Ethanol-based Organosolv Pretreatment of Wheat Straw

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Process Optimization and Lignin Characterization

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- Mission:
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  - Solar energy
  - Wind energy
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ECN

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  - Amsterdam
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Organosolv

Lignocellulose Pretreatment

- Several physical-chemical pretreatment routes to promote enzymatic cellulose hydrolysis under development.

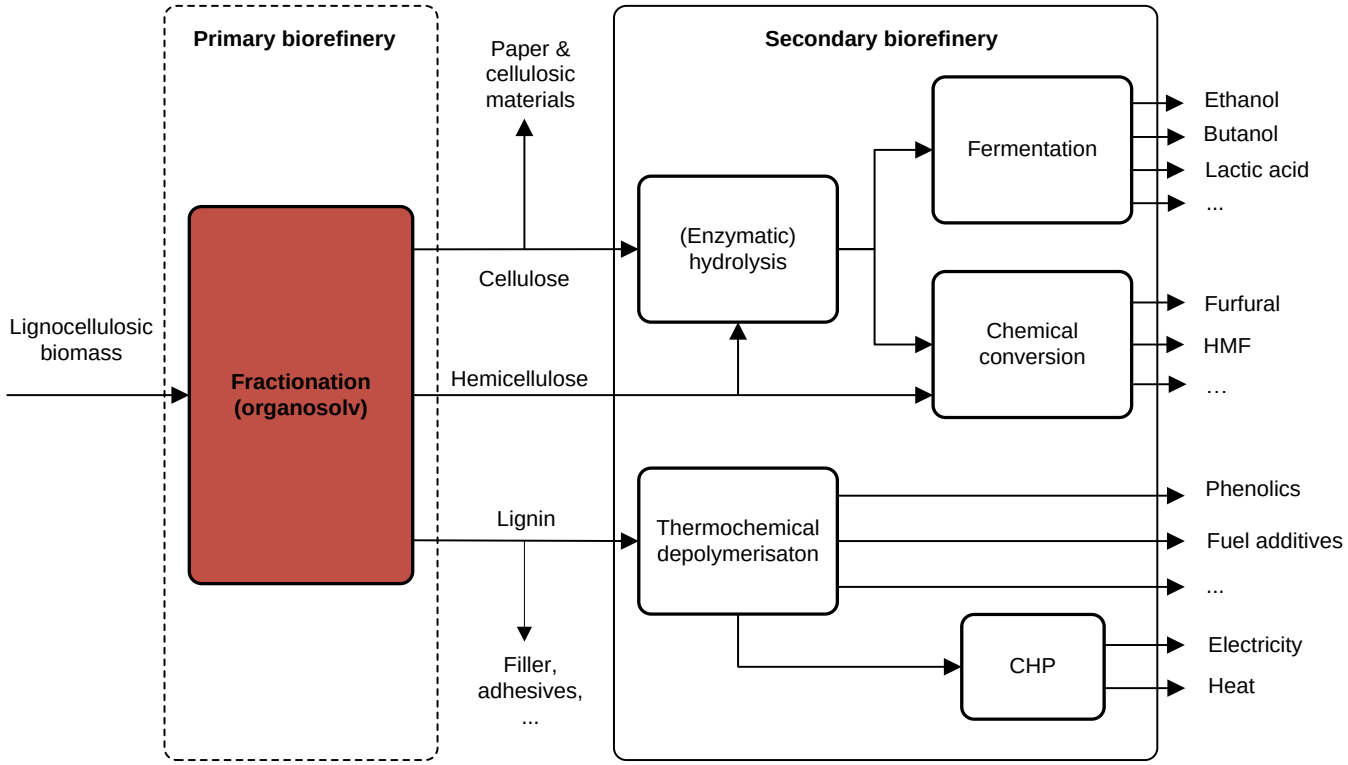
- Main pretreatment routes (pilot-scale):
  - (Dilute) acid pre-treatment.
  - Steam explosion.

