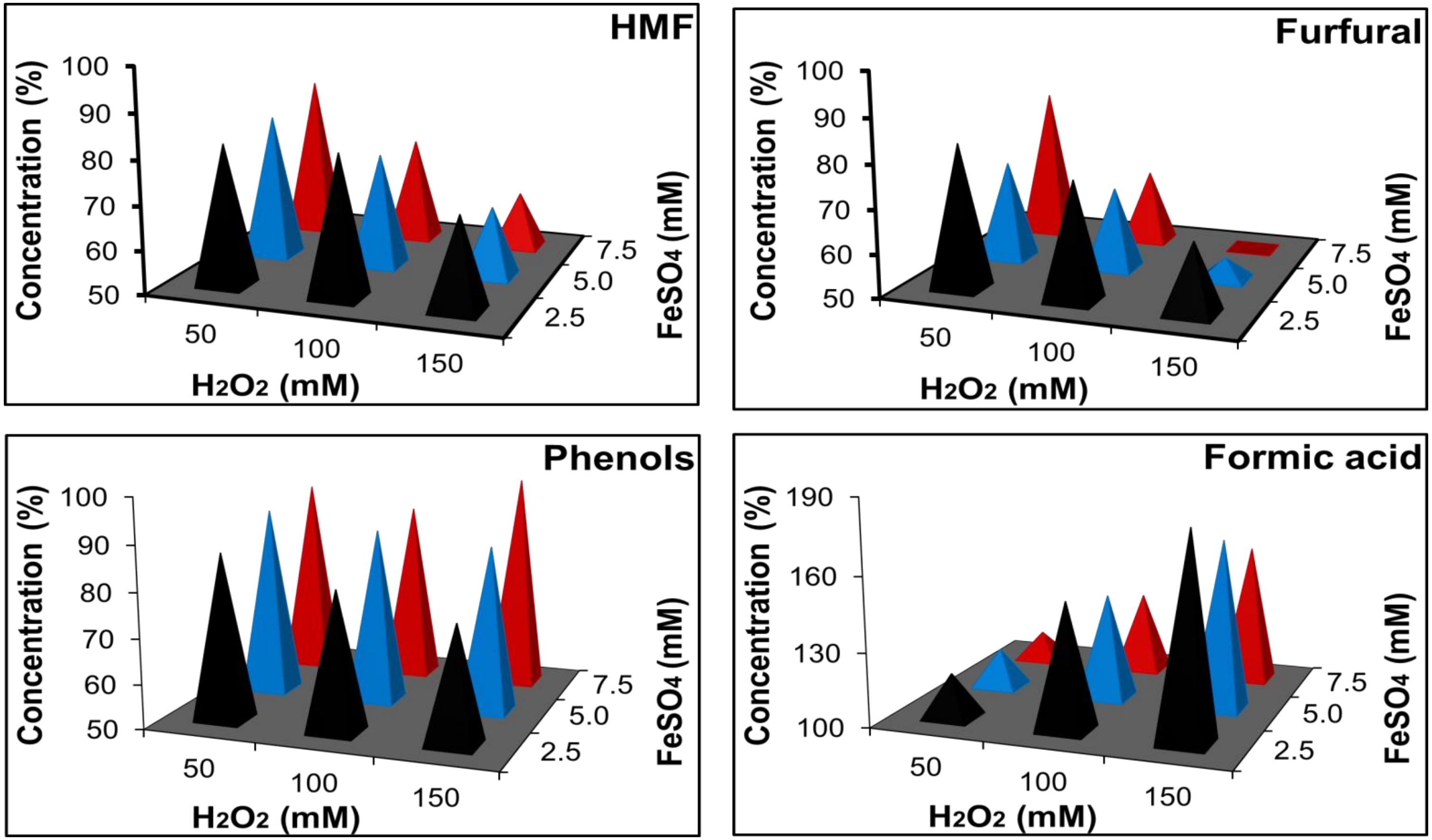
# Inhibitors profile




**Concentrations of inhibitors present in detoxified spruce hydrolysates compare to the non-detoxified hydrolysate.**

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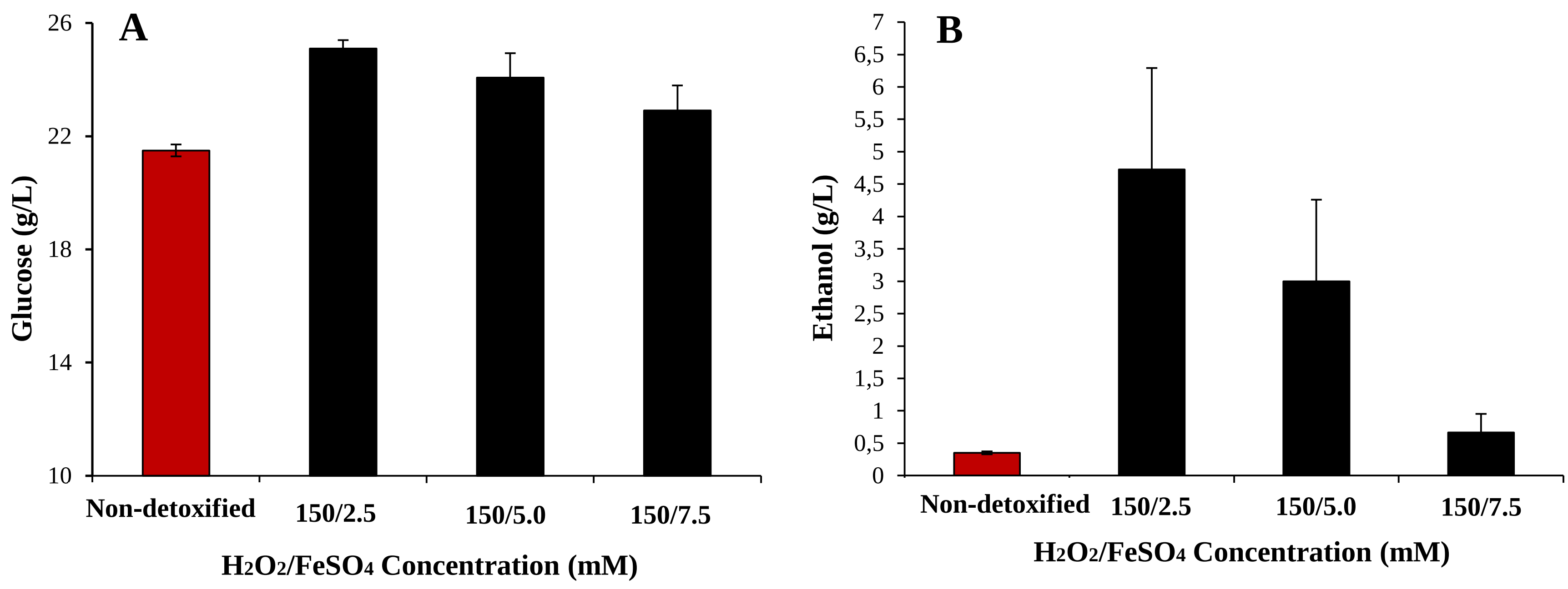
# Enzymatic hydrolysis and fermentation of spruce hydrolysates detoxified with $H_2O_2$ and $FeSO_4$




A: Glucose produced from 72 h enzymatic hydrolysis of Avicel in $H_2O_2/FeSO_4$ detoxified and non-detoxified spruce liquid hydrolysates, B: Ethanol produced from 48 h fermentation of chemically detoxified and non-detoxified spruce liquid hydrolysates.

