Lignin Production by Organosolv Fractionation of Lignocellulosic Biomass

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Lignin & Lignocellulosic Biomass

Lignin major structural constituent of lignocellulosic biomass.

Lignocellulosic biomass:

- Hardwood: e.g., poplar, willow (LignoValue).
- Softwood: e.g., spruce, pine.
- Herbaceous: e.g., miscanthus, wheat straw (LignoValue).

Available in form of:

- (Forestry / agricultural) residues.
- Energy crops.

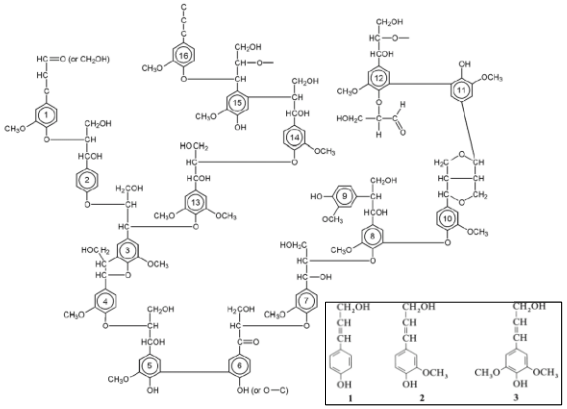
Lignocellulose Constituents

Lignin:

- Polymer of aromatic compounds.

Sugar polymers:

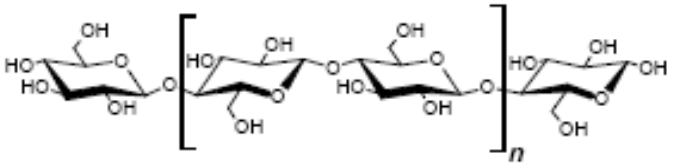
- Cellulose, linear polymer of glucose.
- Hemicellulose, branched copolymer of C5 and C6 sugars.



Lignin (model)

Factors influencing composition:

- Type of plant
- Part of plant (bark, stem, …)
- Age of plant
- …



Cellulose

Based on its chemical composition, lignocellulose potential feedstock for:

- Biofuels (e.g., bioethanol).
- Wide range of chemicals (including aromatics from lignin).

Ultrastructure Lignocellulosic Biomass

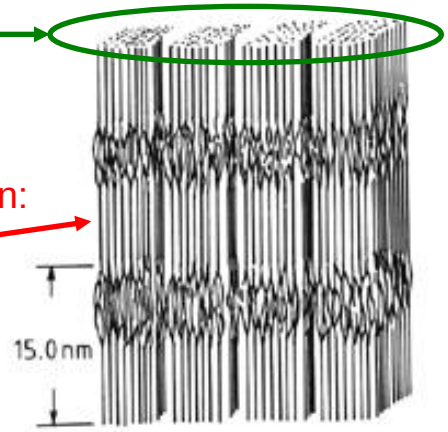
Structural components strongly linked (physically & chemically).

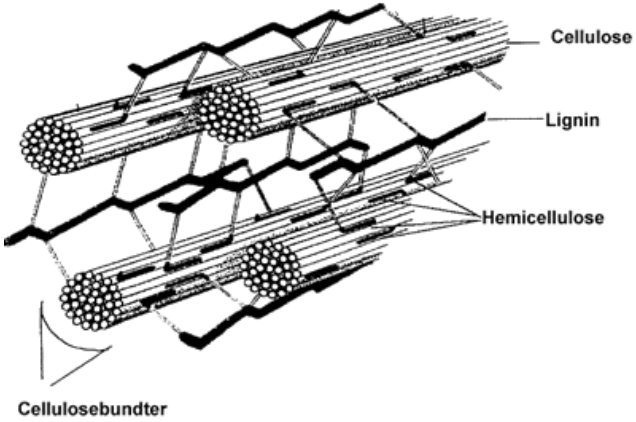
Cellulose:

- Present in fibers.
- Crystalline structure with amorphous regions.
- Cellulose fibrils backbone of wood.

Lignin:

- Functions as ‘glue’, providing physical strength.
- Protection against decay.





Enzymatic Cellulose Hydrolysis

Route for production sugar derivatives including 2G biofuels:

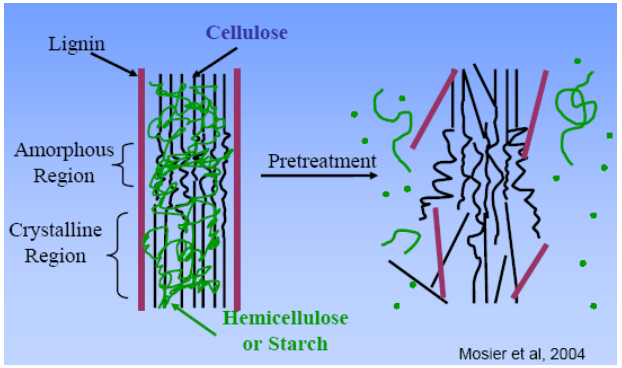
- Enzymatic hydrolysis cellulose to sugars.
- (Bio)chemical conversion of sugars.

