ECN

Energy research Centre of the Netherlands

Modified Organosolv

Fractionation of Lignocellulosic Biomass for Production of High Quality Lignin (and Fermentable Sugars)

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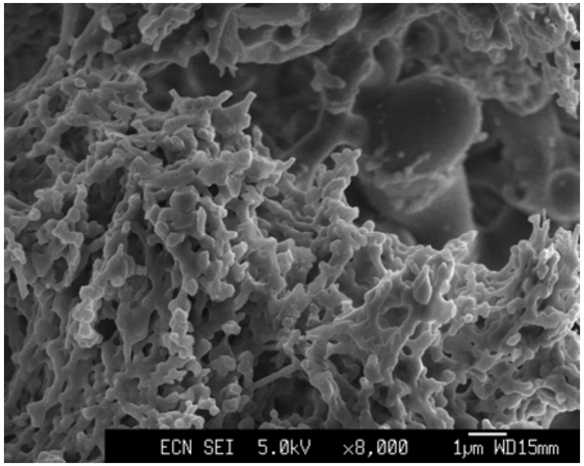
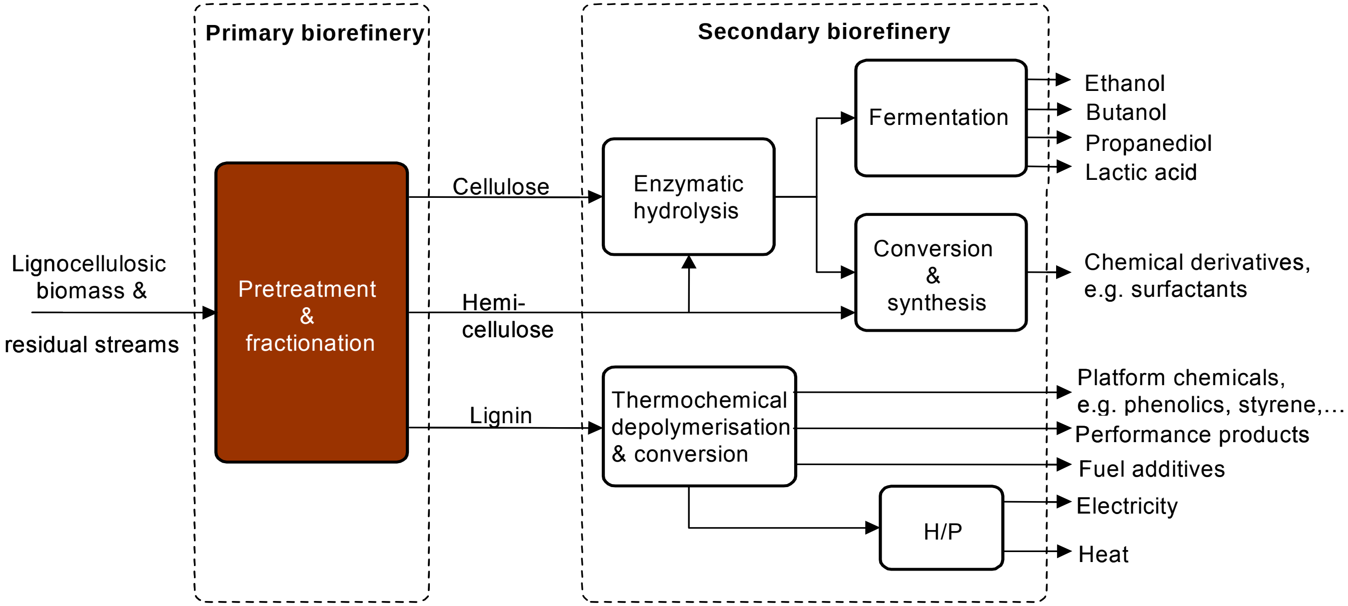


Organosolv lignin

Biorefinery



Goals primary biorefinery:

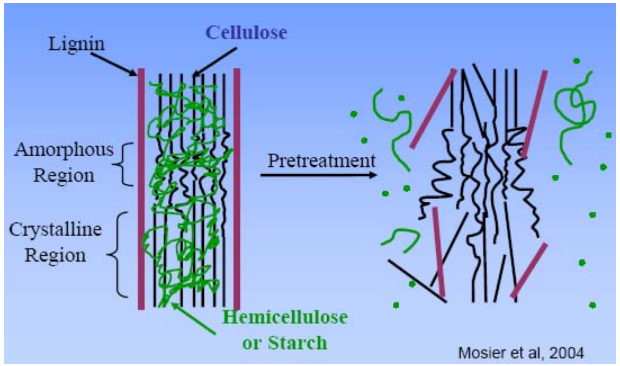
- Enhancement (enzymatic) degradability of cellulose to fermentable sugars.
- Hemicellulose hydrolysis to sugars.
- Extraction of high-quality lignin for production of chemicals.