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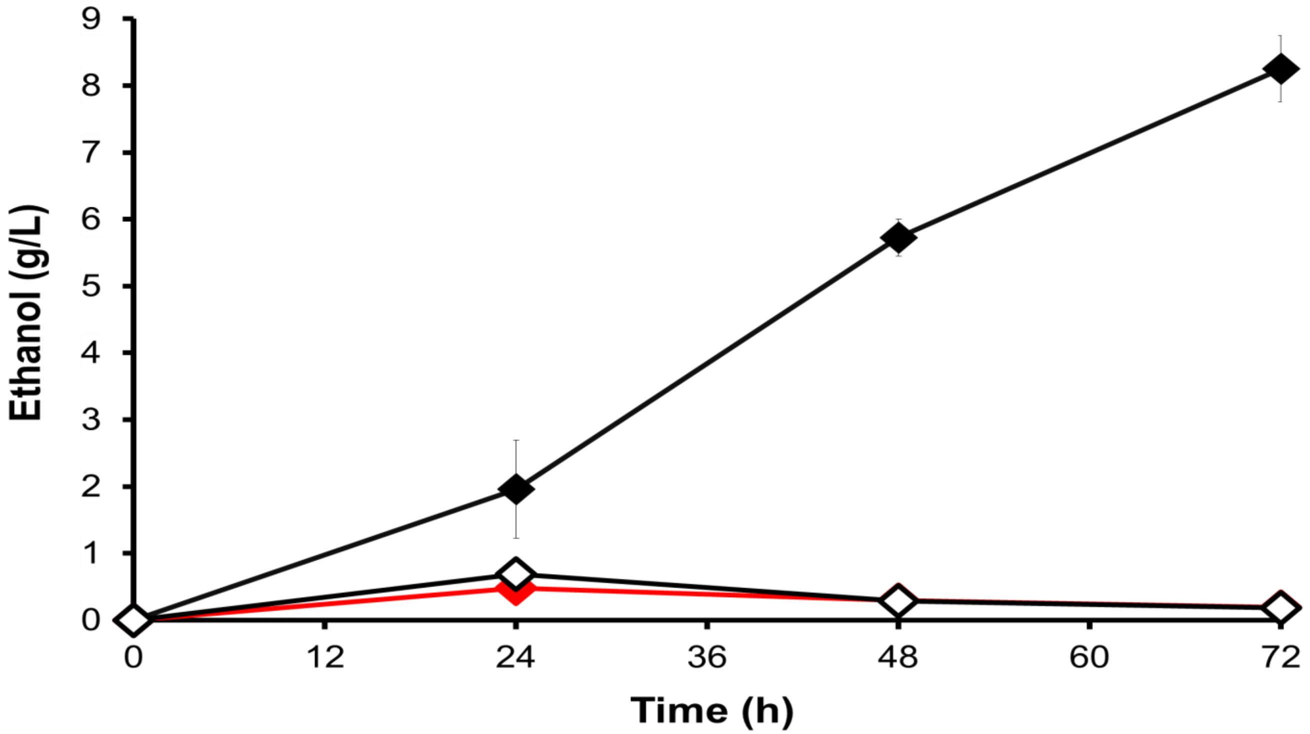
# Inhibitors effect on Fermentation




Ethanol production from spruce hydrolysates, non-detoxified (♦), detoxified with 150 mM $H_2O_2$ and 2.5 mM $FeSO_4{\cdot}7H_2O$ (♦) and detoxified with 150 mM $H_2O_2$ and 2.5 mM $FeSO_4{\cdot}7H_2O$ but the degraded furfural and HMF were recompensed to the levels equal to original concentrations (◊).