→ Pre-treatment: overcoming nature's protection (biomass 'recalcitrance').

Pre-treatment:

Improving accessibility cellulose for enzymes by:

- Removing non-cellulose components (fractionation).
- Reducing crystallinity of cellulose.
- Creating specific surface area.
- ….



Pre-treatment

Several physical-chemical pre-treatment routes under development.

Main pretreatment routes:

- (Dilute) acid pre-treatment
- Steam explosion

Routes effective for cellulose.

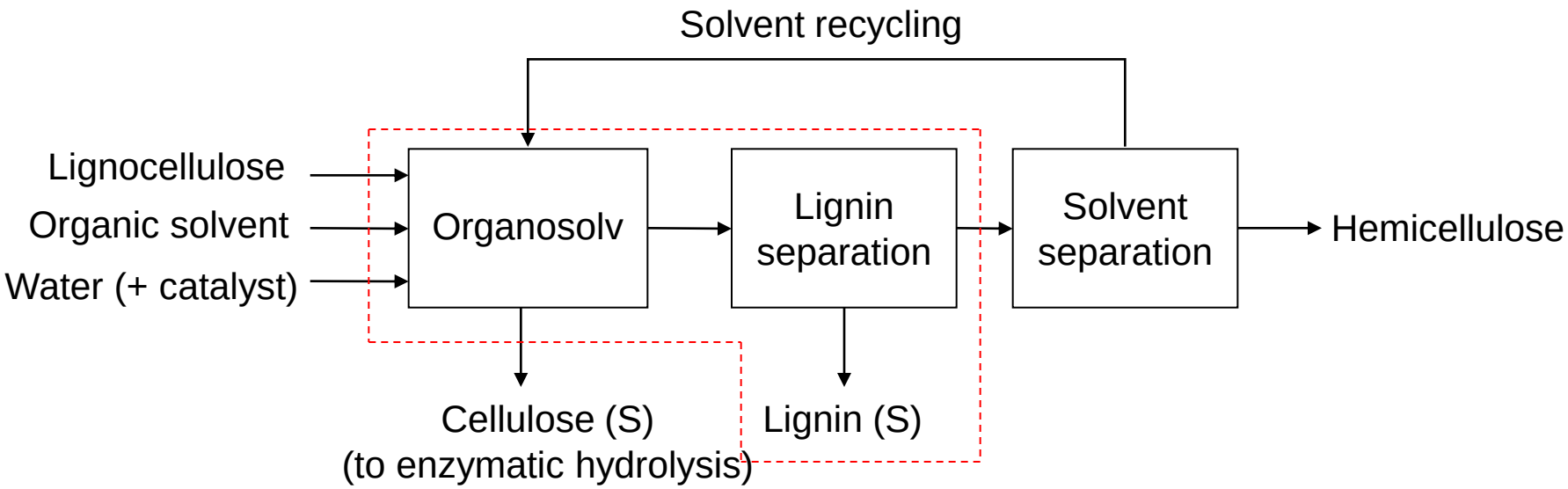
However:

- Lignin ends up in residue (with unconverted sugars, process chemicals, ash, etc).
- Residue generally only suitable for CHP.

Alternative:

- Separation of lignin prior to enzymatic hydrolysis, while preserving the chemical structure of lignin → organosolv.

