



Energy research Centre of the Netherlands

Modified Organosolv

A Fractionation Process of Lignocellulosic Biomass for Co-Production of Fuels and Chemicals

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MODIFIED ORGANOSOLV

A Fractionation Process of Lignocellulosic Biomass for Co-production of Fuels and Chemicals

Wouter Huijgen, Ron van der Laan & Hans Reith



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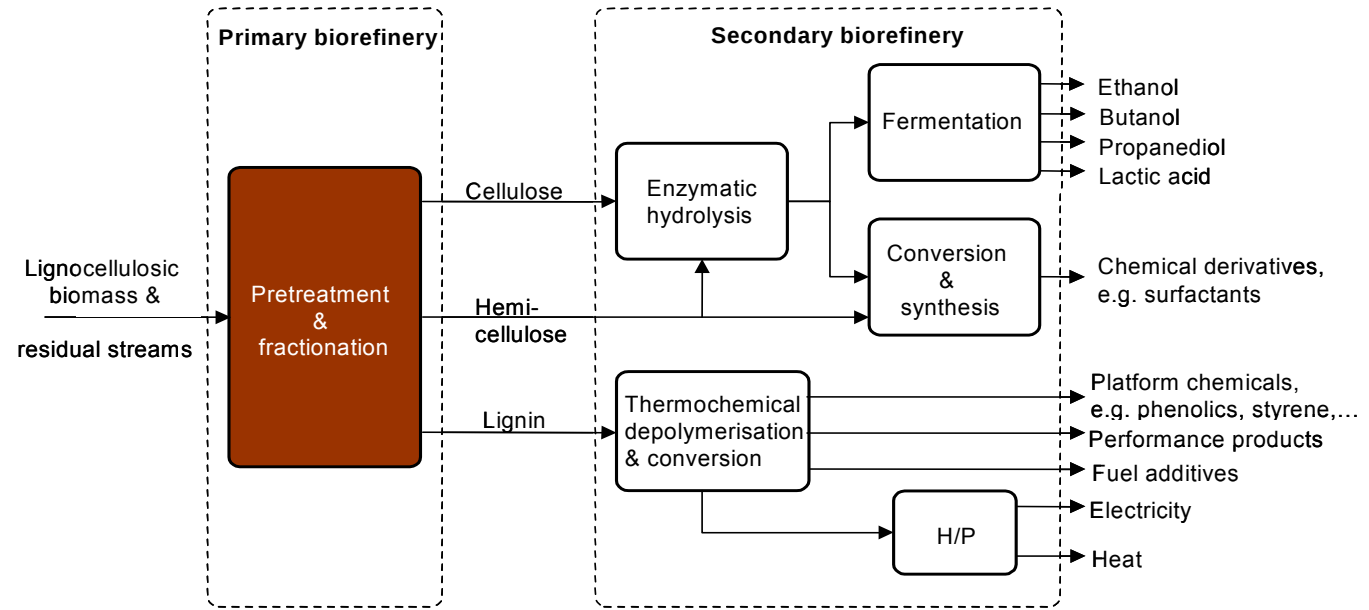
Experimental

Results

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Biorefinery



Goals primary biorefinery:

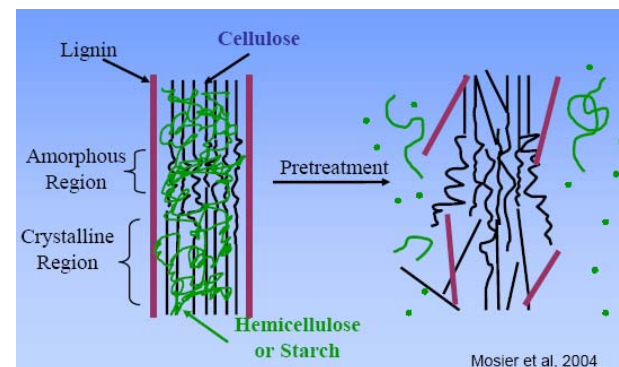
- Enhancement (enzymatic) degradability of cellulose to fermentable sugars.
- Hemicellulose hydrolysis to sugars.
- Extraction of high-quality lignin for production of chemicals.

→ Fractionation of all biomass fractions in a sufficient quality for production of (bio)chemicals.