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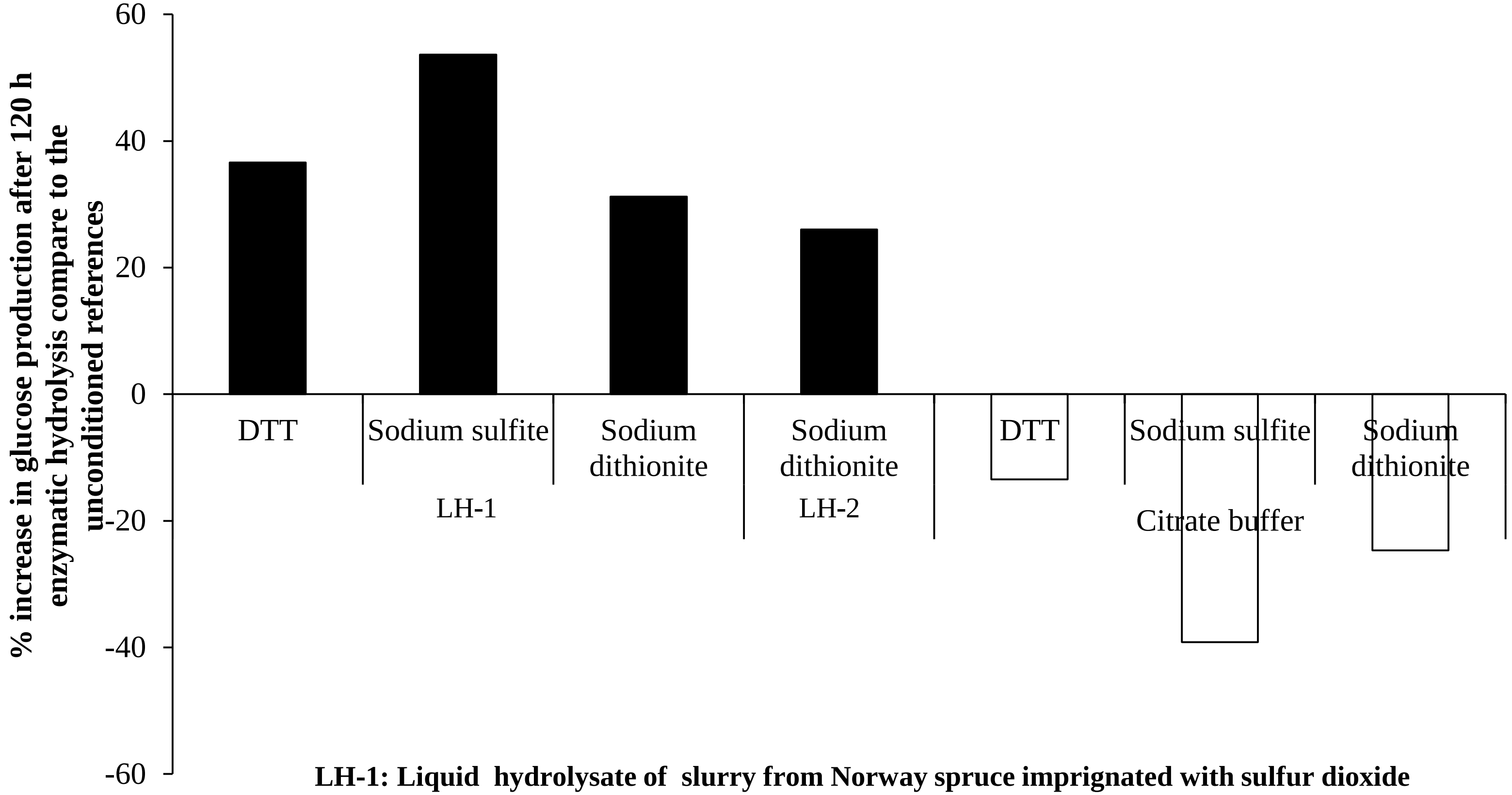
# 2. Detoxification with reducing agents




**LH-1: Liquid hydrolysate of slurry from Norway spruce imprignated with sulfur dioxide**
**LH-2: Liquid hdrolysate from first step of a two-step dilute sulfuric acid hydrolysis of Norway spruce**