→ 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.



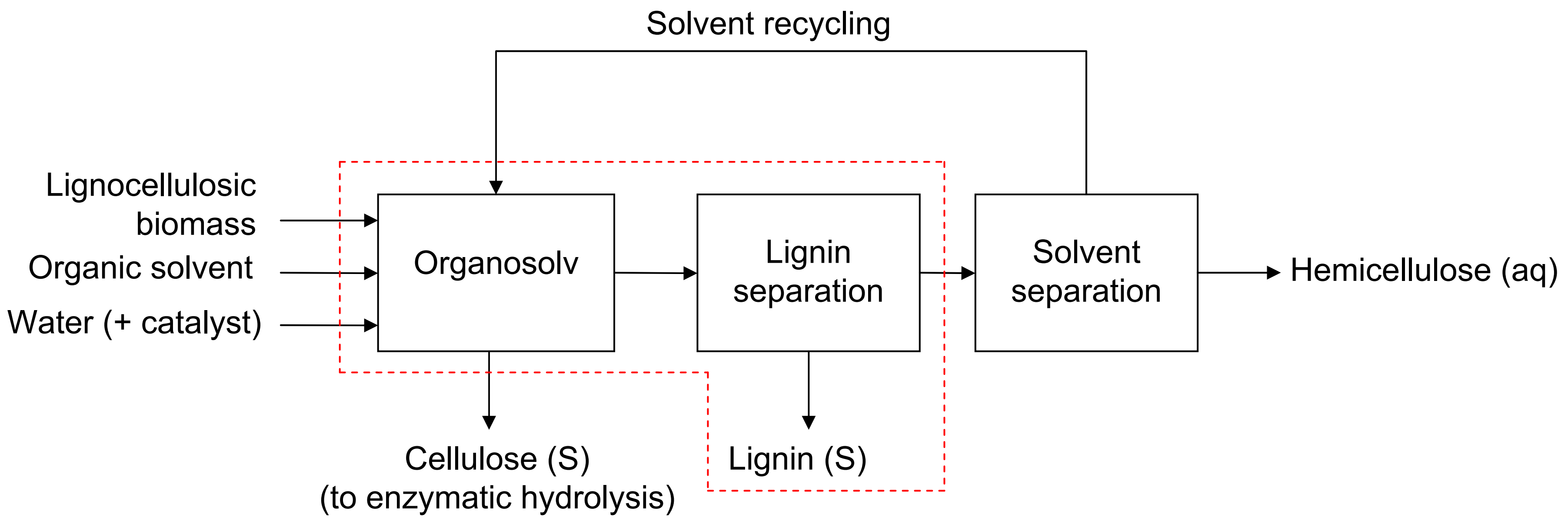
Why organosolv?

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

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).

