Organosolv-based Fractionation of Lignocellulosic Biomass for Co-Production of Fuels and Chemicals within a Biorefinery

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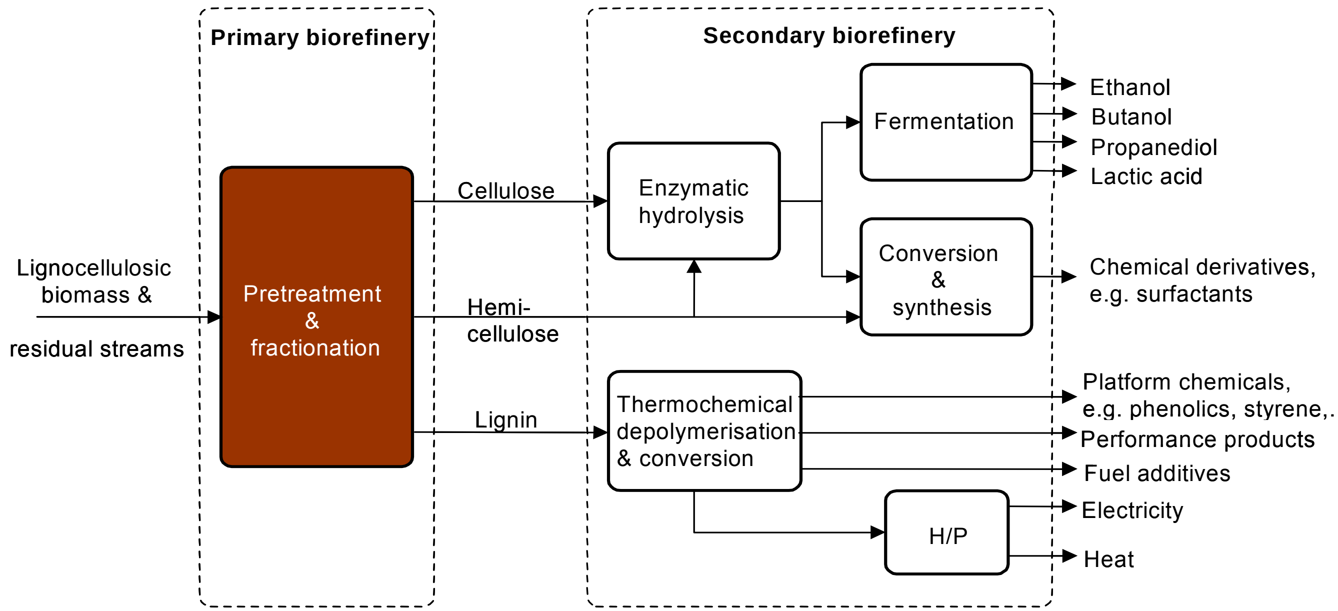
Contents

Biorefinery

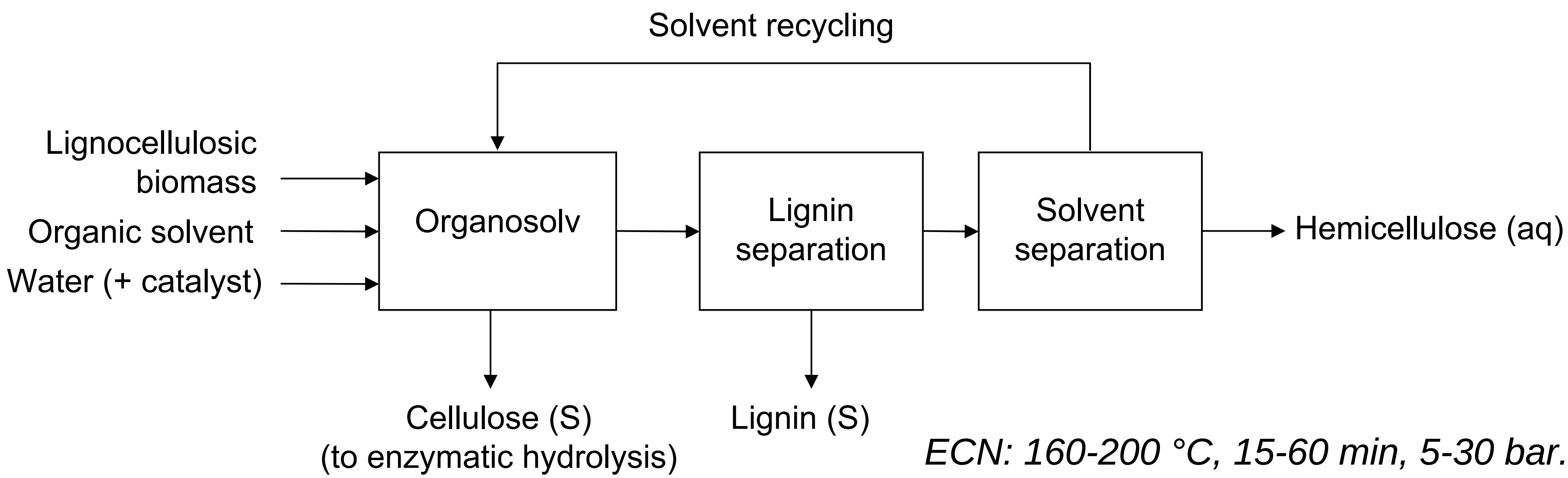
‘The sustainable processing of biomass into a spectrum of marketable products and energy’
(Definition IEA Bioenergy Task 42 on Biorefineries)