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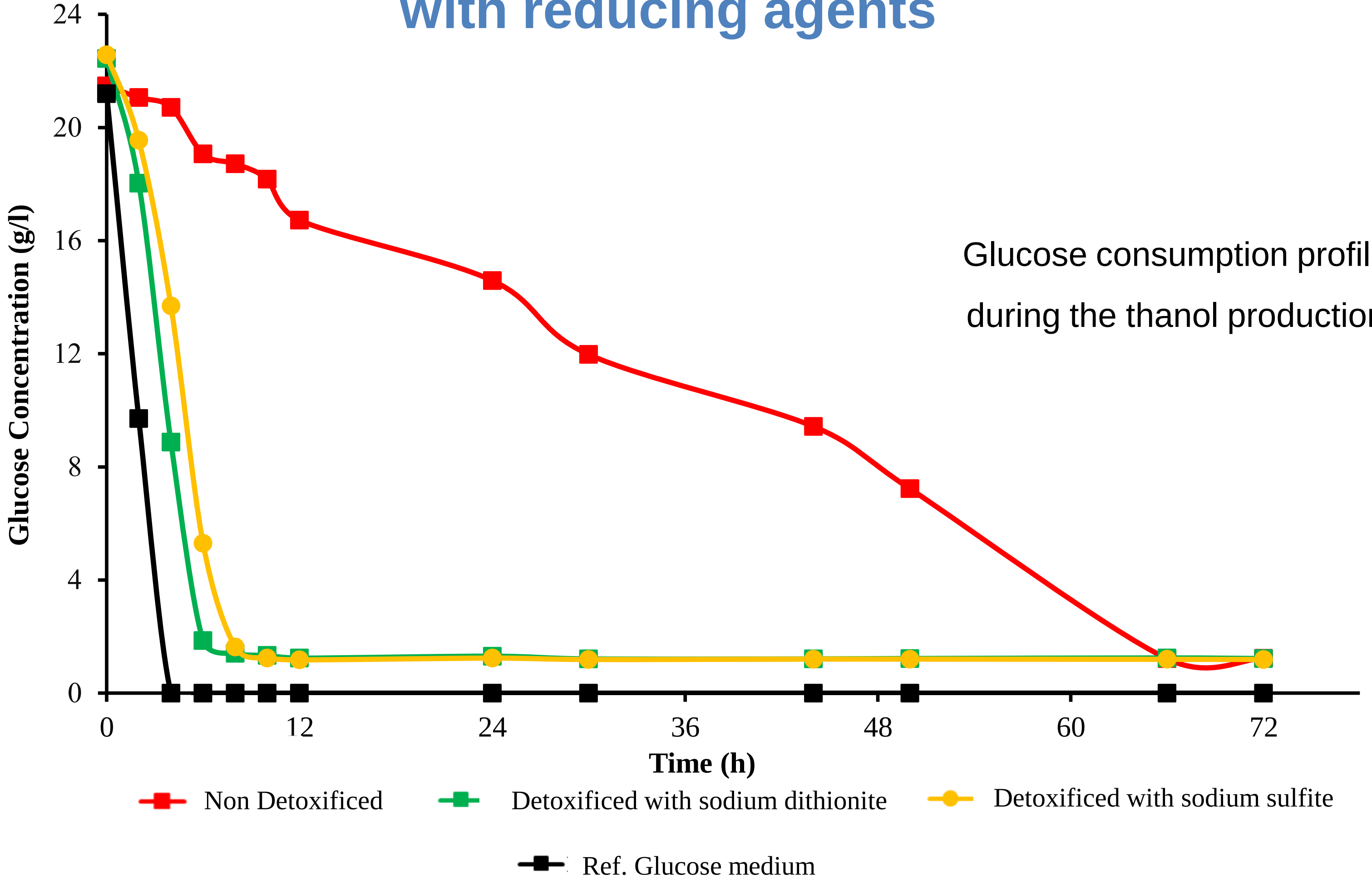
# Fermentation of spruce hydrolysates after detoxification with reducing agents