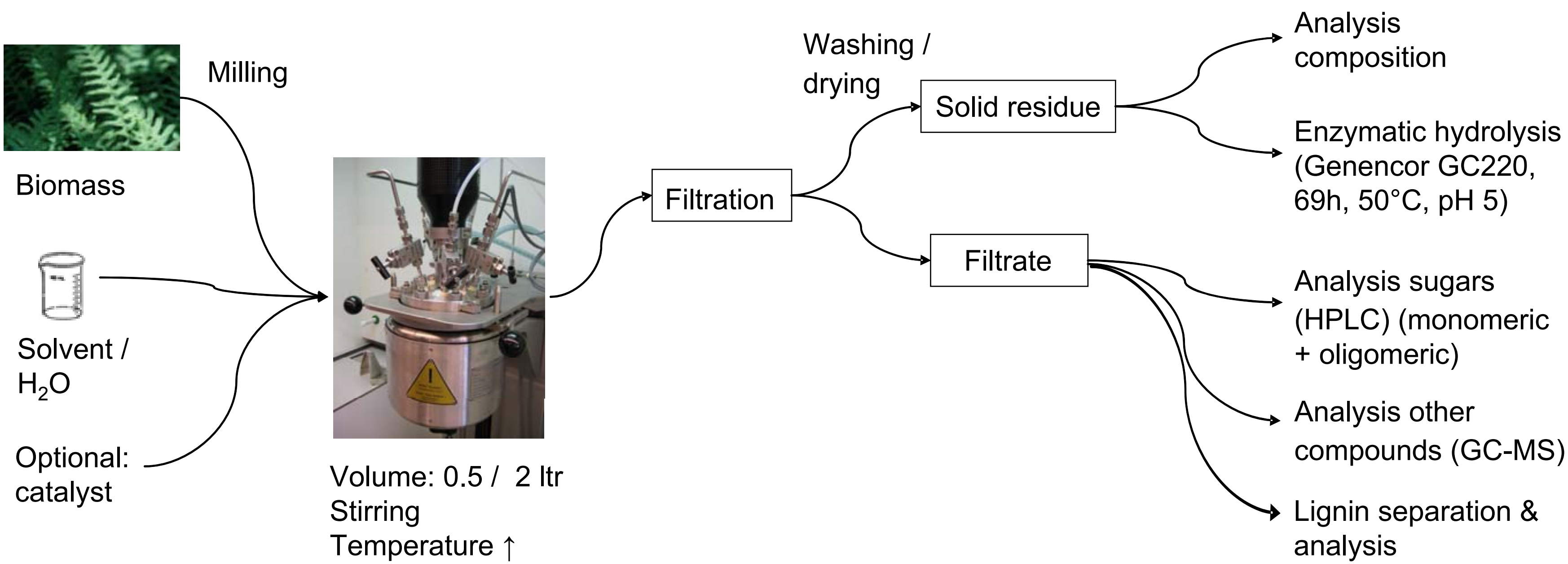
Organosolv process



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

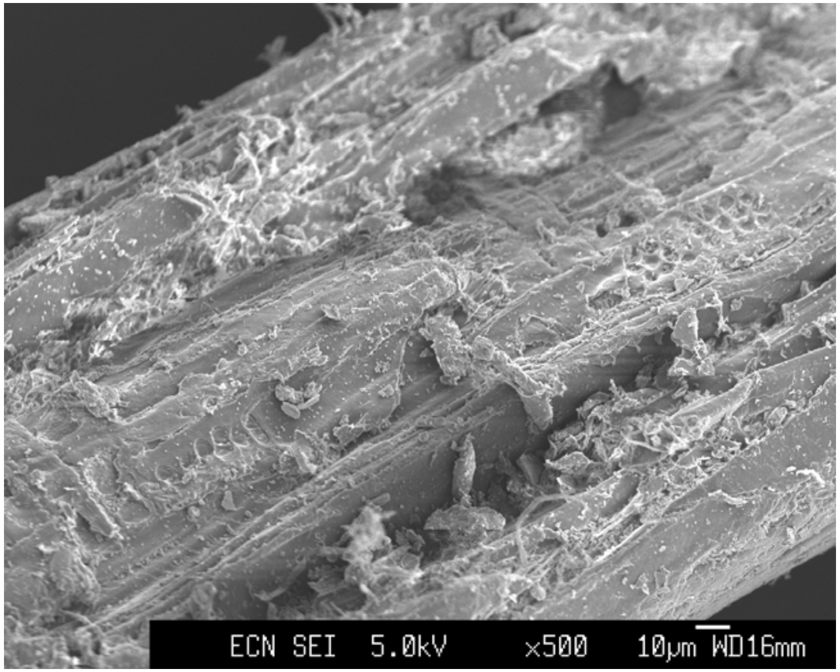
→ Focus today: delignification, lignin separation and lignin quality.