Goals primary biorefinery:

- Fractionation of lignocellulosic biomass into fractions with sufficient quality for production of (bio)chemicals (including lignin).
- Enhancement (enzymatic) degradability of cellulose to fermentable sugars.

Organosolv process

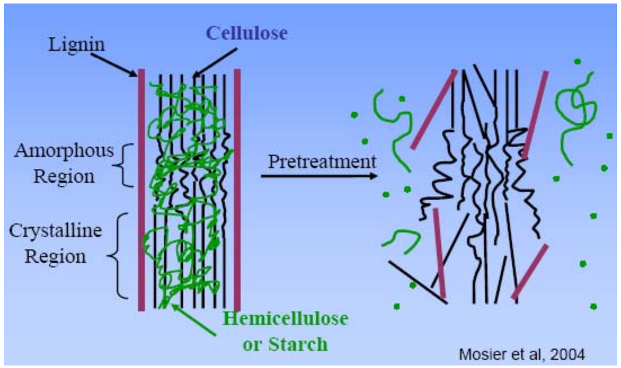


ECN: 160-200 °C, 15-60 min, 5-30 bar.
Organic solvent: ethanol.

History organosolv:

- Original idea: 1931 (Kleinert and von Tayenthal).
- Main developments 1970-90's as alternative pulping process, e.g.:
    - Alcell, ethanol-water, pilot plant 1988, currently Lignol (Canada).
    - Acetosolv etc, acetic and formic acid based, currently CIMV (France, Avidel process).
- R&D challenge: Applicability for biorefinery purposes?

Biomass pre-treatment methods



Various pre-treatment methods, e.g.:

- (Dilute) acid pre-treatment
- Alkaline pre-treatment
- Steam explosion
- Ammonia Fiber Explosion (AFEX)