Biomass pre-treatment

Pre-treatment technologies

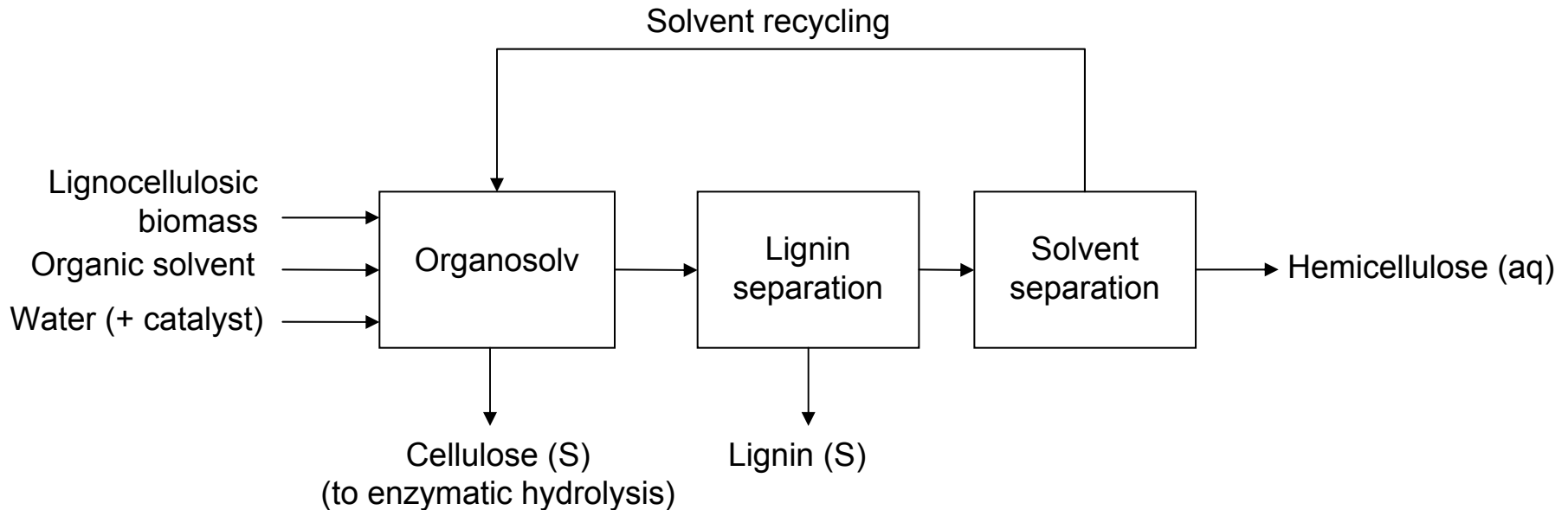
- Many pre-treatment technologies: steam explosion, ammonia fibre explosion (AFEX), acid hydrolysis, alkaline pre-treatment, etc.
- Different functionalities and characteristics.
- Comparison of technologies → selection of organosolv



Why organosolv?

- Other pretreatments generally produce low quality lignin, only suitable for CHP.
- Avoidance waste generation (due to neutralization).
- Minimization formation of fermentation inhibitors.