Experimental set-up



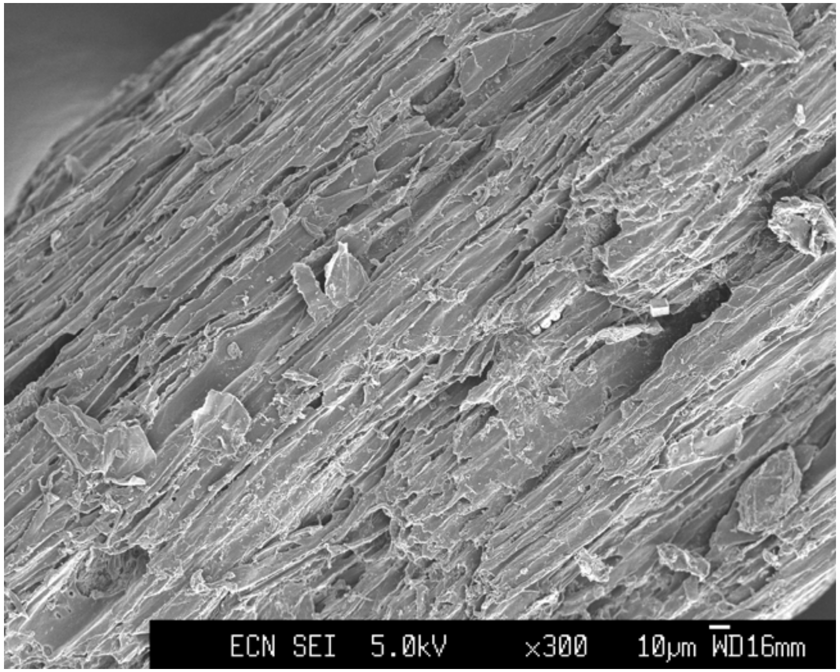
Scanning Electron Micrographs

Fresh willow



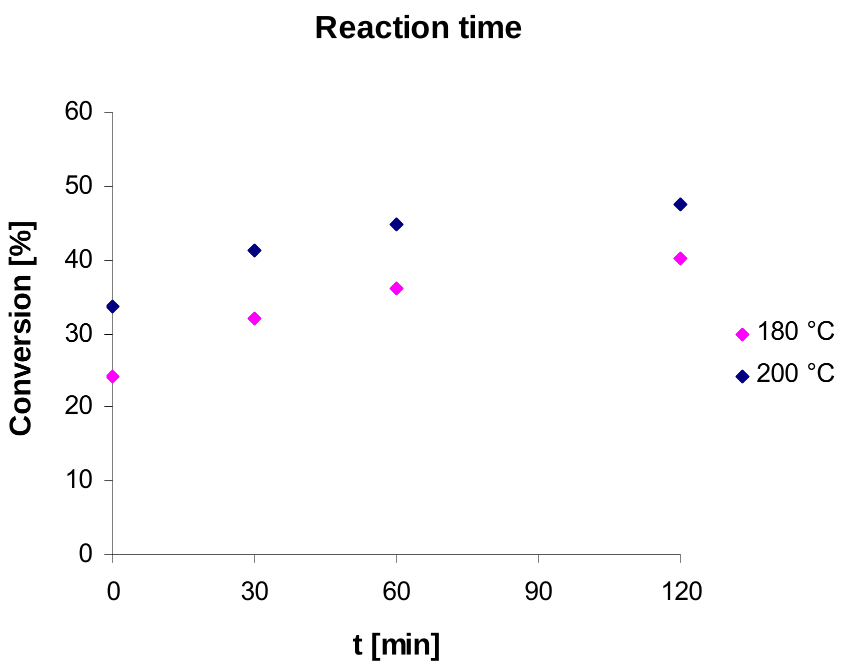
Pre-treated willow

190°C, 60 min, EtOH-H_2O 60:40 (w/w)

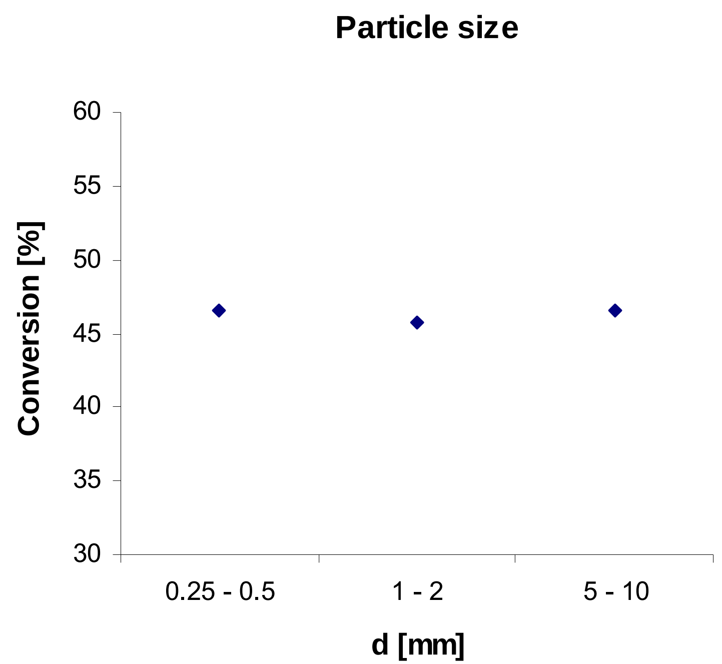


- Cellulose fibrous structure remains intact
- Extraction of hemicellulose and lignin
- More open structure → better access for enzymes

Conversion – Influence process conditions



Willow <0.5 mm, EtOH-H_2O 60:40 (w/w)



Willow, 200 °C, 60 min, EtOH-H_2O 60:40 (w/w)