Glucose consumption profile during the thanol production

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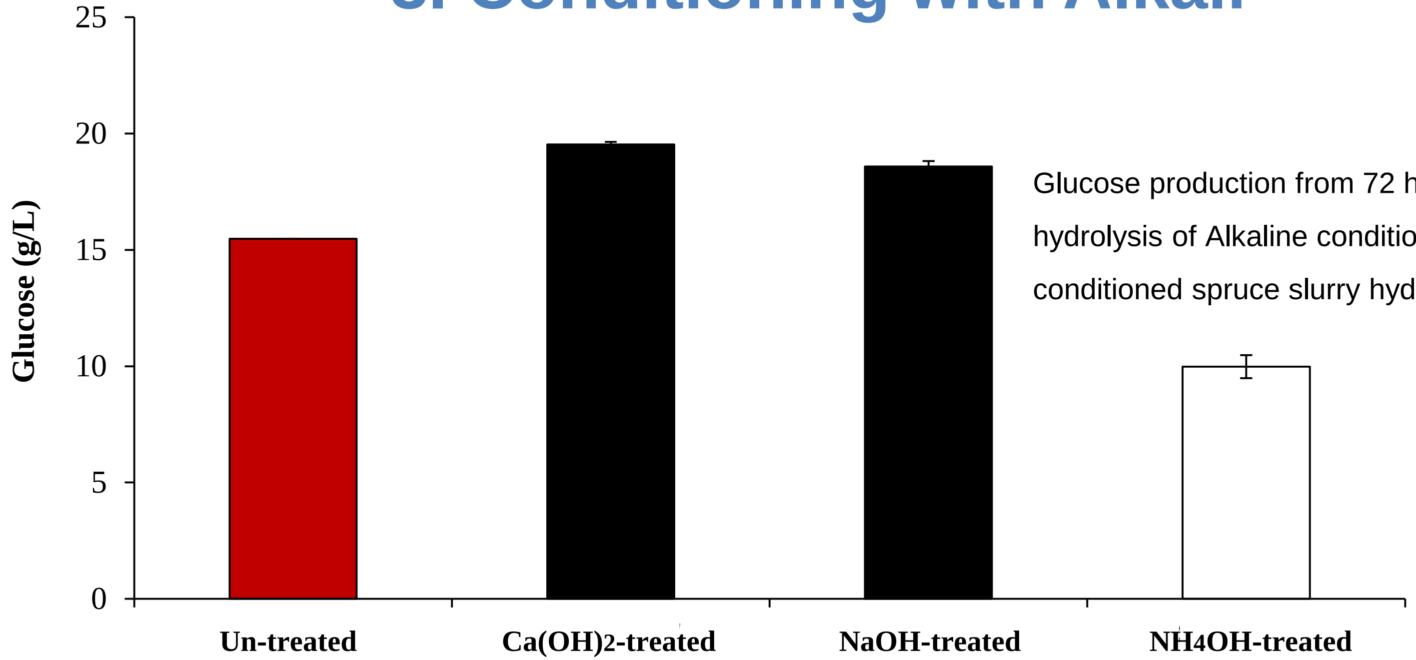
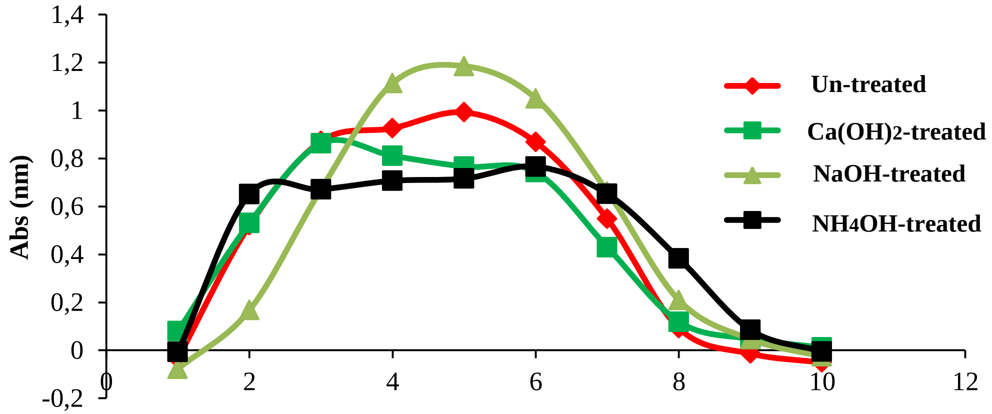
# 3. Conditioning with Alkali




Glucose production from 72 h enzymatic hydrolysis of Alkaline conditioned and un-conditioned spruce slurry hydrolysates.

GPC analyses of the Alkaline conditioned and unconditioned spruce liquid hydrolysates.