Organosolv process

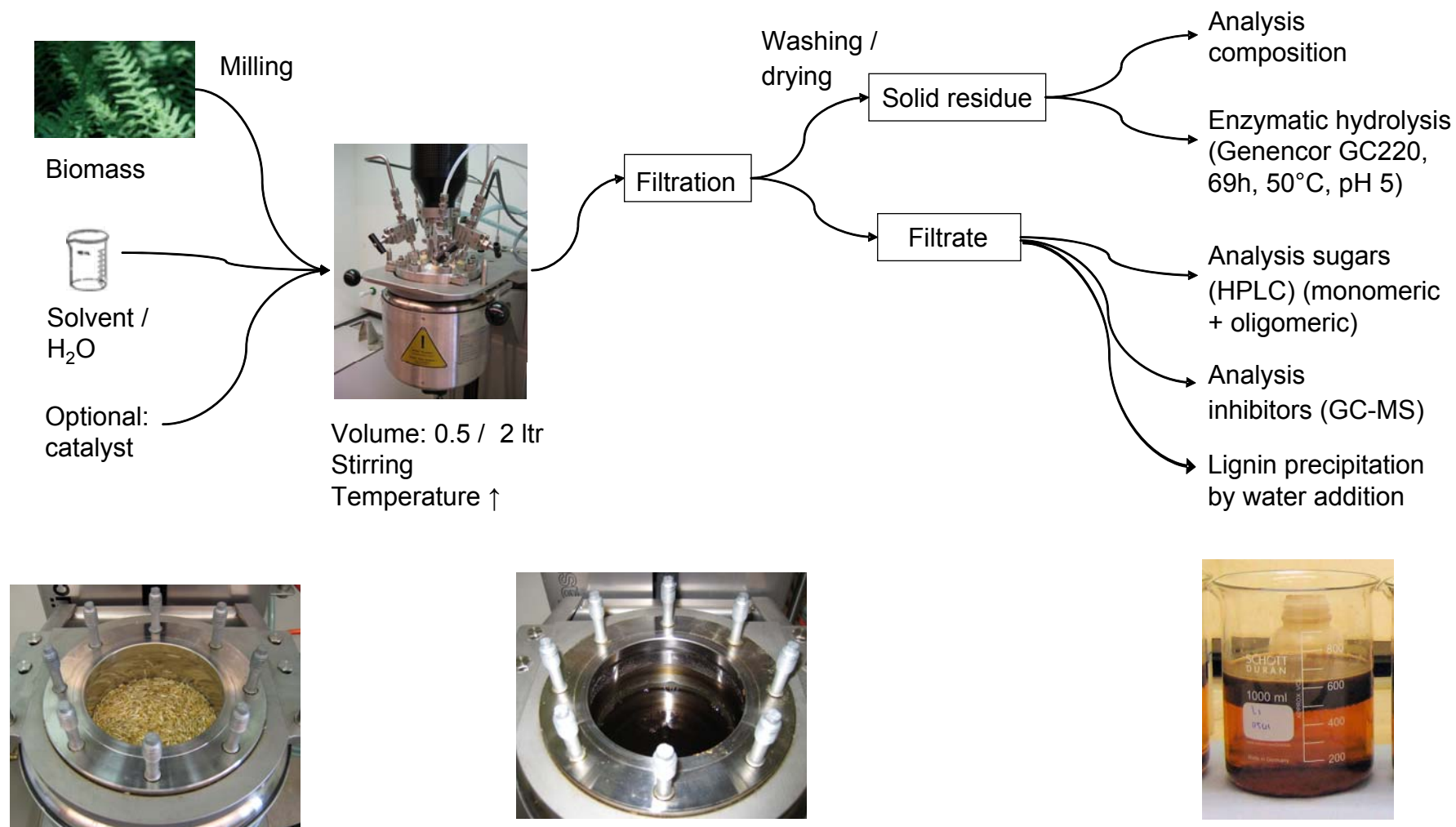


- Typical process conditions (ECN): 160-200 °C, 15-60 min, 5-30 bar.
- Possible solvents: ethanol (standard), methanol, acetone, acetic acid, dioxane, etc.

R&D challenges:

- Organosolv process developed in 70-80's as alternative pulping process.
- Applicability for biorefinery purposes? Adaptations required?
- Reduction of costs and energy consumption (solvent recycling).

Experimental set-up



Effects on Biomass

- General: colour gets darker.
- Structural changes:
 - Function of temperature and stirring rate (mechanical impact).
 - ‘Cardboard’ like appearance.

*Wheat
straw*



Stirring rate: Low (100 rpm)
Fibres

High (500 rpm)
‘Cardboard’

Fresh material (left), pre-treated (right):



Poplar wood

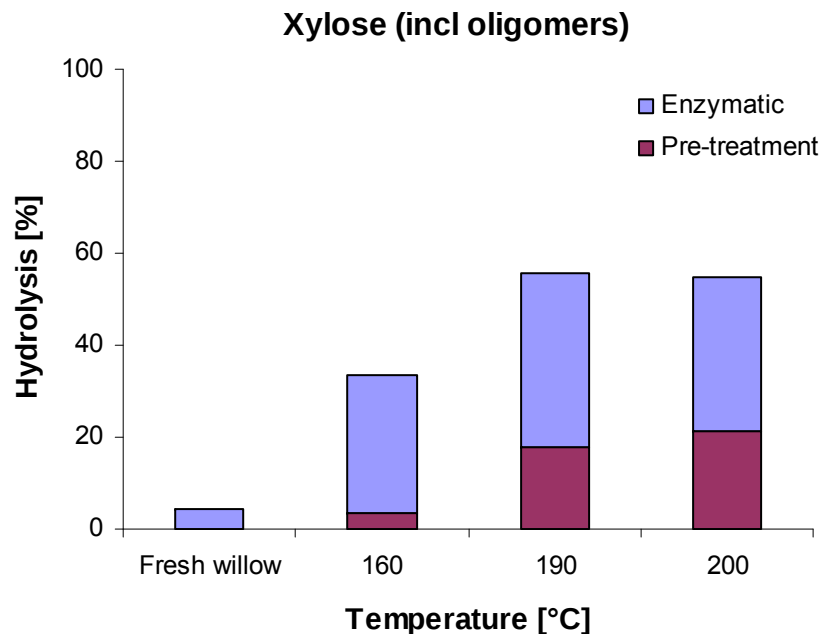
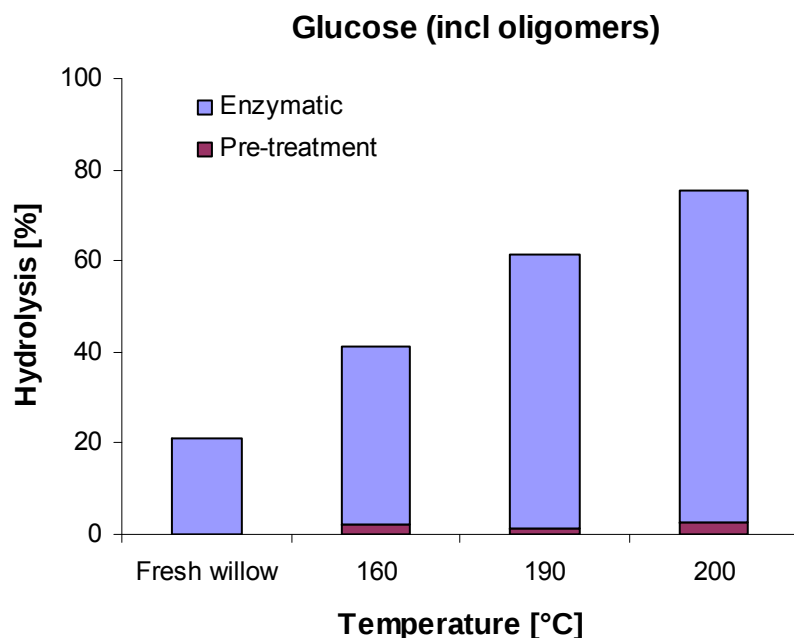