Organosolv Process



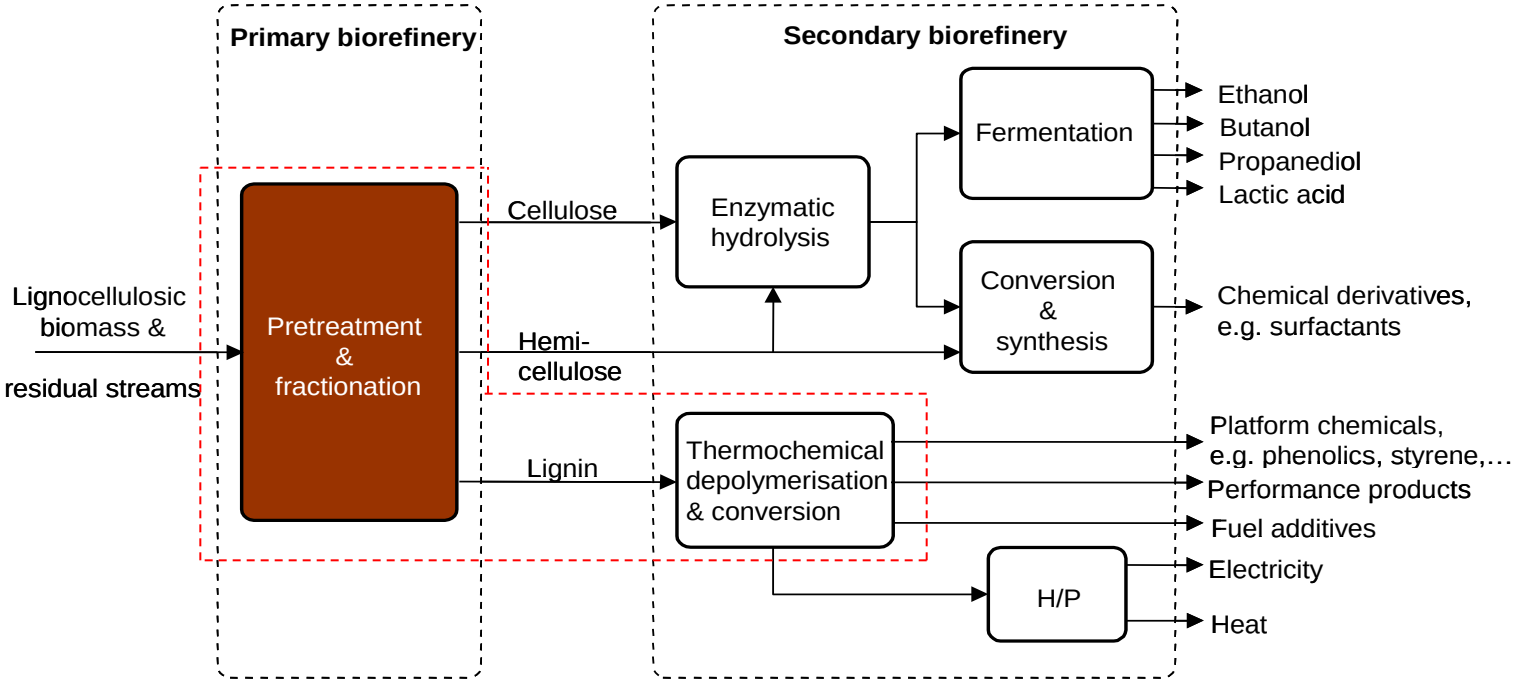
LignoValue organic solvent:

- *Ethanol*

Typical process conditions:

- *160-200 °C, 15-120 min, 5-30 bar.*

Lignocellulose Biorefinery



Aim ECN organosolv technology:

- Fractionation of all major constituents in a sufficient quality for valorisation.
- Including extraction of high-quality lignin for production of chemicals.

Experimental Set-up Organosolv Fractionation

Willow / straw

Milling

EtOH / H_2O

Optional: catalyst

Volume: 0.5 / 2 ltr
Stirring
Temperature ↑

Filtration

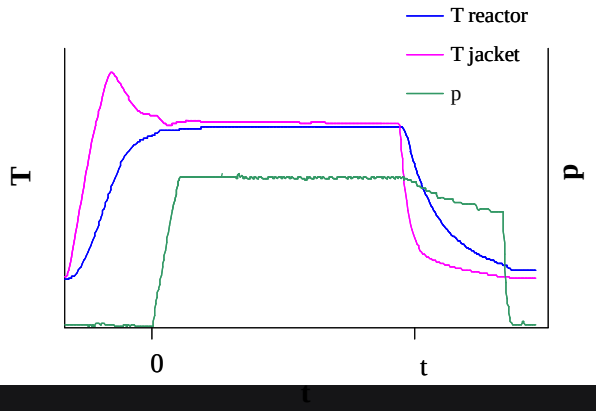
Washing

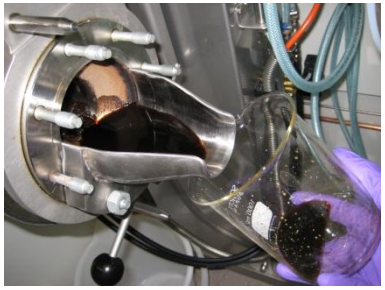
Solid residue

- Analysis composition
- Enzymatic hydrolysis

Filtrate

- Analysis sugars (monomeric + oligomeric)
- Analysis other compounds
- Lignin separation & analysis





Process Parameters

Extensive parametric study performed:

- Ethanol-based fractionation of willow wood and wheat straw.
- Fractionation and enzymatic hydrolysis of cellulose-enriched fraction.

