Recent Advances in Organosolv Fractionation of Lignocellulosic Biomass

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Vienna, Austria

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Energy research Centre of the Netherlands (ECN)

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  - Solar energy
  - Wind energy
  - Policy studies
  - Environment & energy engineering

ECN
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- ~550 employees
- Locations:
  - *Petten (HQ)*
  - *Amsterdam*
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  - *Beijing*

Organosolv

Lignocellulose Pretreatment

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

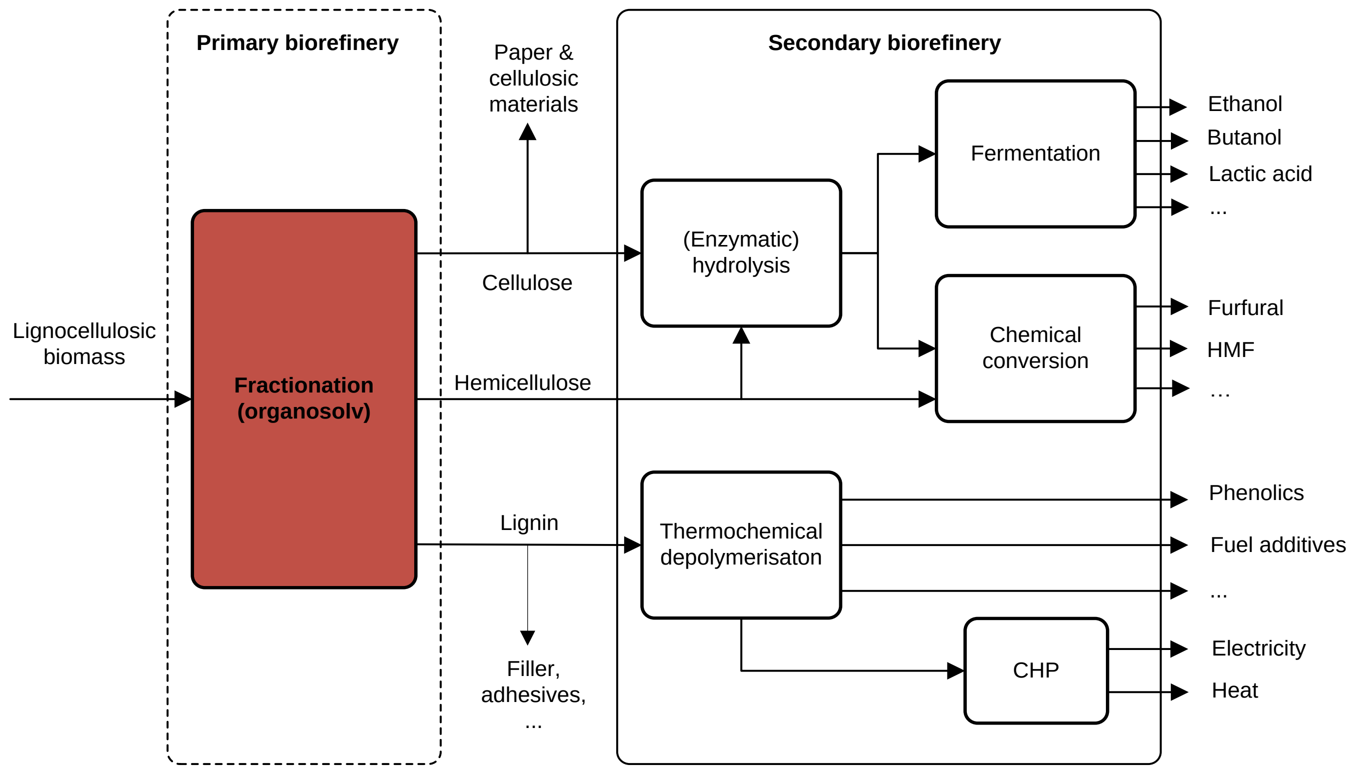
- Main pretreatment routes (demo-scale):
  - Mild acid pre-treatment.
  - Steam explosion.