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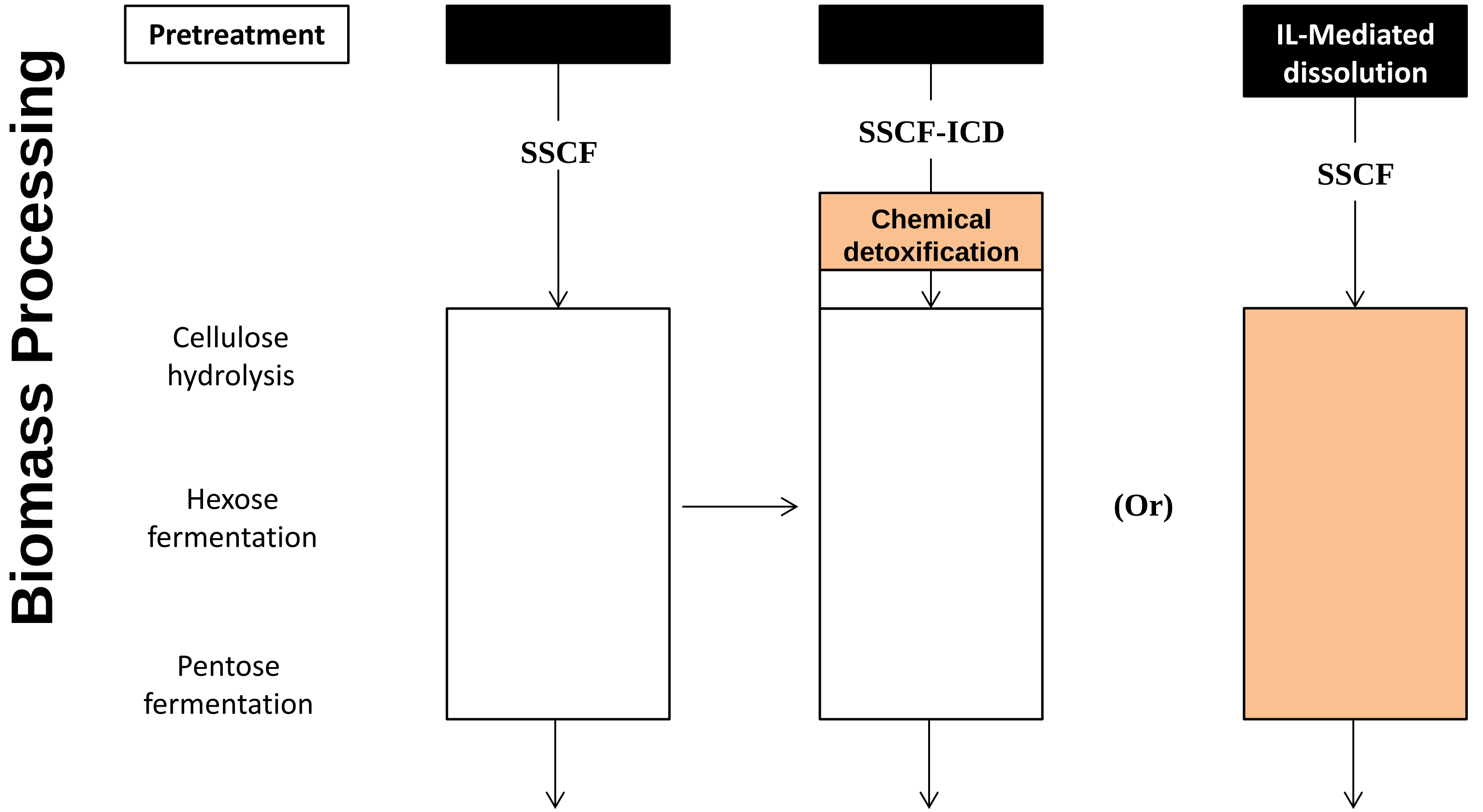
# Conclusions




SSCF: Simultanious Saccharification & Co-Fermentation

SSCF-ICD: Simultanious Saccharification & Co-Fermentation with an Integrated Chemical Detoxification

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➢SEKAB E-Technology AB

❖ Gruop members