Studied variables:

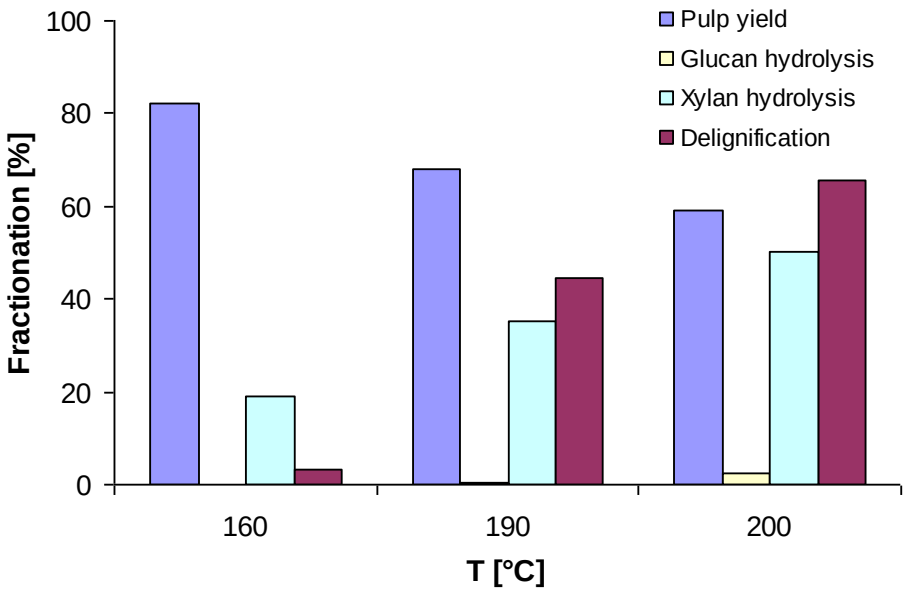
- Particle size (0.25-10 mm)
- Solvent mixture : solid ratio (L/S) (5-20 L/kg)
- Solvent-water ratio (0-85 wt%) ←
- Pretreatment severity: ←
  - Temperature (160-220 °C)
  - Reaction time (0-120 min)
  - Acid catalysts such as H_2SO_4
- Stirring rate (100-500 rpm)

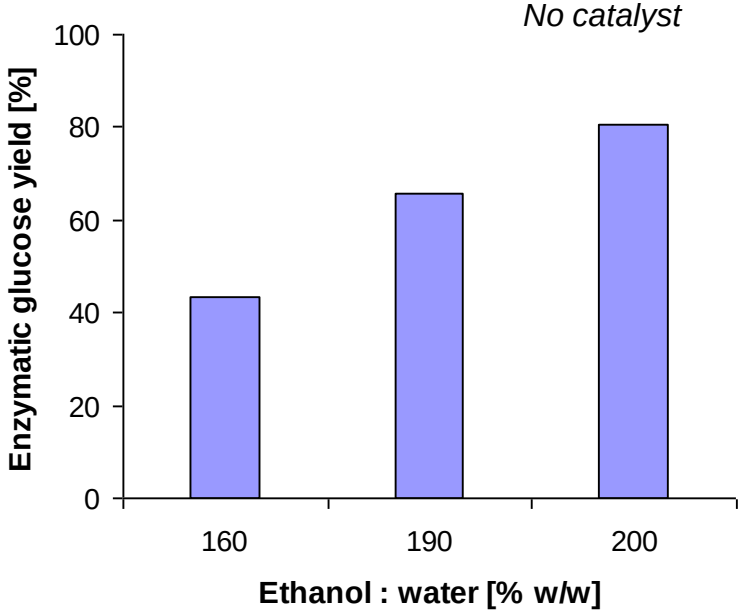
Fresh wheat straw

After organosolv

Process Temperature

Willow
EtOH:H_2O 60:40 wt%
60 min
No catalyst



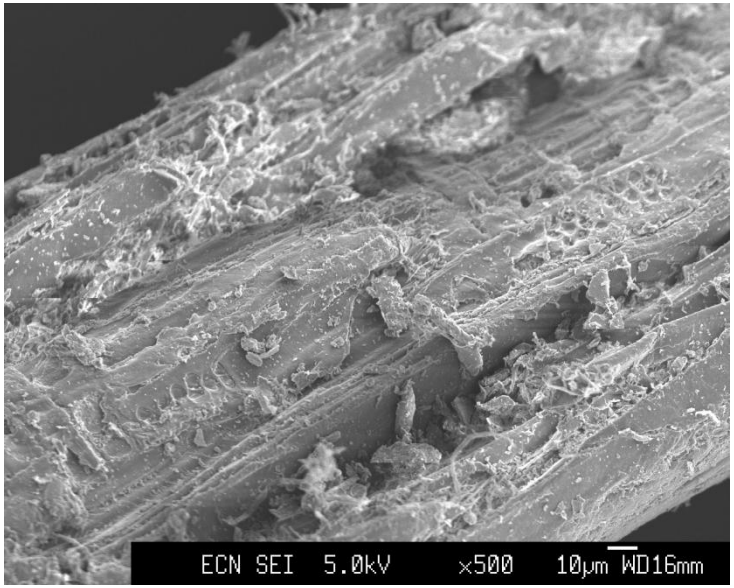


Organosolv fractionation & pre-treatment effective, positive effect temperature:

- Lignin extraction and hemicellulose hydrolysis increase.
- Above 200 ºC, cellulose hydrolysis and degradation of sugars during pre-treatment.
- Large enhancement of enzymatic hydrolysis cellulose (LignoValue: yield up to ~90%).

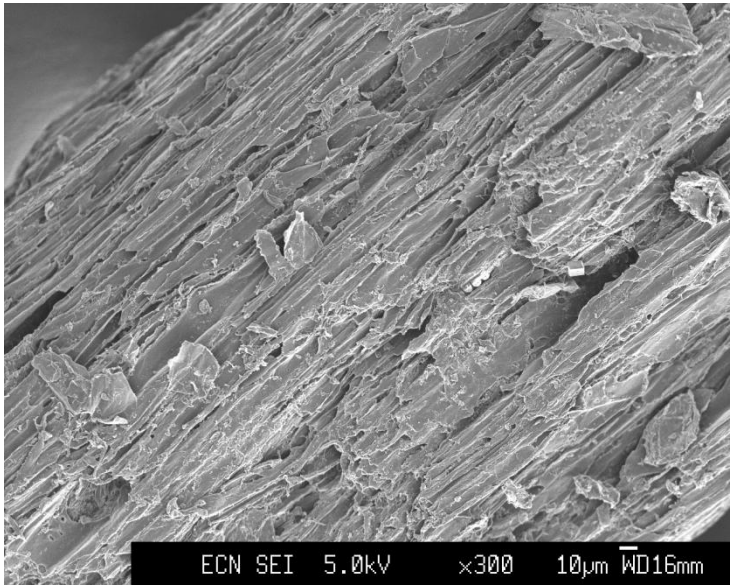
Pre-treatment Effect

Fresh willow



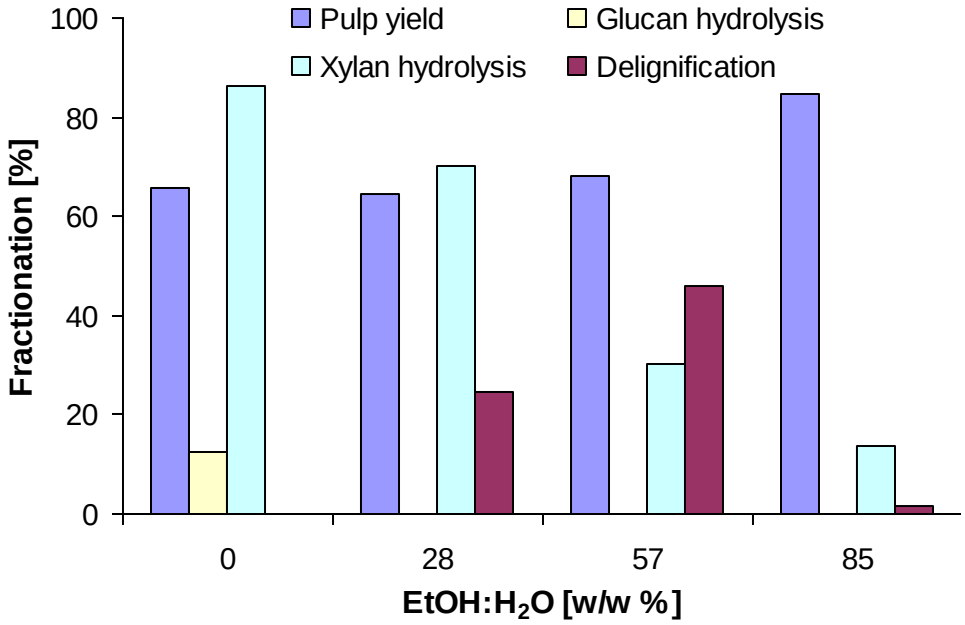
Pre-treated willow

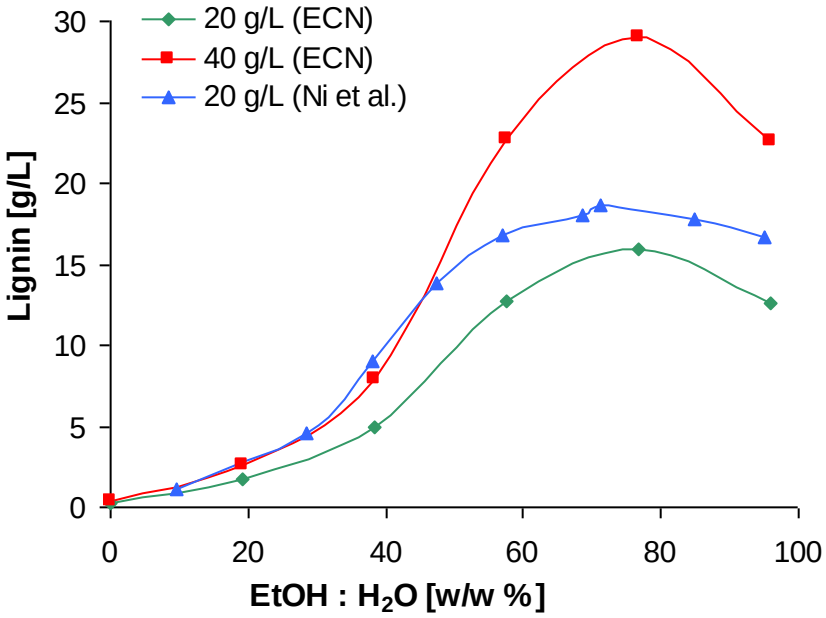
(190°C, 60 min, 60wt% EtOH)



- Cellulose fibrous structure remains intact.
- Extraction of hemicellulose and lignin.
- More open structure → better access for enzymes.

Solvent-Water Ratio: Fractionation