Wheat straw

T = 200 °C, solvent: ethanol/water.

(Hemi)Cellulose Hydrolysis – Effect of Temperature

Cumulative hydrolysis during pre-treatment and enzymatic hydrolysis:

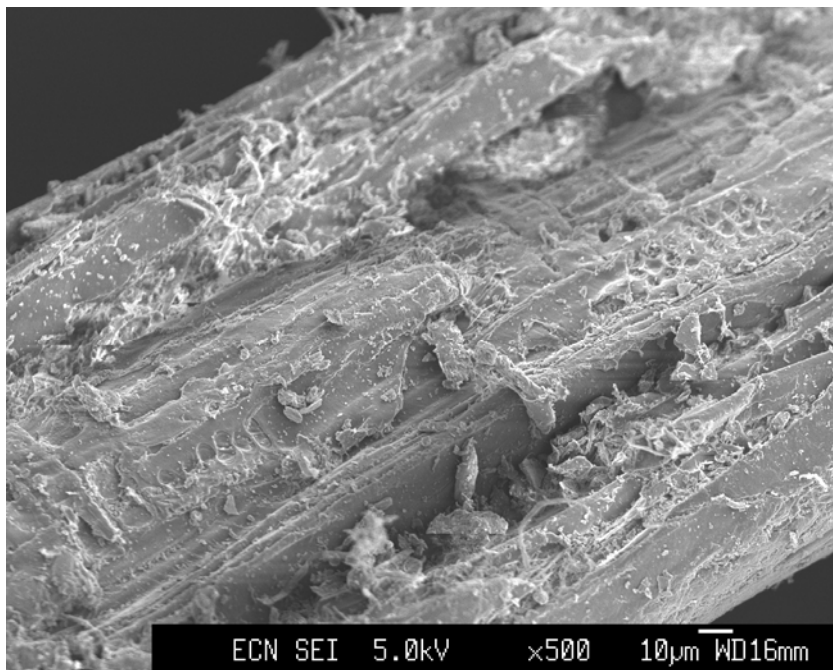


- Temperature key process parameter.
- Cellulose hydrolysis during pre-treatment negligible, hemicellulose $\pm 20\%$.
- Large enhancement of enzymatic hydrolysis cellulose (max $\pm 75\%$).
- Inhibitor formation: increase with temperature, high (≥ 200 °C).