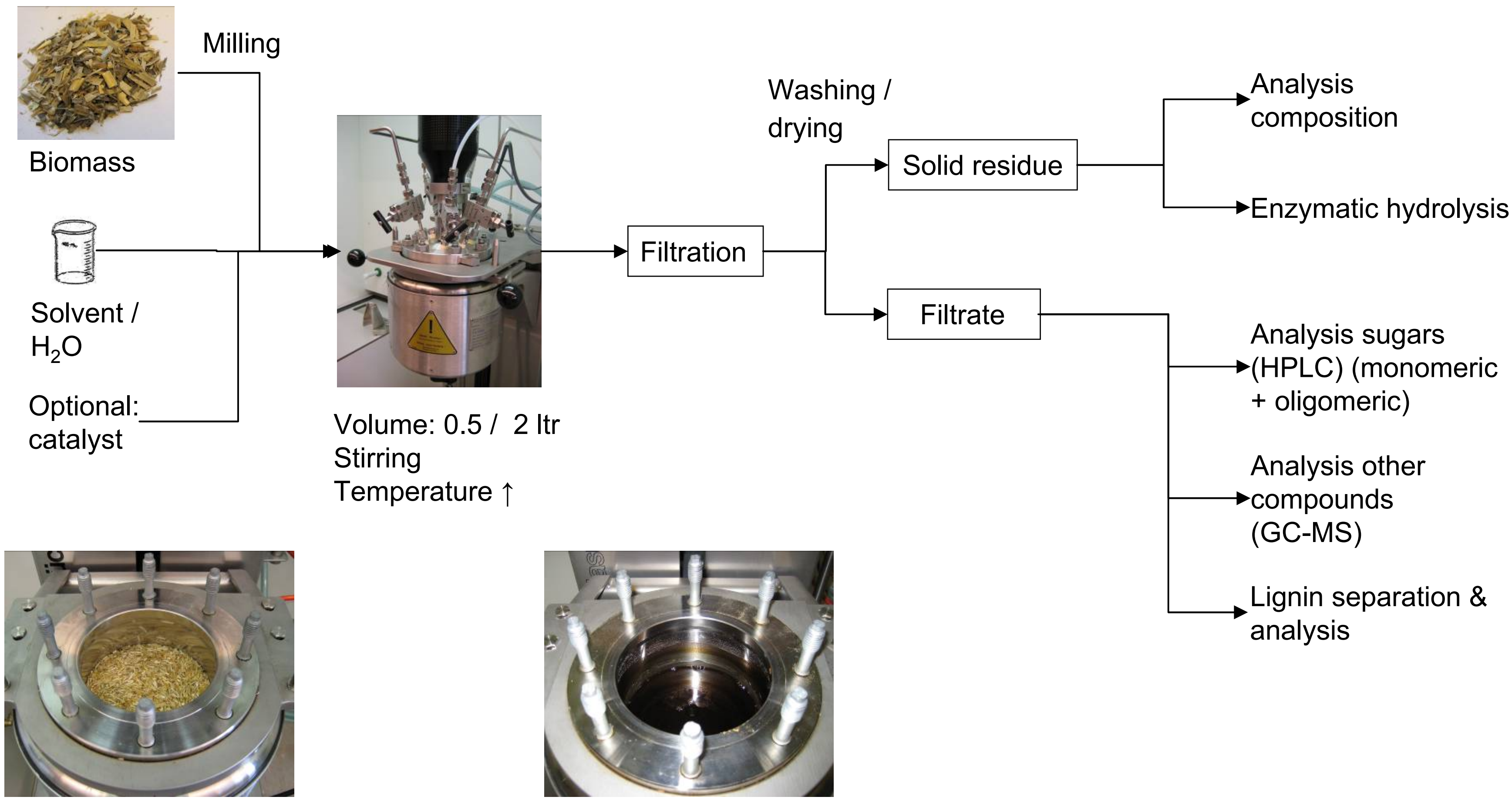
Advantages organosolv:

- Separation lignin before enzymatic hydrolysis & fermentation:
  - High-quality lignin (lignin other pretreatments generally only suitable for CHP).
  - Potentially lower enzyme consumption.
- Avoidance waste generation (due to neutralization).
- Minimization formation of fermentation inhibitors (e.g., furfural).

Disadvantages organosolv:

- Potentially higher costs and energy consumption due to use organic solvent (separation and recycling) and pressurized equipment.

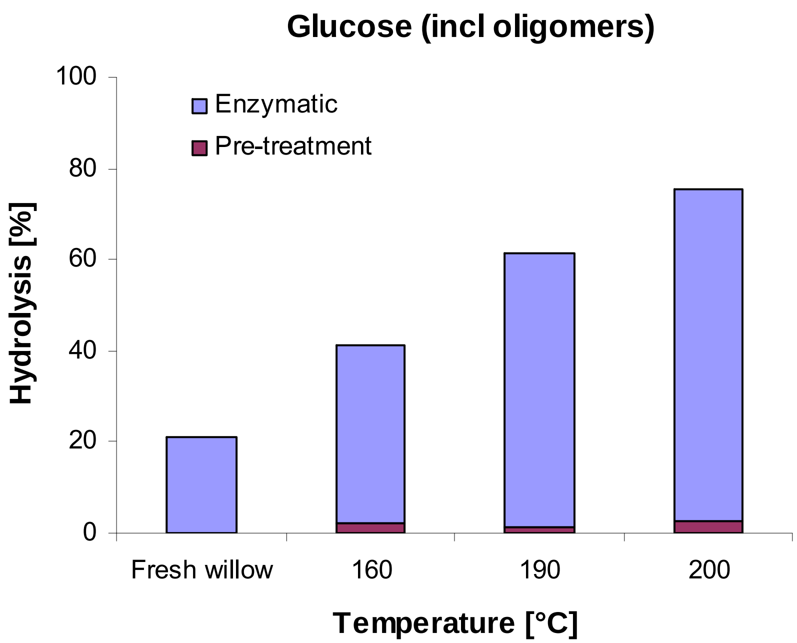
Experimental set-up lab-scale fractionation