- Ethanol major influence on delignification and hemicellulose hydrolysis.
- Optimum EtOH-H_2O ratio for delignification (~60 wt% EtOH).
- Solubility of lignin (fragments) dependent on solvent mixture composition.

Willow
190 °C
60 min
No catalyst

Solvent-Water Ratio: Enzymatic Hydrolysis

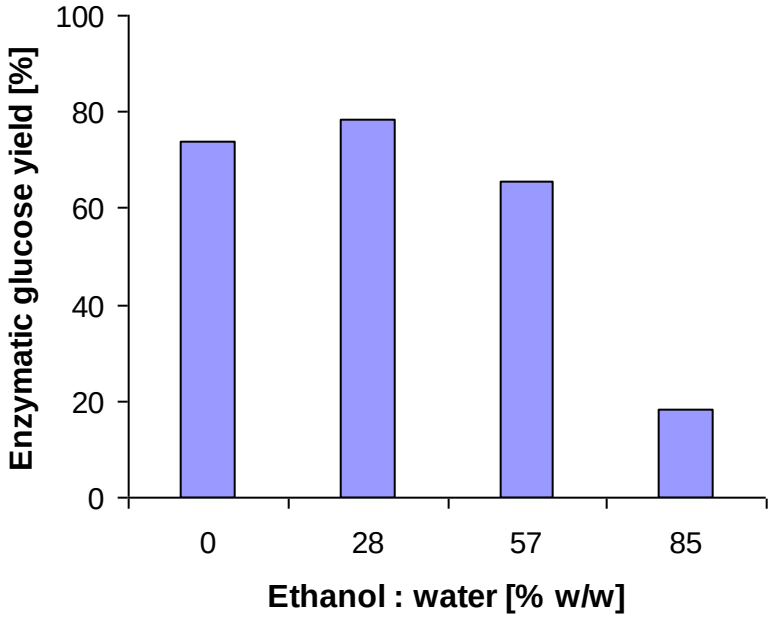
Enzymatic digestibility very low at high EtOH percentage (poor fractionation).

Cellulose digestibility optimum around 30% w/w EtOH (trade-off delignification and hemicellulose hydrolysis).

Optimization process conditions dependent on revenues various products.

LignoValue:

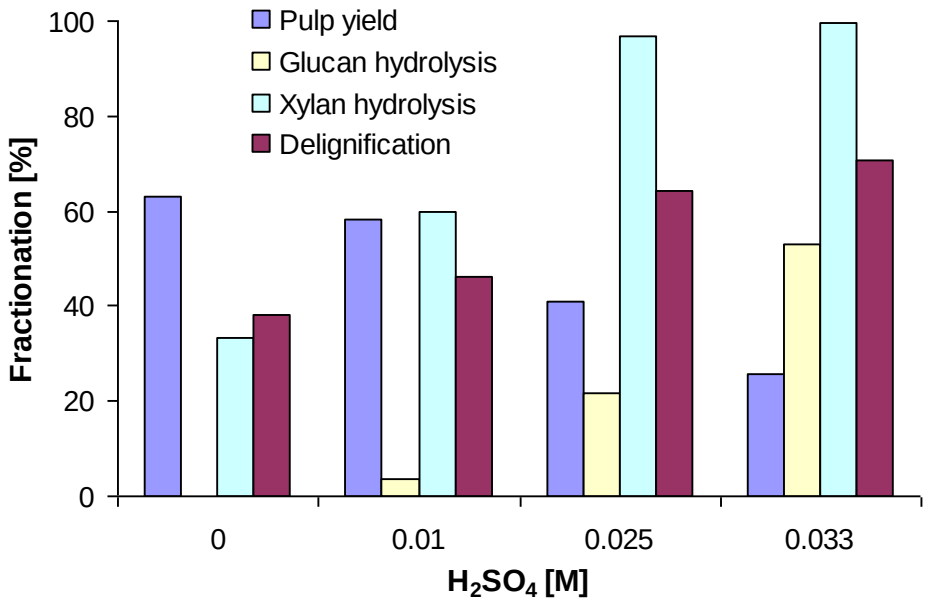
- Focus on lignin.
- Ethanol-water ratio ~60% w/w selected.

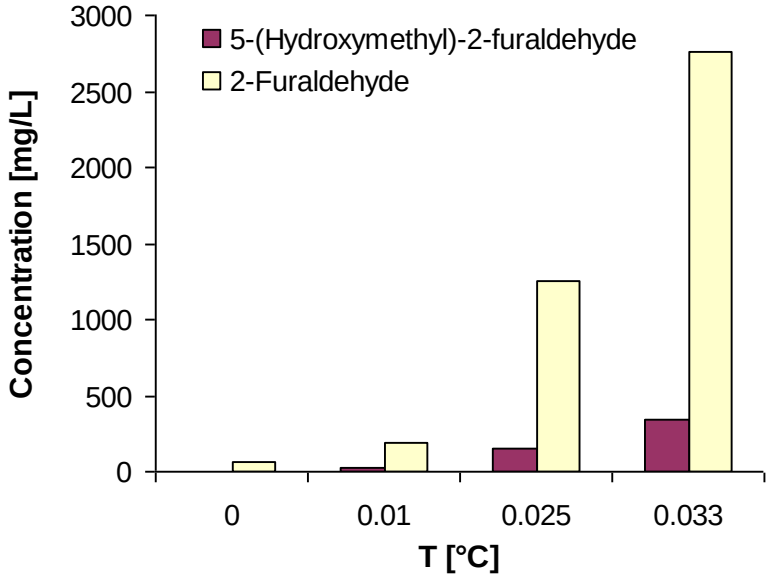


Willow
190 °C
60 min
No catalyst

Catalysts

Willow
60:40% w/w EtOH-H_2O
200 °C
30 min





Addition of H_2SO_4:

- Improved fractionation (especially hemicellulose hydrolysis, but also delignification).
- Increase enzymatic digestibility pretreated willow.
- However, cellulose hydrolysis during fractionation and increase degradation reactions.

Feedstocks

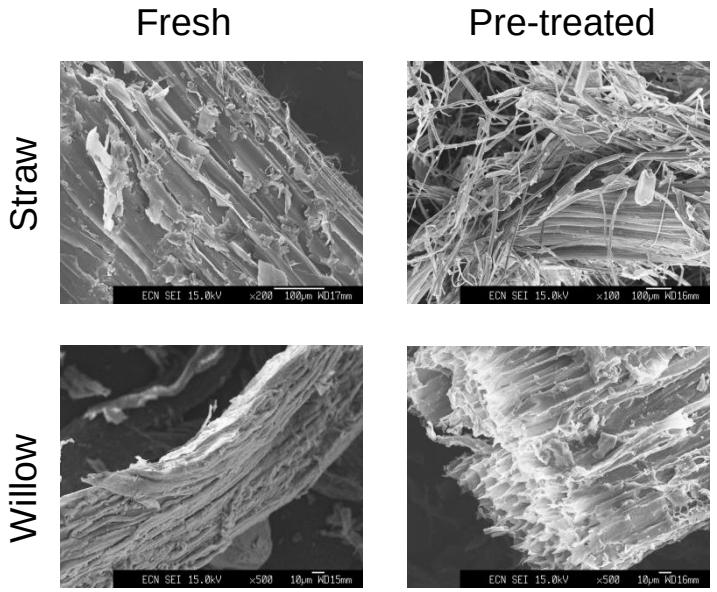
Effectiveness organosolv dependent on type of lignocellulosic biomass.

In general:

- Organosolv less effective for softwoods and (more dense) hardwoods.
- More severe pretreatment conditions or use of catalyst required.

LignoValue:

- Organosolv effective for both willow wood and wheat straw.
- Organosolv particularly suitable for straw.