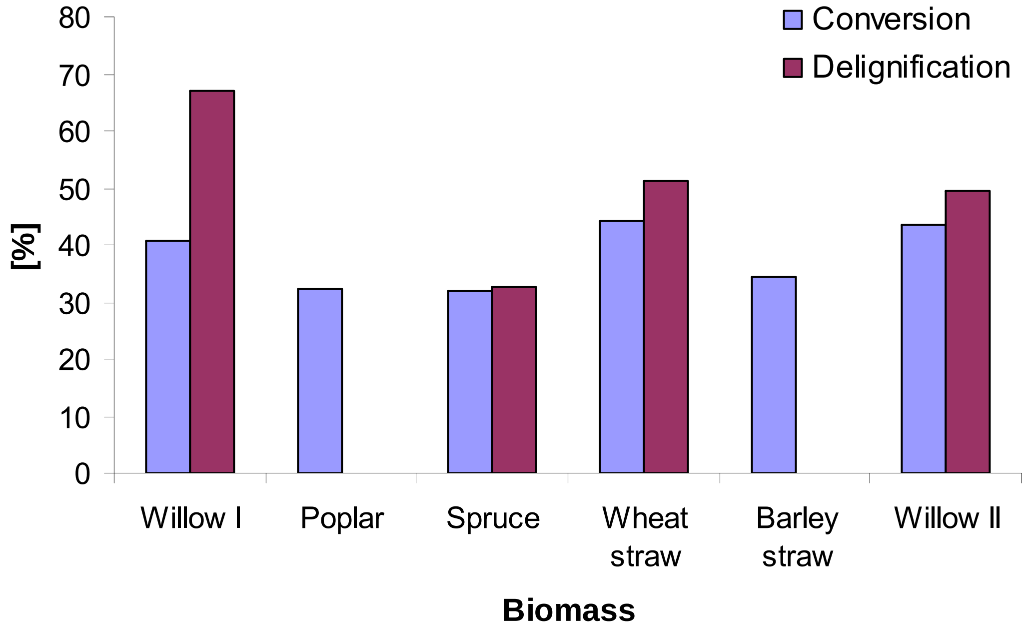
- Influence reaction parameters on conversion tested.
- No effect particle size (0.5-10 mm), L/S-ratio (7-20 L/kg) and stirring rate (100-500 rpm).
- Conversion dependent on biomass, residence time, temperature & solvent composition.

  → delignification.

Biomass type & batch

• Large differences in conversion and delignification between biomass types.

• Also between different batches significant differences occur.



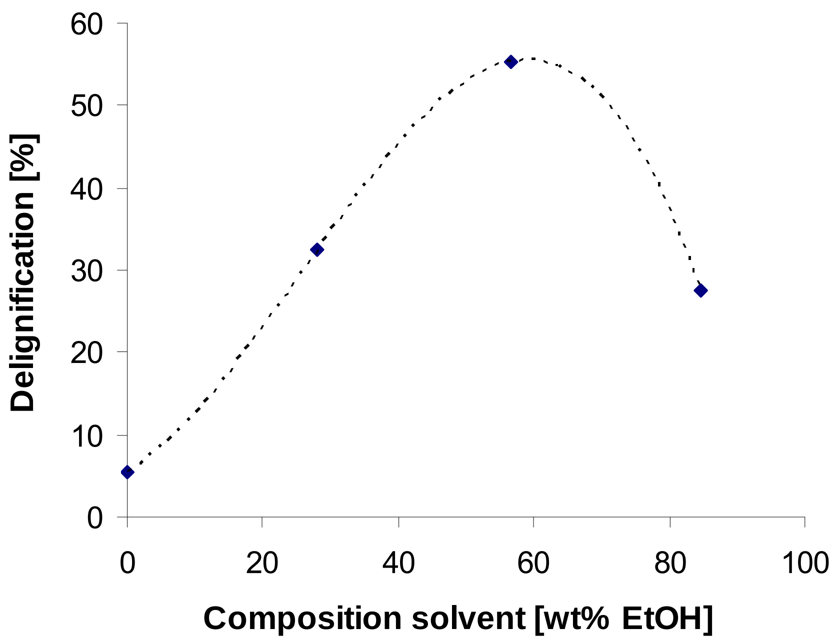
Fresh material (left), pre-treated (right):

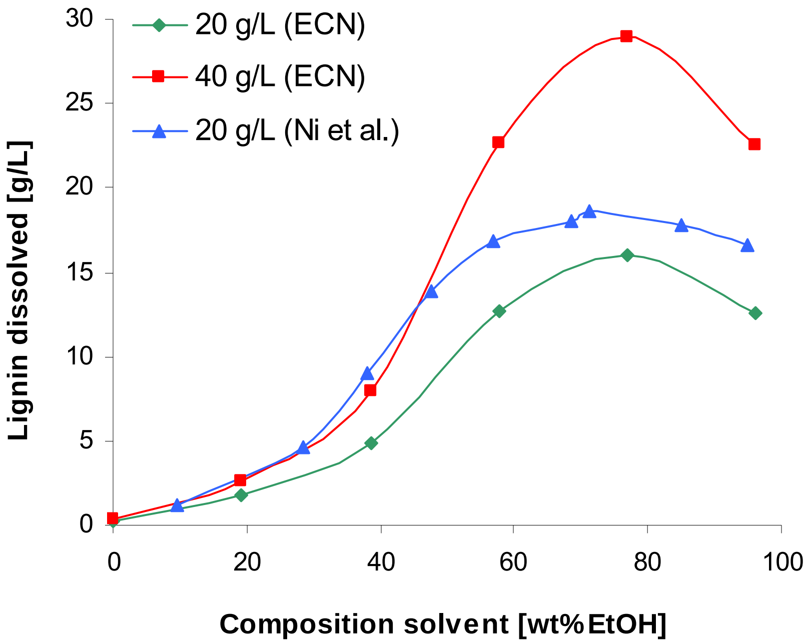
Poplar wood

Wheat straw

200°C, 60 min, EtOH-H_2O 60:40 (w/w)