- Routes effective for cellulose, however:
  - Lignin ends up in residue (with unconverted sugars, process chemicals, ash, …).
  - Residue generally only suitable for CHP.

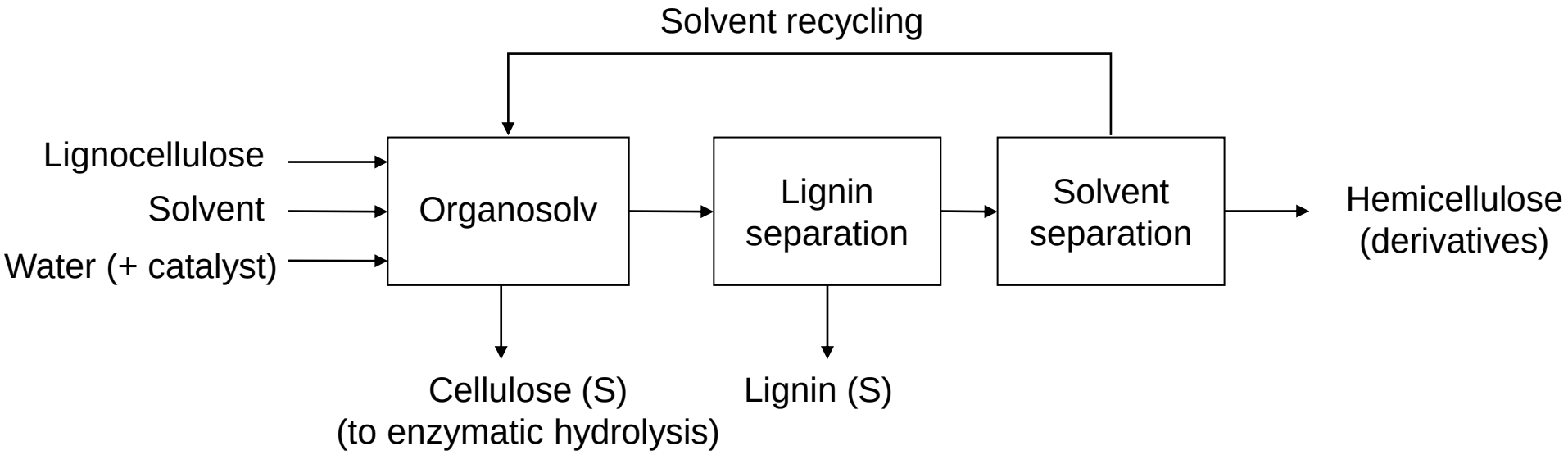
- Alternative:
  - Separation of lignin prior to enzymatic hydrolysis.
  - Preserving native chemical functionalities of lignin.

} Organosolv

Lignocellulose Biorefinery



Organosolv Process



- Solvents: aqueous ethanol, acetone, …
- Catalyst: H_2SO_4, ...
- Typical process conditions: 160-200 °C, 30-120 min.

General information: Reith et al. (2011) A step towards the development of a Biorefinery, NPT procestechnologie, 18(1), 26-28

Process Optimization Wheat Straw

Process Optimization Study

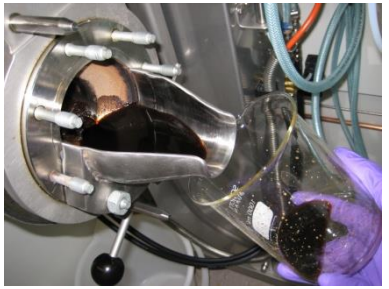
- EU-FP7 project BIOCORE:
  - Four feedstocks selected: wheat straw, birch, poplar and rice straw.
  - Focus of optimisation study: wheat straw.

- Wheat straw:
  - Origin: northern France.
  - Milled to <10mm and stored ambient-dry.
  - Composition: 10.2% extractives, 35.4% glucan, 19.8% xylan, 2.1% arabinan, 1.4% galactan, 17.6% lignin and 3.5% ash.