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

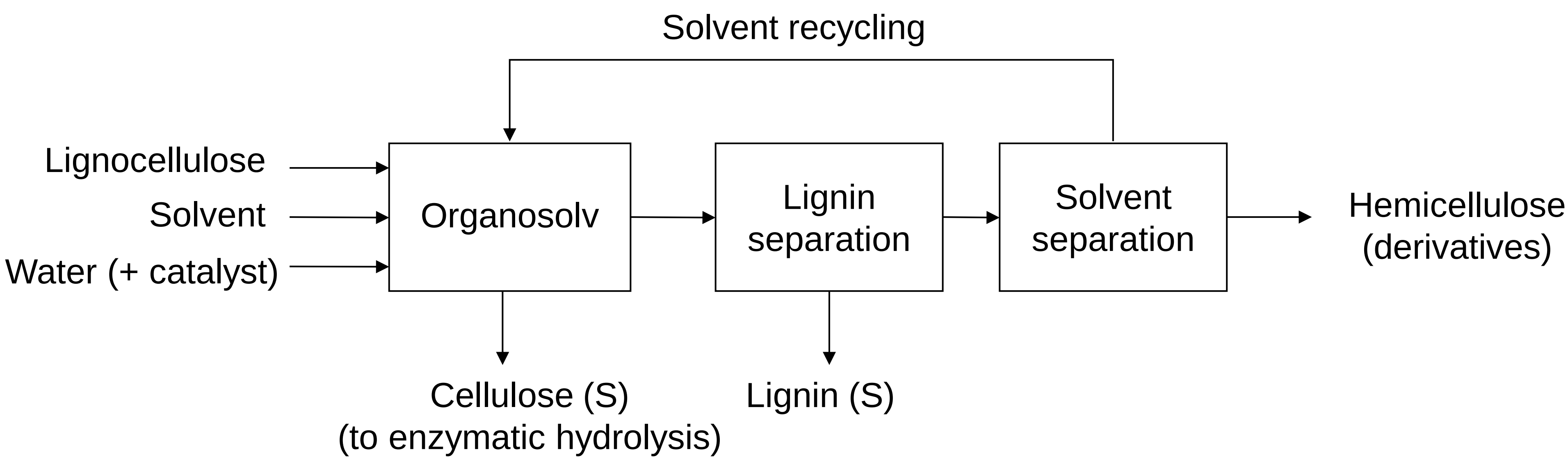
- Alternative:
  - Separation of lignin prior to enzymatic hydrolysis.
  - Using native chemical functionalities of lignin.