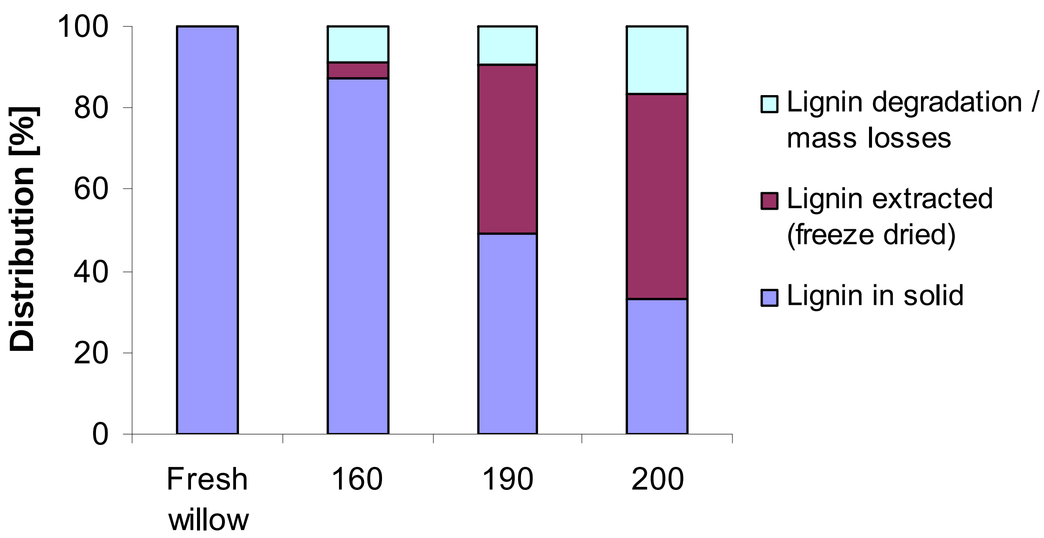


Process parameters

- Extensive parametric study based on willow wood.
- Effect on 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%) ←
  - Temperature (160-220 °C) ←
  - Reaction time (0-120 min) ←
  - Stirring rate (100-500 rpm)
  - Addition of H_2SO_4 as catalyst (0-0.033 M) ←
- Results presented at RRB4.
- Organosolv probably not mass-transfer limited (within ranges process conditions tested).

Reaction temperature





- Cellulose hydrolysis during pre-treatment negligible.
- Large enhancement of enzymatic hydrolysis cellulose (max ±75%).
- Substantial delignification of willow wood achieved (max ±70%).
- Degradation of sugars and lignin substantial at ≥200°C.

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

Types of biomass

• Effectiveness organosolv strongly dependent on type of biomass.

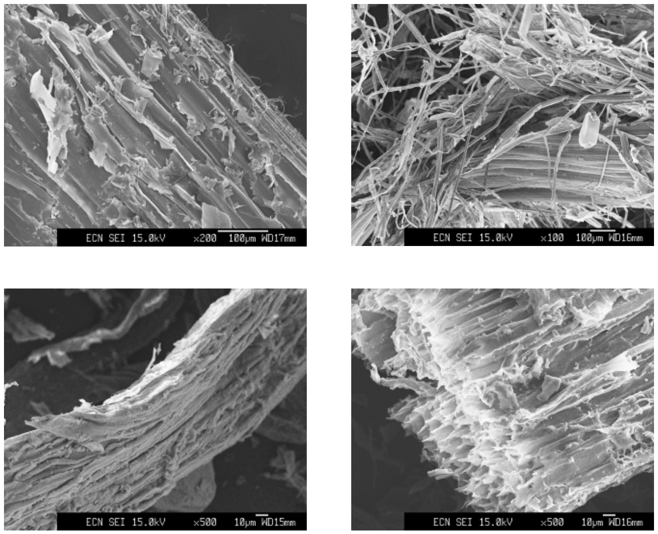
• Organosolv less effective for softwoods and (more dense) hardwoods.