- Reference:
  - Wildschut et al. (2013) EtOH-based organosolv fractionation of wheat straw for the production of lignin and enzymatically digestible cellulose, Bioresour. Technol., 135, 58-66 .

Experimental

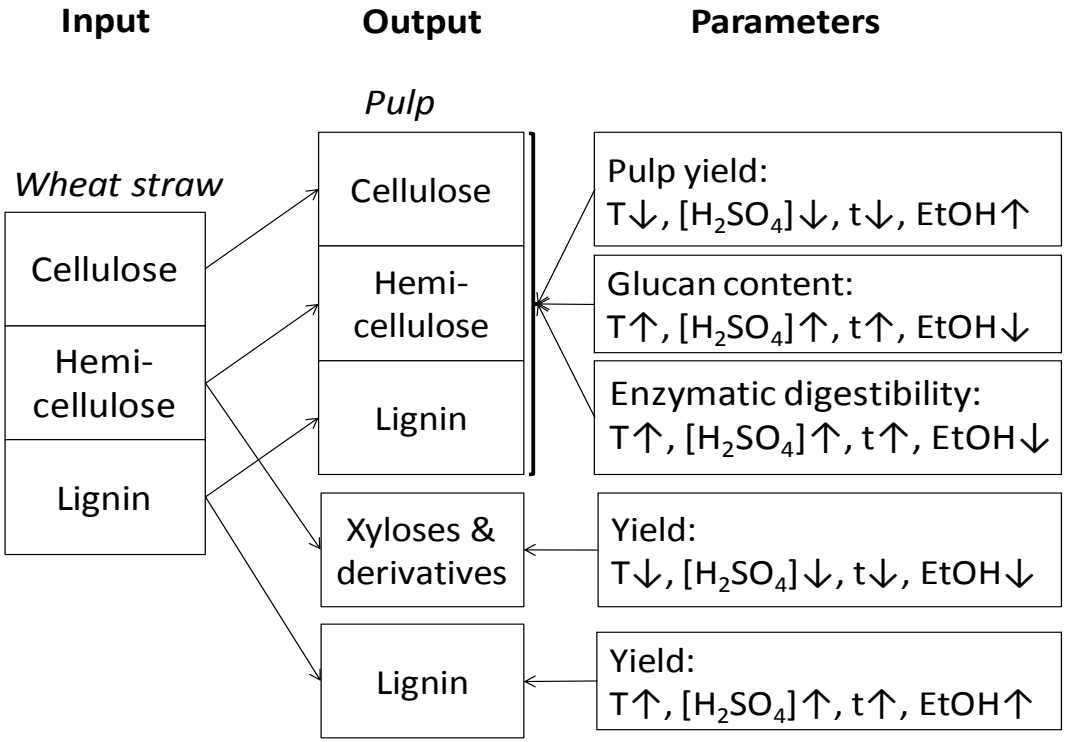
- Organosolv:
  - Batch autoclave reactor (0.5L).
  - Parameter screening:
    - Temperature (160-210 °C).
    - Ethanol concentration (50-80 % w/w aqueous ethanol).
    - Reaction time (60-120 min).
    - Catalyst dose (0-30 mM H_2SO_4).
  - Optimisation study:
    - 16 experiments with high/low for other parameters.



- Enzymatic hydrolysis:
  - NREL protocol.
  - Accellerase 1500 (DuPont Industrial Biosciences).
  - 20 FPU/g dw substrate, 3% w/v consistency, pH 4.8, 50 °C, 72h.

Optimization

- Based on process-product relations, optimization towards enzymatic digestibility.



	Autocatalytic	Catalytic
Process conditions	210 °C 90 min 50% w/w EtOH	190 °C 60 min 60% w/w EtOH 30 mM H_2SO_4
Enz. digestibility (%)	86	89
Delignification (%)	59	76
Lignin yield (%)	84	86
Xylan hydrolysis (%)	81	95

Lignin Characterization

Lignin Characterization Study

- Goal: influence organosolv process conditions → properties of lignins.