Ethanol-water ratio





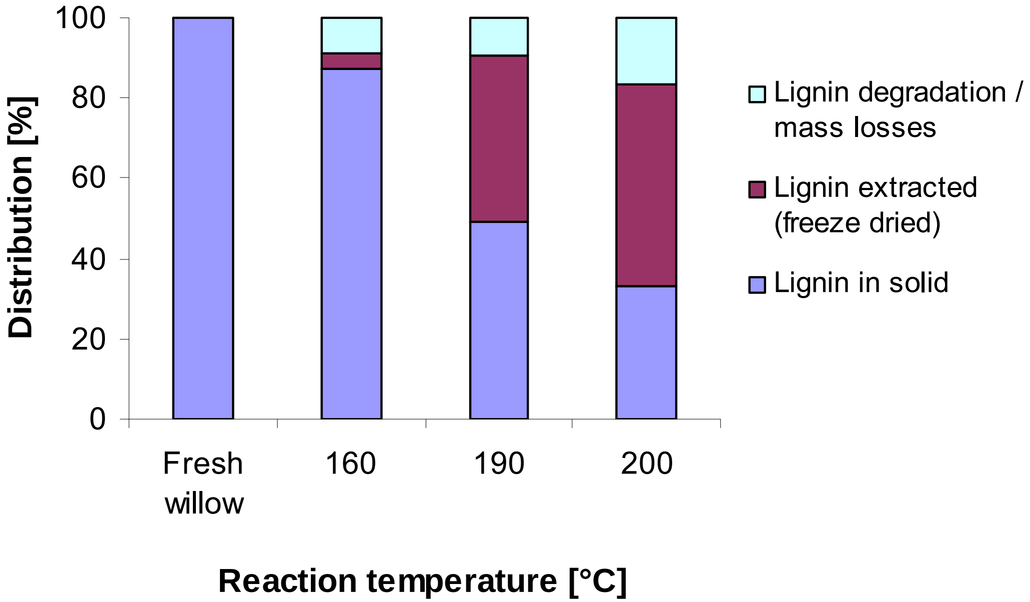
Willow <0.5 mm, 190°C, 60 min

- Ethanol-water ratio solvent major influence delignification (opt around 60 wt% EtOH).
- Solubility of lignin (fragments) dependent on solvent mixture composition.

Temperature

- Substantial delignification of willow wood achieved (max ±70%).

- Temperature key process parameter & degradation (inhibitor formation). Significant at ≥200°C (similar to hemicellulose hydrolysis).