Willow
EtOH:H₂O 60:40 wt%
60 min
No catalyst
500 rpm

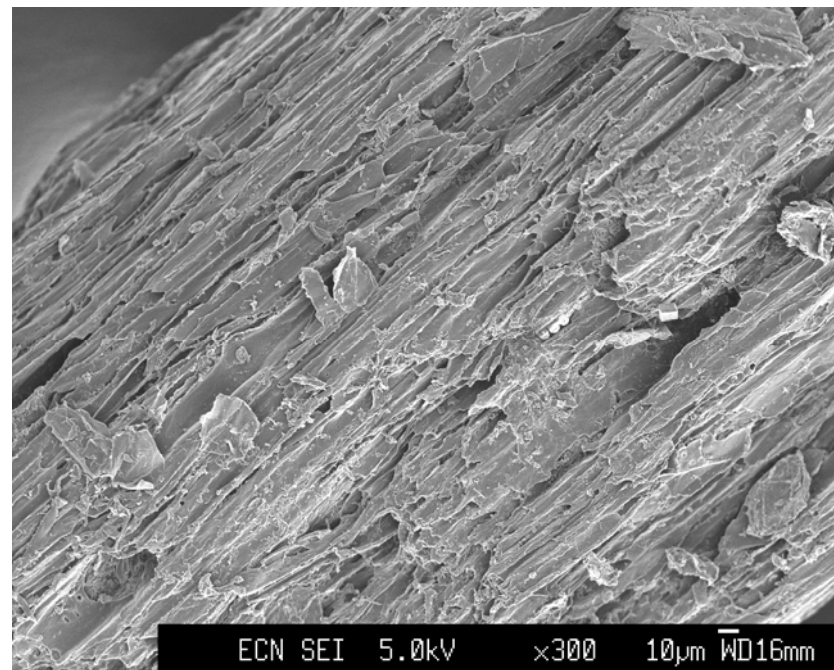
Scanning Electron Micrographs

Fresh willow



Pre-treated willow

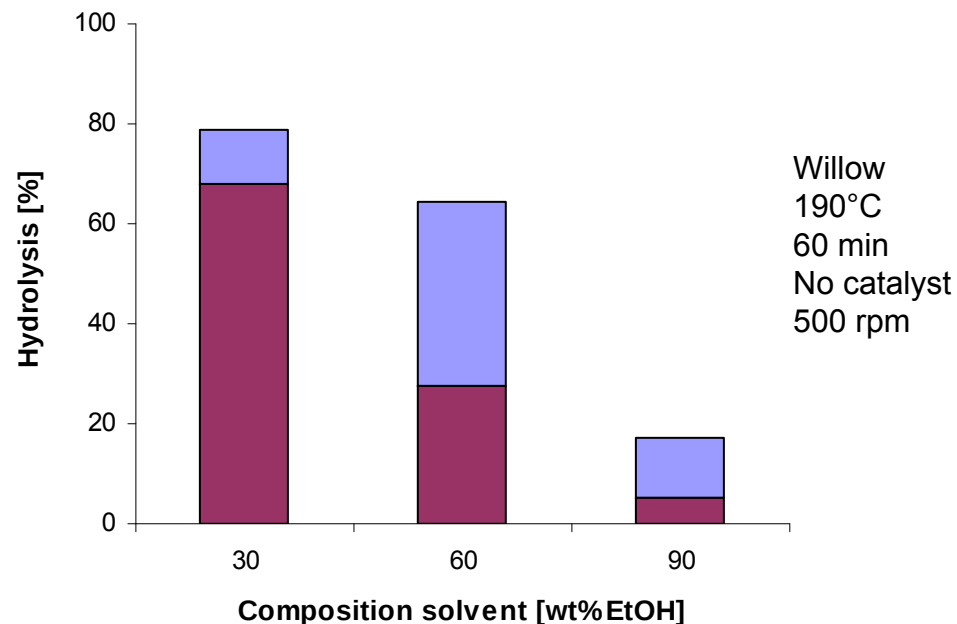
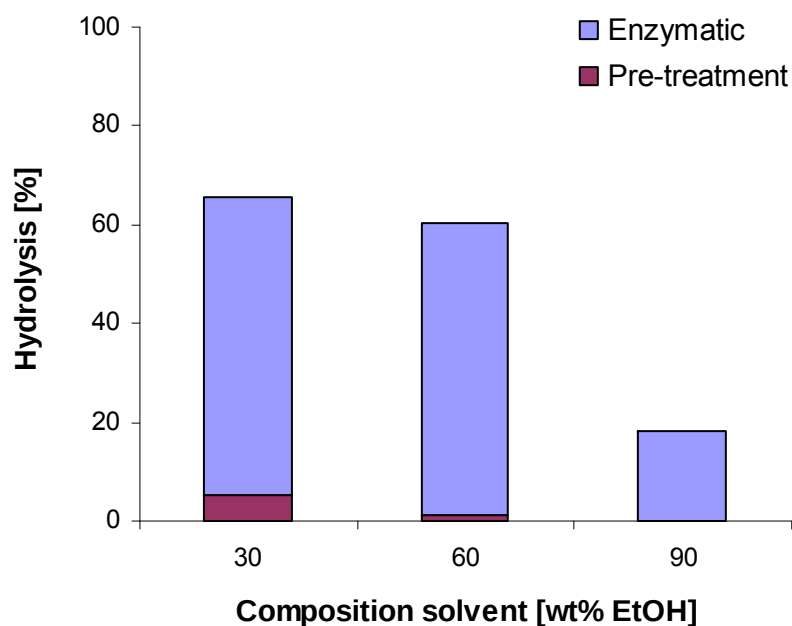
(190°C, 60 min, 60wt% EtOH)



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

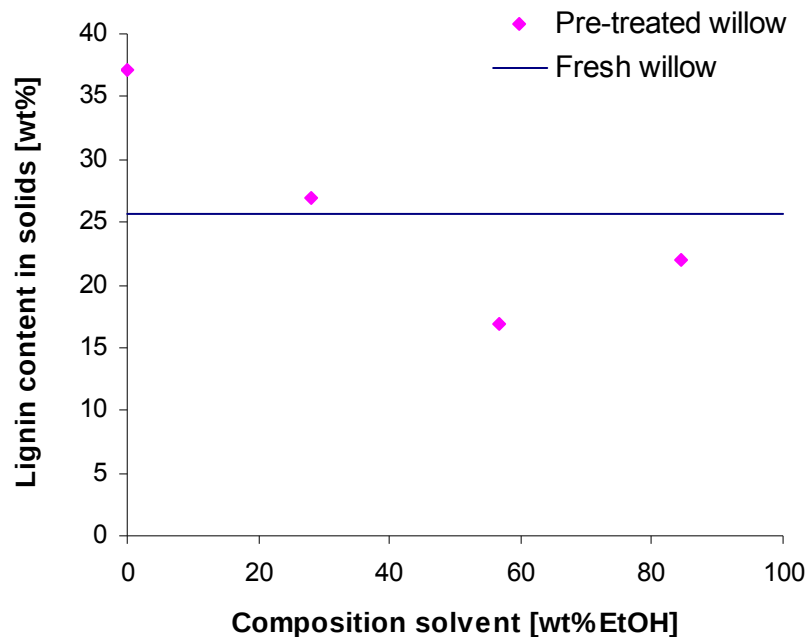
(Hemi)Cellulose Hydrolysis - EtOH:H₂O ratio