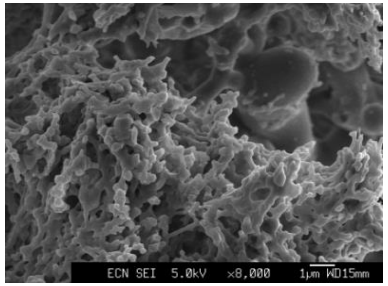
- 11 samples selected from parametric study on wheat straw:
  - Influence process parameters: T, t, [H_2SO_4] & EtOH:H_2O.
  - Optimum conditions: enzymatic hydrolysis & lignin yield.
  - Alcell lignin used as reference.

- Analyses performed:
  - Composition (NREL protocol LC biomass → purity, carbohydrates impurities).
  - Ash content (TGA).
  - Molecular Weight Distribution (alkaline SEC).
  - Functional groups (both titrations and 31P-NMR).
  - Tg (DSC).

Properties Organosolv Lignins

- Light brown to black (compacted) powder.

- High purity (>>90 wt%).
  - Main contaminant oligomeric xylose (hemicellulose).
  - Lignin sulphur (≤0.1 wt%) and ash free.

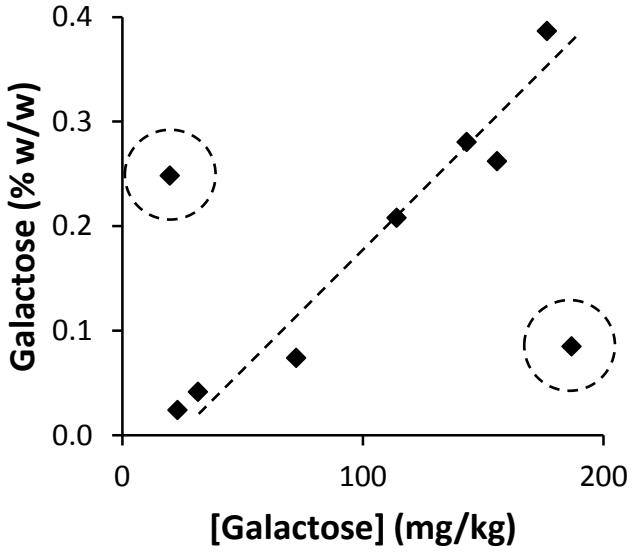


- Molecular weight:
  - Low average (2000-3500 g/mol).
  - Narrow MW distribution.

→ Organosolv lignin: promising properties for valorisation.