  } <u>Organosolv</u>

Lignocellulose Biorefinery



Organosolv Process

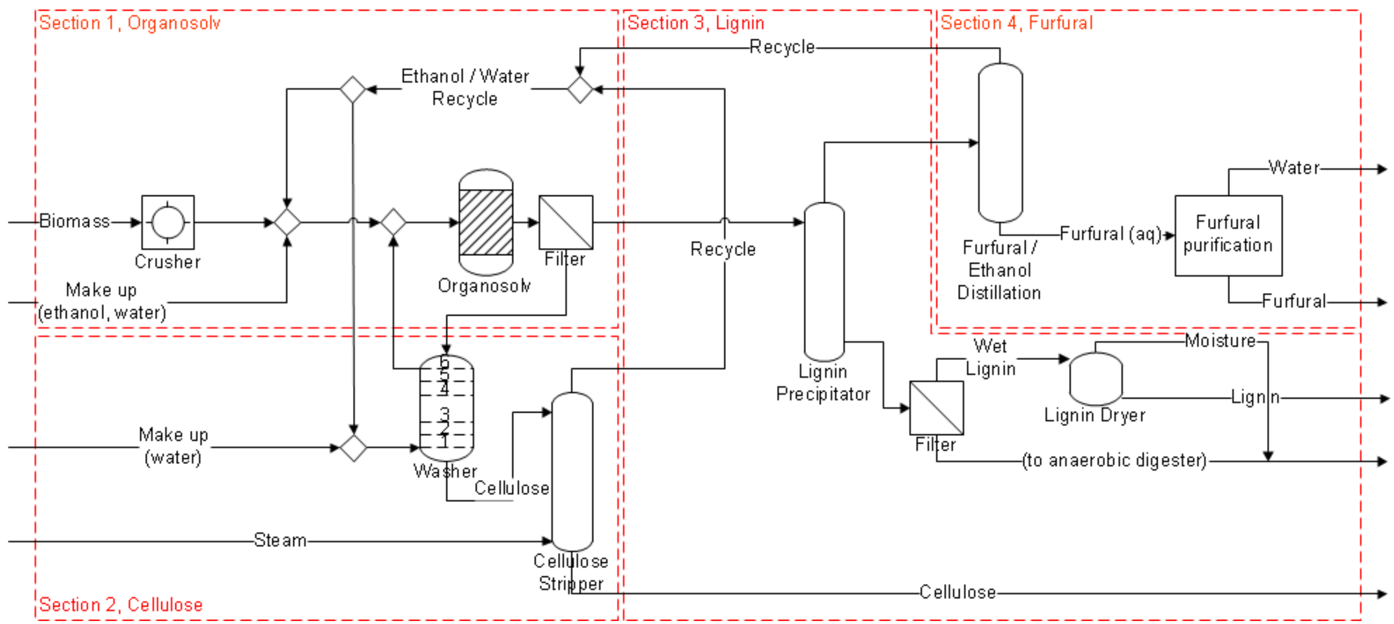


- Solvents: aqueous ethanol, acetone, ...
- Catalyst: H_2SO_4, ...
- Typical process conditions: 170-210 °C, 30-120 min.

Mild ketone-based organosolv

Solvent Recovery

- Techno-economic evaluation of ‘classical’ EtOH organosolv process.
- Recycling of organic solvent crucial for economy!
- Hardly any solvent mass balances in organosolv literature.



Van der Linden et al. (2012) Ethanol-based Organosolv Biorefineries… , Nordic Wood Biorefinery Conference, Helsinki (FIN).

Challenges Classical EtOH Organosolv

- Solvent losses:
  - Due to incomplete recycling:
    - Previous work shows conceptually energetic and economic feasibility.
  - Due to reactions:
    - Autocondensation of ethanol.
    - Reaction of ethanol with lignin.
    - Reaction of ethanol with hemicellulose sugars.

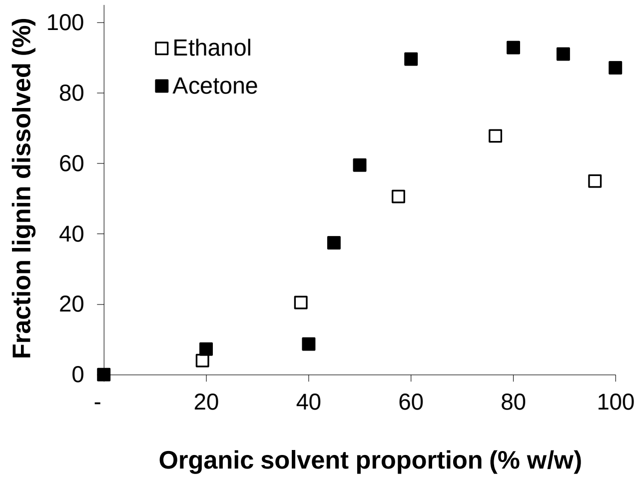
- Low yield of hemicellulose sugars:
  - Either substantial losses by furfural-lignin condensation due to high T.
  - Or formation of ethylated xylose. What to do with ethylated xylose?

➡ **Fractionation at low temperature (mild) using non-reacting solvent.**

Ketone-based Organosolv

- Ketones: excellent lignin solvents.

- Key features process:
  - Typical temperature: 190 → 140 °C.
  - Solvent: ethanol → acetone.
  - H_2SO_4 dose used for wheat straw: 20 → 60 mM.