Cumulative hydrolysis during pre-treatment and enzymatic hydrolysis:



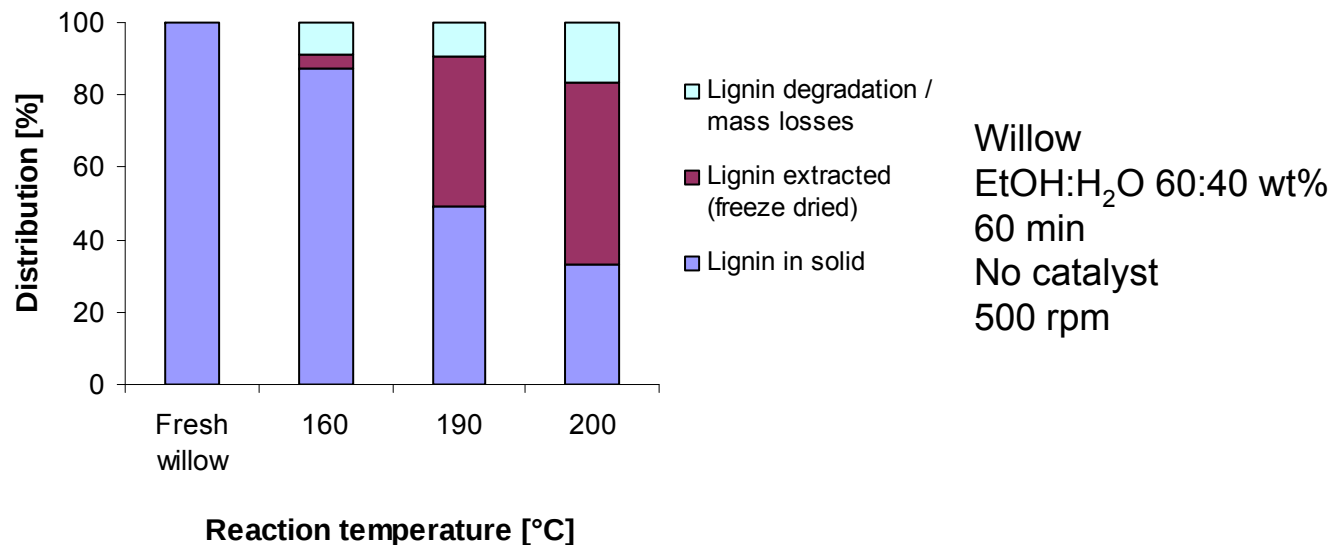
- Large effect on hemicellulose hydrolysis during pre-treatment.
- Enzymatic degradability cellulose remains similar at low EtOH:H₂O ratio.

Extraction of Lignin – EtOH:H₂O ratio



- Ethanol:water ratio solvent major influence delignification (opt 60 wt% EtOH).
- Delignification optimum at higher EtOH-H₂O ratio, in contrast to hemicellulose hydrolysis.
- Solubility of lignin (fragments) dependent on solvent mixture composition.