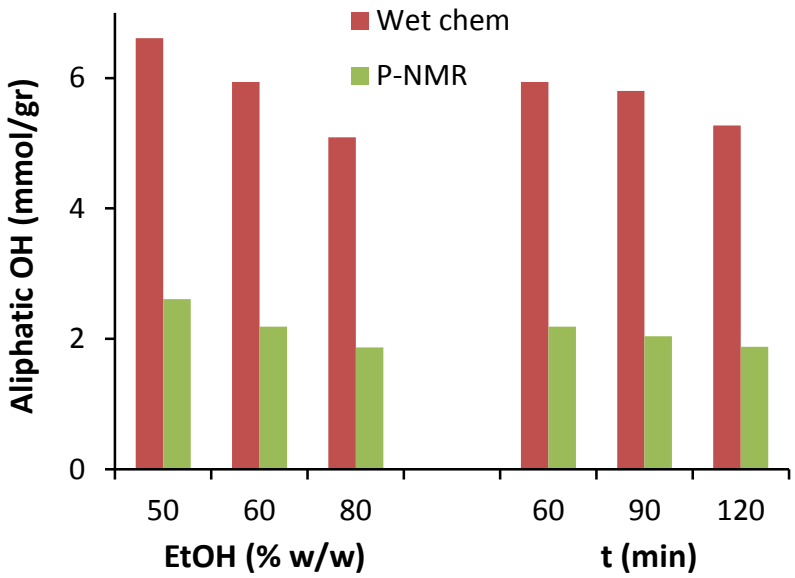
Carbohydrate Impurities

- Lignin powders:
  - Production by precipitation upon water dilution, centrifugation, decantation and drying.
  - Lignins used have not been washed.
- Correlation between 'total sugars in organosolv liquor' and 'carbohydrate impurities in lignin':
  - Carbohydrate impurities originate from adhering diluted organosolv liquor.
  - Not from LignoCarbohydrate Complexes (LCC).
- Deviation of the same two lignins from the correlation for each sugar:
  - Different process conditions (80% EtOH, 30 mM H_2SO_4).



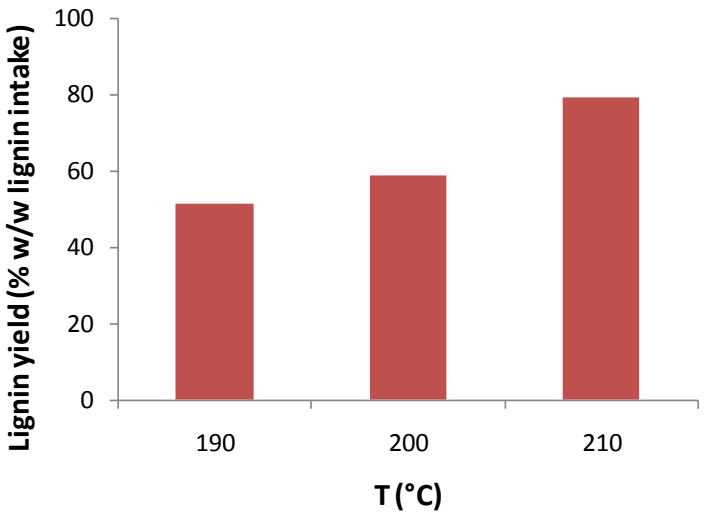
Analytical Challenges

- Large differences between functional groups determined by ^{31}P-NMR and wet chemistry methods.
  - Absolute values differ substantially, mostly trends are the same.
  - Reasons for discrepancies unclear.
- Difficulties in determining Tg in some samples.



Organosolv Process Temperature

- Increase delignification & lignin yield.
- Reduction of carbohydrate impurities.
- Reduction of functional groups:
  - More lignin condensation.
  - More pseudo-lignin formation (incl lignin-furfural condensation).



Lignin characteristics

T (°C)	AIL + ASL (% w/w)	Carbohydrates (% w/w)	OH phen+OH COOH (mmol/gr)
190	90.9	3.6	2.1
200	95.5	1.6	1.7
210	96.6	1.0	1.6

Ongoing and Future Work

- Lignin application tests with industrial partners.
- Construction bench-scale continuous organosolv reactor.
- Partnering for further technology development & commercialisation.

2007

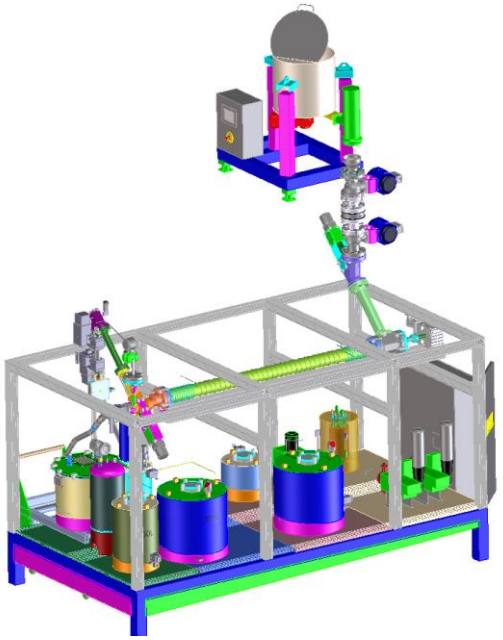
0.1 L

0.5 & 2 L

2010

20 L

2013



Continuous biomass pretreatment reactor

Thank you for your attention

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