• Good pre-treatment of some hardwoods and straws (focus ECN).

Fresh | Pre-treated

`Straw

Hardwood



Biomass	Pulp yield (dw%)	Xylan hydrolysis (%)	Delignification (%)	Enzymatic degradability (% cellulose feedstock)
Barley straw	51	80	57	92
Wheat straw	62	45	55	60
Willow	66	50	64	71
Poplar	71	28	ND	39
Spruce	73	NA	33	ND

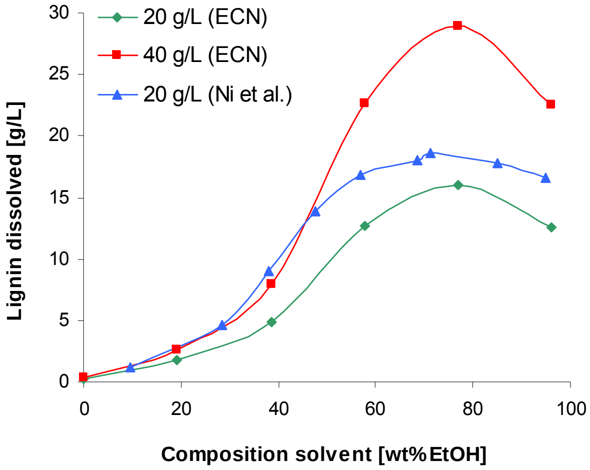
200°C
60 min
EtOH-H_2O 60:40 (w/w)

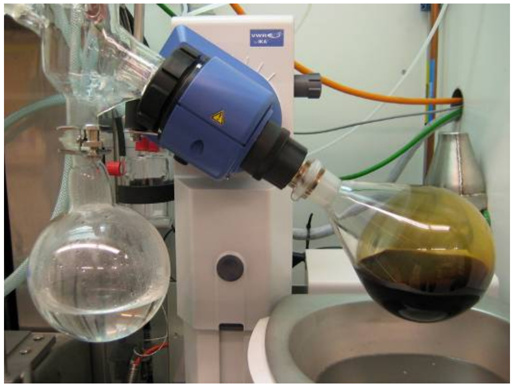
Lignin separation from organosolv filtrate

• Separation by adjusting ethanol-water ratio.

• Lab protocol developed based upon water addition
→ rapid & efficient separation of lignin from filtrate.

• Process simulations: large additional water stream detrimental for energy consumption process.





• Alternative: ethanol evaporation.

• 100% ethanol evaporation not feasible because of structural changes lignin.

• Partial evaporation followed by water addition
→ factor 4 reduction of water consumption.

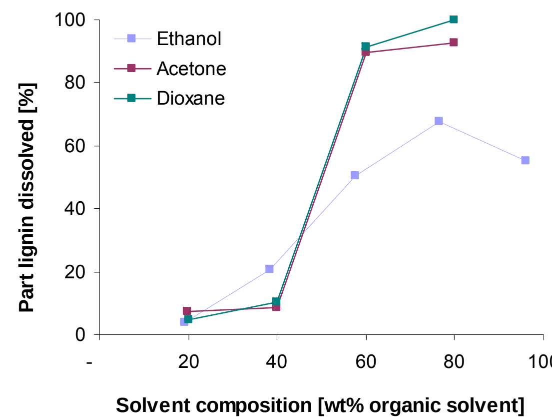
Lignin characterisation

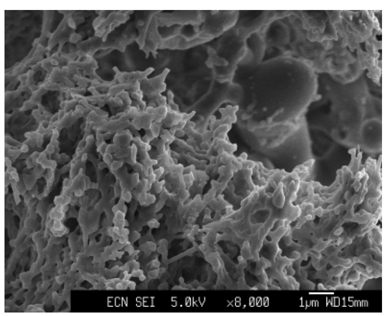
• Lignin: light brown to black (compacted) powder.
• Colour and structure dependent on process conditions organosolv, biomass type and contaminants.

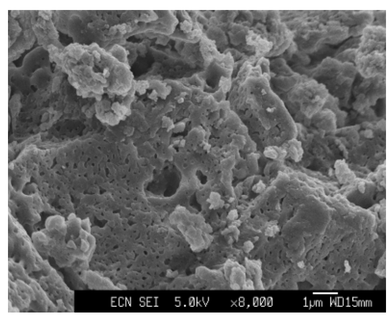
• Lignin relatively pure (88-97 wt% without washing).
• Main contaminant xylan (hemicellulose).
• Purity even higher after washing (Alcell lignin >99%).
• Lignin sulphur- and ash-free (max 0.1 wt% S).