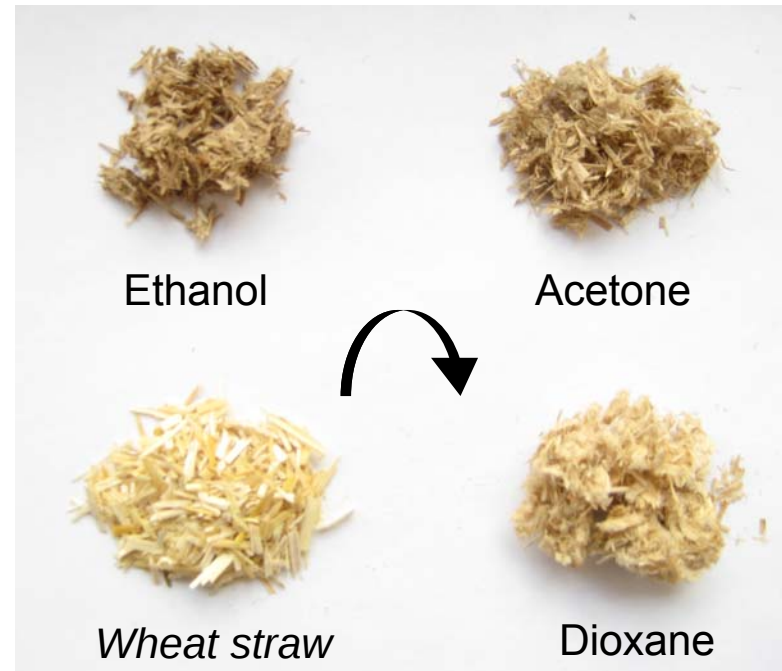
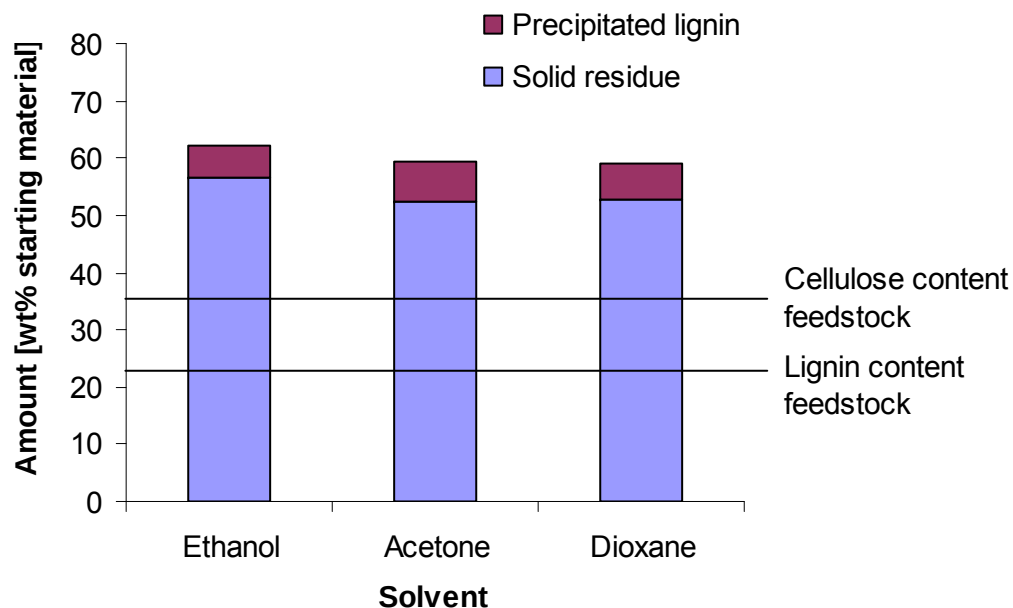
Lignin extraction and recovery – Temperature



- Substantial delignification of willow wood achieved (max ±70%).
- Similarly to hydrolysis: temperature key process parameter & degradation (inhibitor formation) significant at ≥200°C.
- Separation of lignin from filtrate possible by precipitation.
- Delignification at milder process conditions → alternative solvents & catalysts.

Alternative solvents

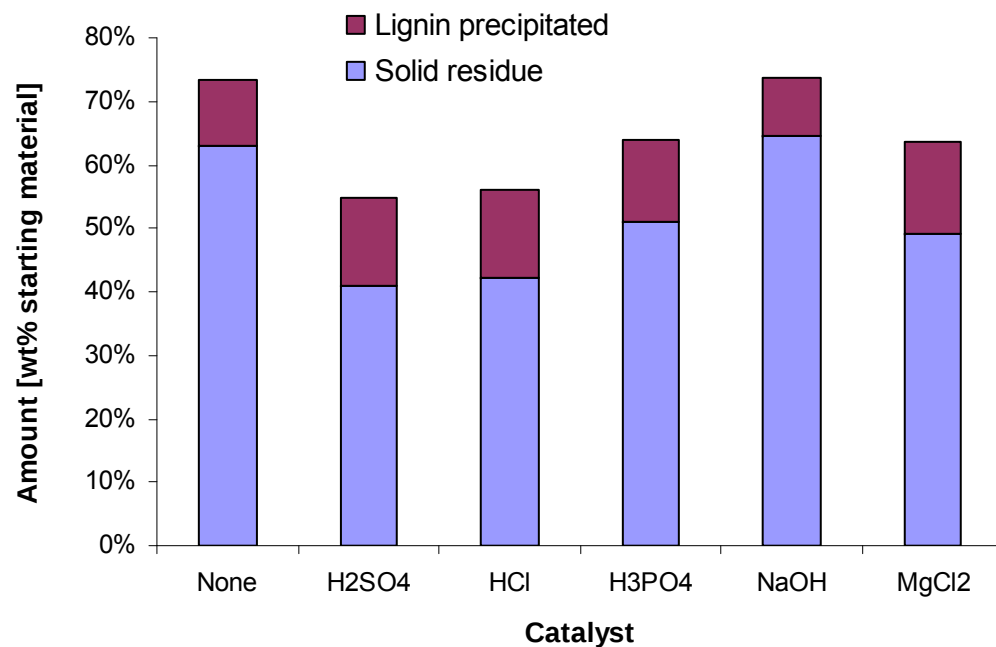
- Solvents known as good lignin solvents tested.
- Colour and structure of biomass indicative for enhanced delignification wheat straw.
- However, differences in conversion and amount of lignin precipitated small.