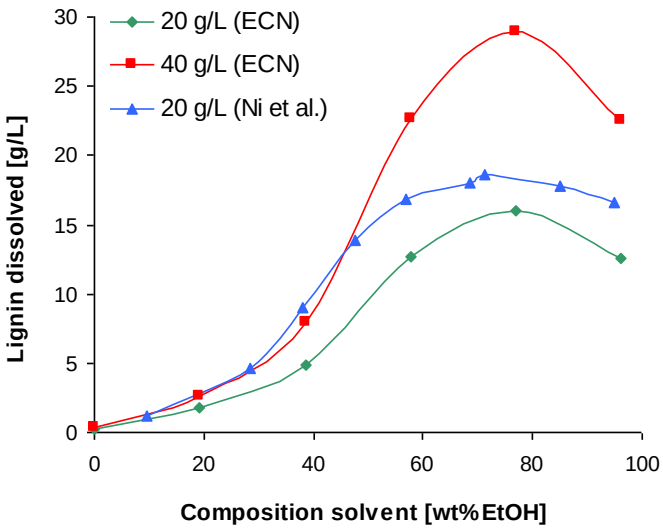
Lignin Separation from Organosolv Liquor

Lignin dissolved in ethanol-water liquor together sugars, soluble ash minerals, etc.

Separation by adjusting ethanol-water ratio.

Lab protocol:

- Preconcentration and water addition.
- Rapid & efficient separation of lignin from filtrate.
- Maximum lignin yield obtained LignoValue feedstocks: ~70%.



Lignin Characterisation

Lignin appearance:

- Light brown to black (compacted) powder.
- Colour and structure dependent on process conditions organosolv, biomass type and contaminants.

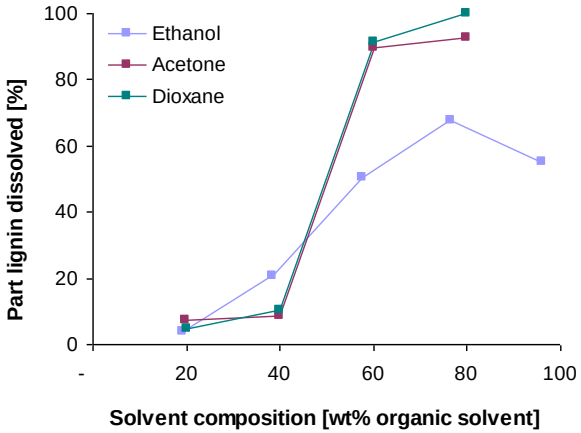
160, 180, 200, 220 °C

Purity:

- Lignin relatively pure (>90 wt%, up to 96% for wheat straw derived lignin).
- Main contaminant oligomeric xylose (hemicellulose).
- Lignin sulphur- and ash-free (max 0.1 wt% S).

Solubility:

- H_2O (none), ethanol, acetone & dioxane (good).



Lignin Characterisation - II

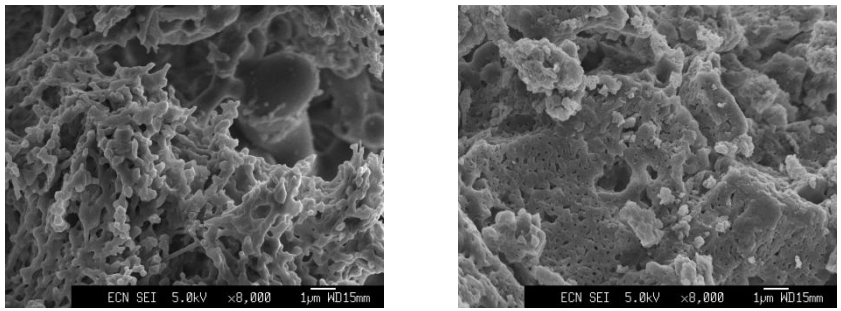
Molecular weight:

- Low mean molecular weight (2000-3500) relative to other types of lignins.
- Relatively narrow distribution.

^{31}P-NMR:

- Identification of functional groups.
- SGH type lignins in different ratios depending on feedstock.

→ Organosolv lignin promising properties for valorisation (relative to other types of lignin).



Organosolv lignin

Conclusions

Fractionation & pre-treatment:

- Ethanol-based organosolv able to fractionate willow wood and wheat straw.
- Enzymatic hydrolysis cellulose improved substantially (up to ~90% for wheat straw).
- Organosolv particularly effective for straw.
- Recycling organic solvent crucial process element to be studied further.

Organosolv lignin:

- Efficient separation of lignin.
- High purity (up to 96% for wheat straw derived lignin).
- Promising properties for production of chemicals and performance products.

Thank you for your attention!

More information:
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http://www.lignovalue.nl/
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