Huijgen et al. (2010) Ind Eng Chem Res 49, 10132-40

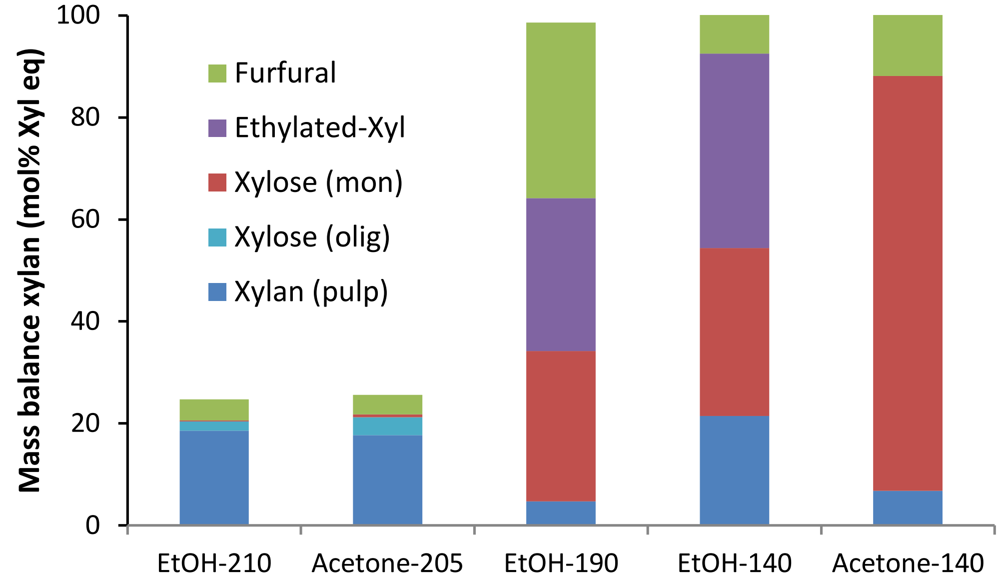
- Effective pulping at milder conditions:
  - High cellulose pulp purity & enzymatic digestibility.
  - Lignin: good yield and more native / less condensed.
  - Also feasible with longer chain ketones e.g. butanone.

- Self-condensation of acetone at conditions applied limited.

Smit, Grisel & Huijgen, patent WO 2015/009145.

Hemicellulose Products

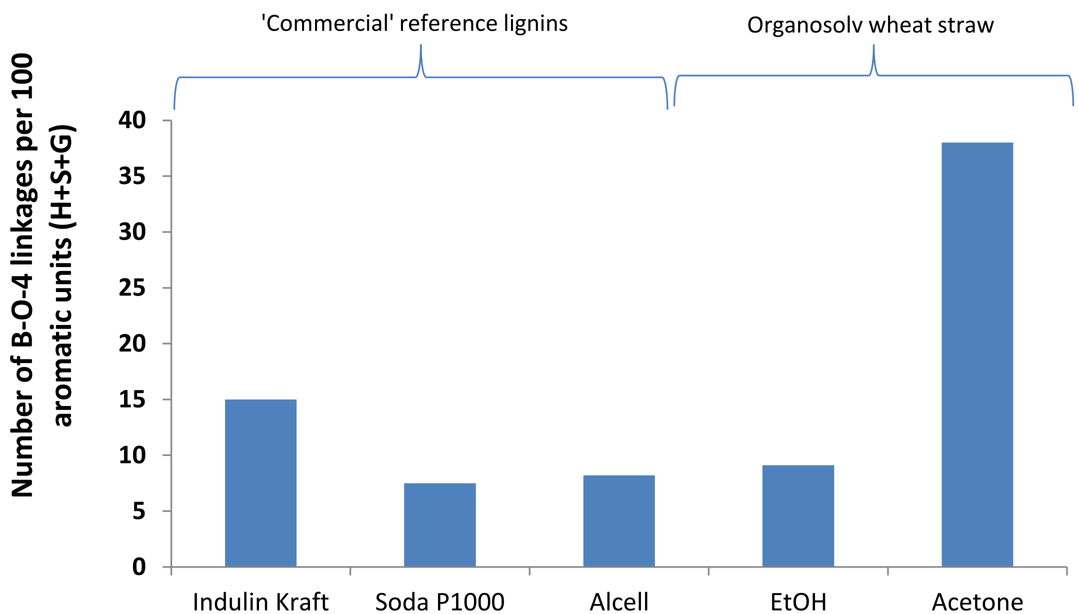
- Example: organosolv fractionation of wheat straw
- Autocatalytic, ≥ 200 °C:
  - HC products <10%.
- T↓ to 190 °C (30 mM H_2SO_4):
  - Roughly equal Xyl, Et-Xyl and furfural.
- T↓ to 140 °C (60 mM H_2SO_4):
  - Reduction of furfural formation.
- Acetone @140 °C (60 mM H_2SO_4):
  - Yield monomeric xylose: 81%