Wheat straw
60:40 wt% solvent:water
200 °C
30 min
100 rpm

Effect of Catalysts

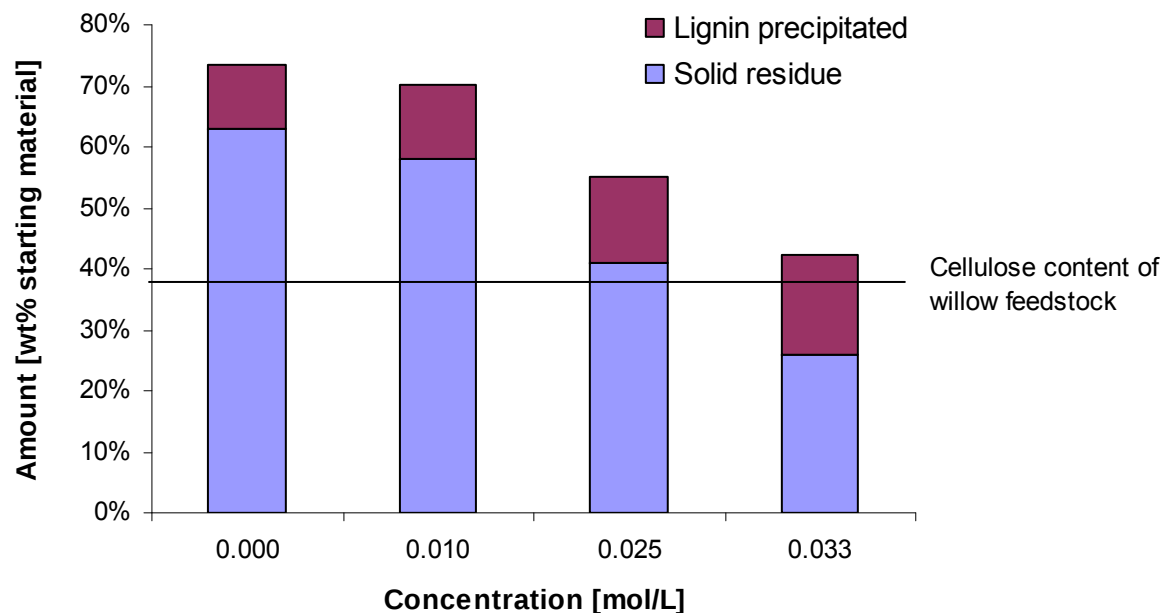
Screening:



- Addition of acids effective.
- H₂SO₄ most effective.
- NaOH not effective due to neutralisation (at this concentration).
- MgCl₂ potentially interesting catalyst since it does not lower the pH by itself.

Willow
60:40 wt% EtOH-water
200 °C
30 min
100 rpm
0.025M catalyst

Catalyst – H_2SO_4



Willow
60:40 wt% EtOH-water
200 °C
30 min
100 rpm

- Hemicellulose hydrolysis and delignification are improved.
- Up to 2/3 of lignin isolated (i.e., extracted and precipitated).
- At high concentrations: even cellulose hydrolysis.
- Not required (and high formation of inhibitors and higher costs)

Lignin characterisation

Performed by A&F (NL) & VTT (FI).

- Lignin produced relatively pure (94-100 wt%).
 - Main contaminant: xylose (mostly oligomers).
 - Mean molecular weight (MW) and polydispersity (PD):
 - Comparable with commercial organosolv lignin.
 - Low relative to other types of lignins.
 - Mean lignin particle size (volume-based): 61 μm (poplar) and 10 μm (wheat straw).
 - Further characterisation in progress.
- ⇒
- Purity and MW distribution indicate suitability of lignin for chemical production.
 - Conversion tests of lignin into e.g. phenols to be performed.

Feedstock / sample	Mw	PD
Poplar	2419	3.5
Barley straw	3006	4.1
Willow	3452	4.1
Alcell®	2985	3.6

Conclusions

- Organosolv suitable for fractionation within biorefinery:
 - Hemicellulose hydrolysis (max $\pm 80\%$).
 - Delignification (max $\pm 70\%$).
- Cellulose fraction: enzymatic degradability strongly enhanced.
 - Enhancement of enzymatic degradability (max $\pm 75\%$).
- Lignin seems of sufficient quality for chemicals production.

Further R&D:

- Process optimization: particularly higher delignification at milder process conditions.
- Further characterization of lignin & conversion to products.
- Conceptual process design.

Thank you for your attention!

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This work is in part performed in the context of:



BIOsynergy



SenterNovem EOS-LT