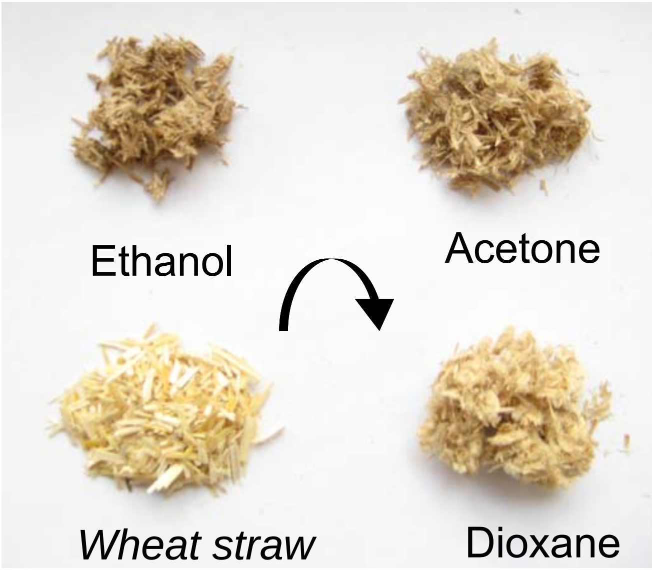


Willow <0.5 mm, EtOH-H_2O 60:40 (w/w), 60 min

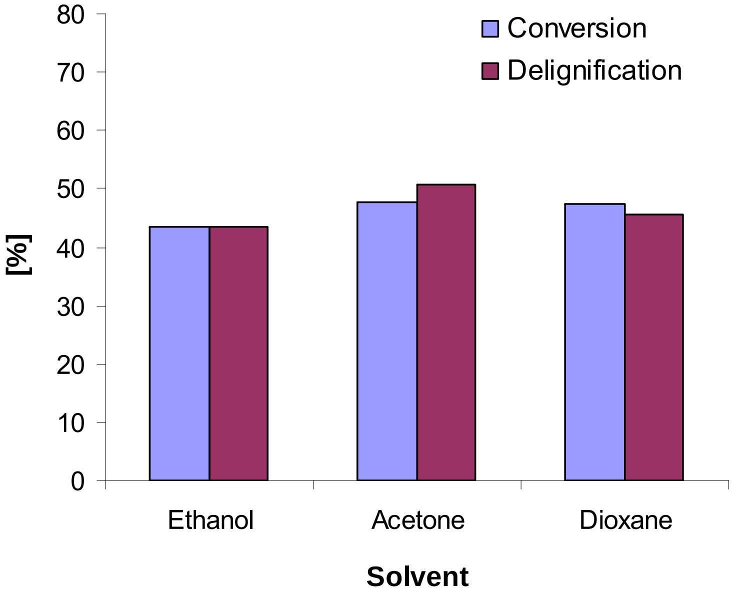
- Delignification at milder process conditions → alternative solvents & catalysts.

Alternative solvents

- Various solvents tested:
  - Good lignin solvents
  - Including acetone and dioxane
- Colour and structure of biomass indicative for enhanced delignification wheat straw.
- However, differences in conversion and delignification small.
- Lignin solubility in ethanol not limiting at conditions applied?

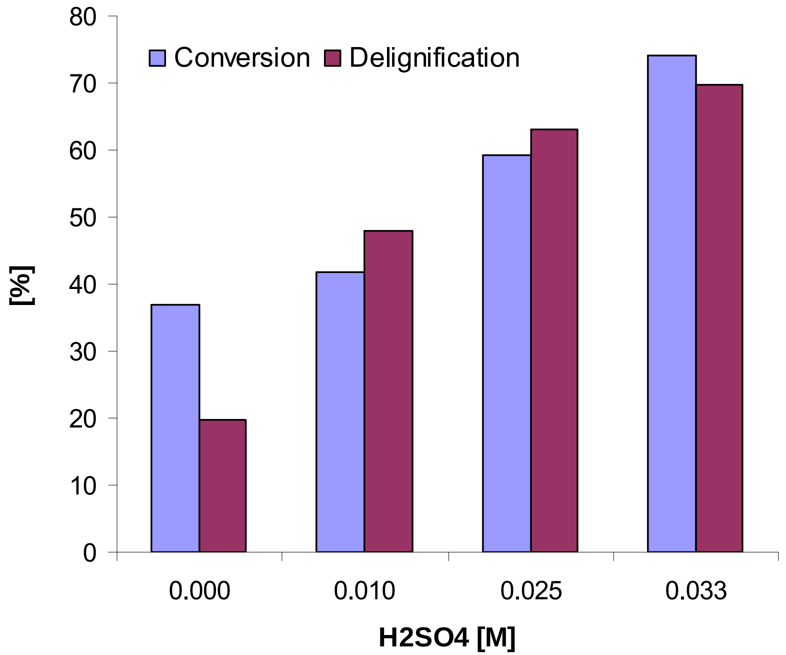


Wheat straw
60:40 wt%
solvent-water
200 °C
30 min



Catalysts

- Different acids, bases and salts were screened.
- Addition of H_2SO_4 resulted in improved delignification.
- Up to 2/3 of lignin extracted.
- Also higher hemicellulose hydrolysis and enzymatic degradability of cellulose.
- However, high formation of degradation products / inhibitors and higher costs.
- Performance at lower temperatures?



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

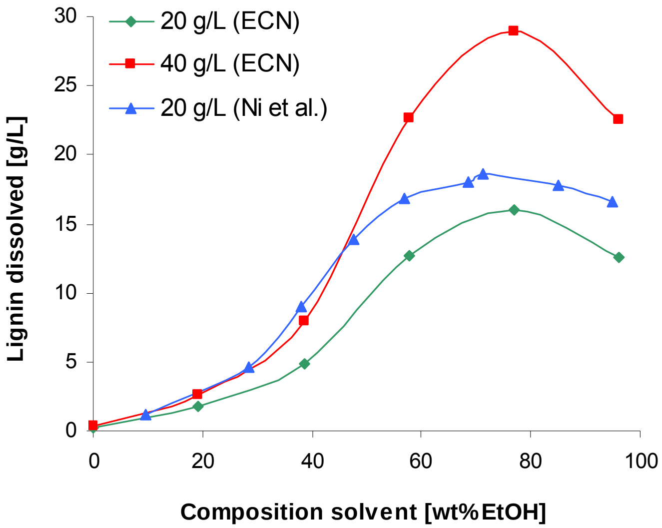
Lignin separation

- Adjustment solvent-water ratio.
- Current protocol based upon water addition.
- Future: solvent evaporation to improve energetic performance organosolv process.