EtOH-190&210: Wildschut et al. (2013), Bioresource Technol 135, 58-66
Acetone-205: Huijgen et al. (2010) Ind Eng Chem Res 49, 10132-40

Remarkable Lignin Characteristics

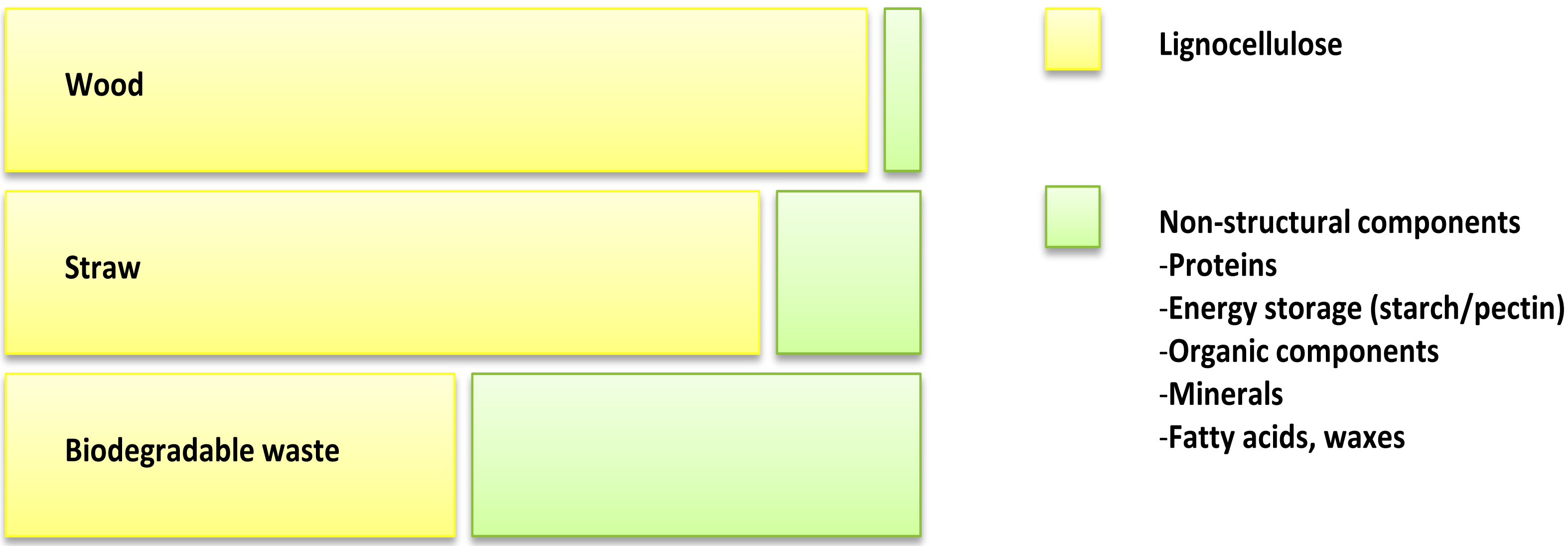
- High number β-O-4 ether linkages.
  - Suggests more native lignin.
  - Crucial for many chemocatalytic depolymerisation routes.



Constant et al., Multitechnique Comparative Characterisation of Various Technical Lignins Including by NMR and SEC Studies (in prep)

Pre-extractions

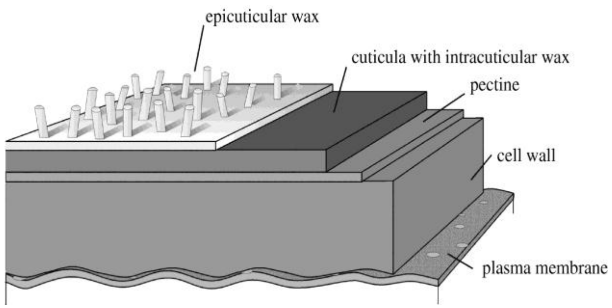
Pre-extractions



- Goal: Development of a feedstock-flexible organosolv biorefinery
  - Ability to process heterogeneous lignocellulosic biomass sources.
  - Reduction of compositional differences between various feedstocks.
  - Reduction of compositional variability between feedstock batches.

Pre-extractions

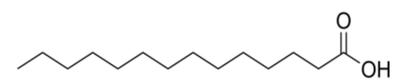
- Process:



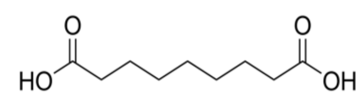
Plant epicuticular layer

1 → Water extraction:
Salts, proteins etc

2 → Organic extraction: fatty acids



resins

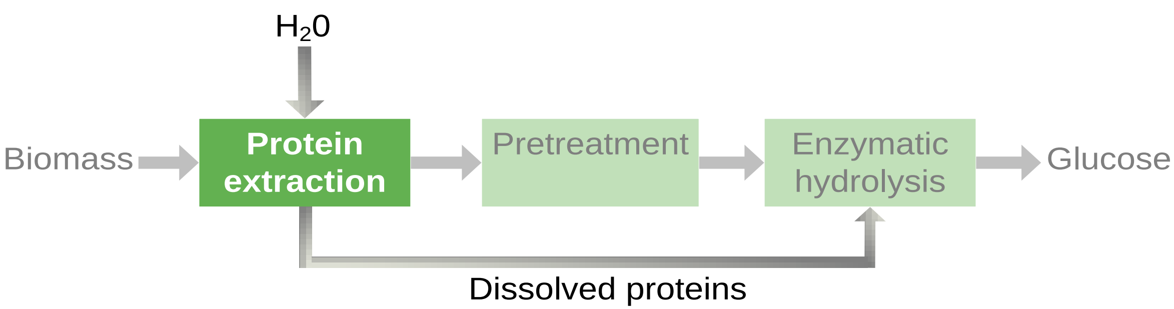


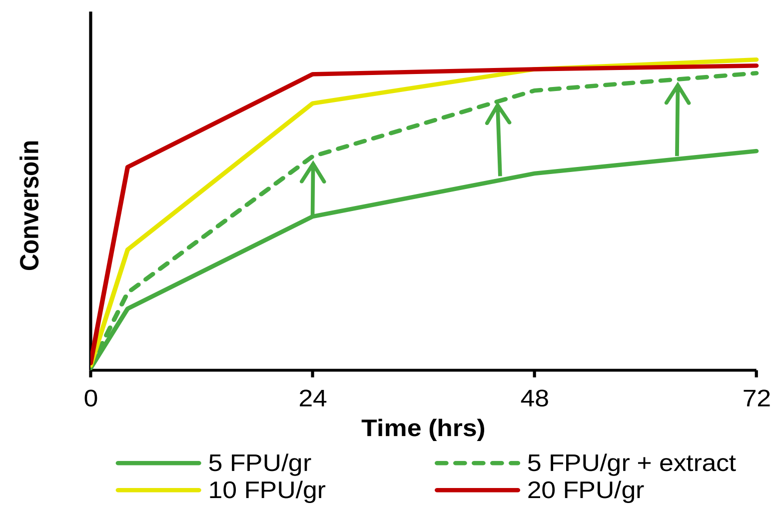
- Results:
  - Less condensed lignin (incl less fatty acids).
  - Higher cellulose pulp purity.
  - But also, better enzymatic digestibility!

Smit, Huijgen & Grisel, patent WO 2014/126471.

Cellulase Saver

- Method to reduce enzyme costs in production of 2G sugars.
  - Reducing enzyme binding to lignin.
- Also applicable to other pretreatments than organosolv.





Smit & Huijgen, patent WO 2014/098589.

Thank you for your attention

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