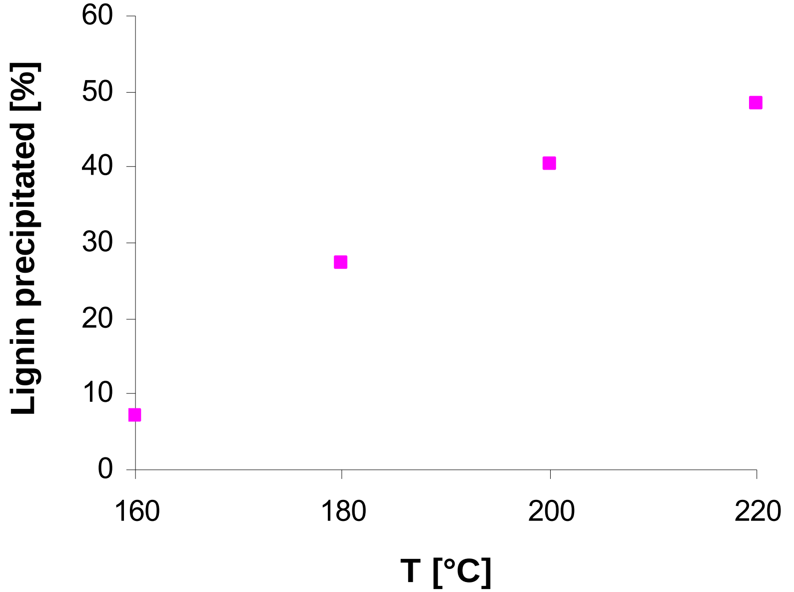
- Tested parameters for development protocol:
  - Amount of water
  - Temperature water
  - Stationary phase
  - Rate of addition (presence of air bubbles)
  - pH
  - Settling time

→ Rapid flocculation of lignin.

- Separation by centrifugation and decantation.



Lignin production



160, 180, 200, 220 °C

- Max lignin yield willow (based on lignin content feedstock):
  58% (200°C, 120min) or 68% with addition of H_2SO_4.
- Maxima comparable to delignification determined → almost all lignin separated from filtrate.
- Lignin appearance dependent on process conditions.

Lignin characterisation - I

- Lignin samples produced from willow, poplar and barley straw.
- Organosolv at 180 & 200 °C, 60 min, EtOH-H_2O 60:40 (w/w).
- Subsequent separation by water addition, flocculation & centrifugation.
- No washing applied.

- Elemental composition (200°C):

[wt%]	C	H	N	O	S
Willow	61.6	6.0	0.9	29.2	0.1
Poplar	63.1	5.9	0.1	29.1	0.0
Barley straw	63.8	6.2	0.7	28.0	0.1

- Biochemical composition (200 °C):

[wt%]	Lignin	Xylan	Other	Sum
Willow	87.9	2.3	1.3	91.5
Poplar	93.7	0.5	0.6	94.7
Barley straw	96.7	1.7	1.2	99.6

- Willow from lignin: first trial. Current precipitation protocol → >94wt% pure lignin.
- Lignin: relatively pure and sulphur-free (main contaminant xylan).

Lignin characterisation - II

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

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

- Mean molecular weight (MW) and polydispersity (PD):
  - Comparable with Alcell lignin.
  - Low relative to other types of lignins.

- Mean lignin particle size (volume-based): 61 µm (poplar) and 10 µm (wheat straw).

- ^{31}P-NMR:
  - SGH type lignins in different ratios.
  - Lower production temperature (180 instead 200°C): less carboxylic acid groups, more aliphatic OH groups (higher sugar content?).

→
- Purity and MW distribution indicate suitability of lignin for chemical production.
- Conversion tests of lignin into e.g. phenols to be performed.

Conclusions

- Delignification very dependent on biomass type, temperature and solvent mixture.
- Lignin produced seems relatively good feedstock for production of chemicals.
- Up to 2/3 lignin isolated with lignin precipitation protocol. However,
    - For delignification high temperature and/or H_2SO_4 use required.
    - For separation large amount of H_2O required.

Future research

- Optimisation organosolv process in order to produce lignin at milder process conditions.
- Development new lignin separation/precipitation protocol based upon evaporation.
    - Solvent integrity and recycling.
    - Development of lignin separation apparatus.
- Lignin conversion tests (see poster P. de Wild).

Thank you for your attention!

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This work is in part performed in the context of:

SIXTH FRAMEWORK PROGRAMME

SenterNovem EOS-LT