• Solubility: H_2O (none), ethanol & acetone (good).

160, 180, 200, 220 °C







Organosolv lignin

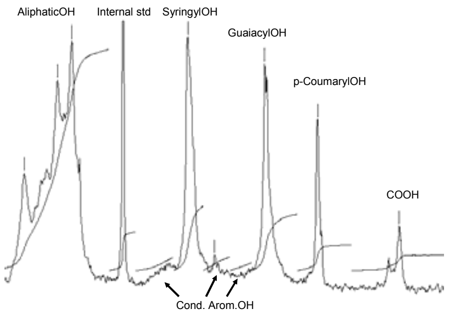
Lignin characterisation - II

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

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

- ^{31}P-NMR:
  - Identification of functional groups.
  - SGH type lignins in different ratios depending on feedstock.

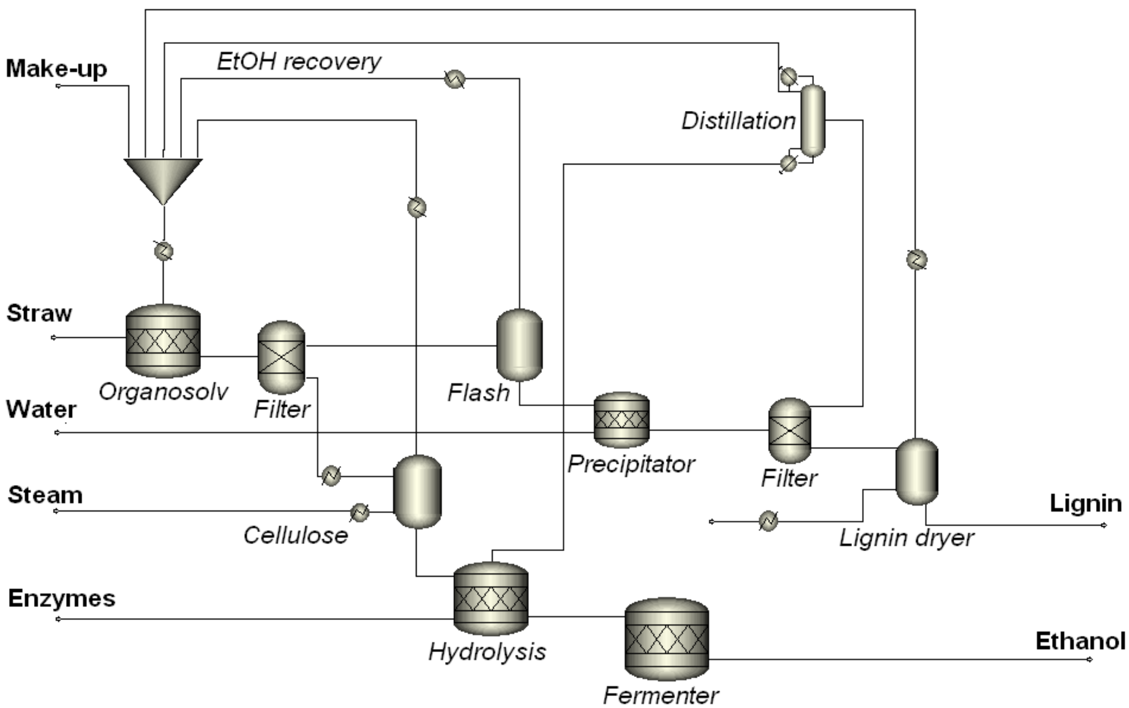
- Characterisation indicates suitability organosolv lignin as feedstock for chemical production.



- Commercial application routes of lignin in general large challenge.
- Conversion tests of ECN organosolv lignin underway.
- Main focus at ECN on lignin pyrolysis & catalytic conversion to produce phenol(ics).

Simulation organosolv process

- Preliminary results.
- Process design made in ASPEN → determination of streams and energy consumption.
- Feedstock: wheat straw.
- Process: 200 °C, 60 min, EtOH:H_2O 60:40, 5 L/kg.



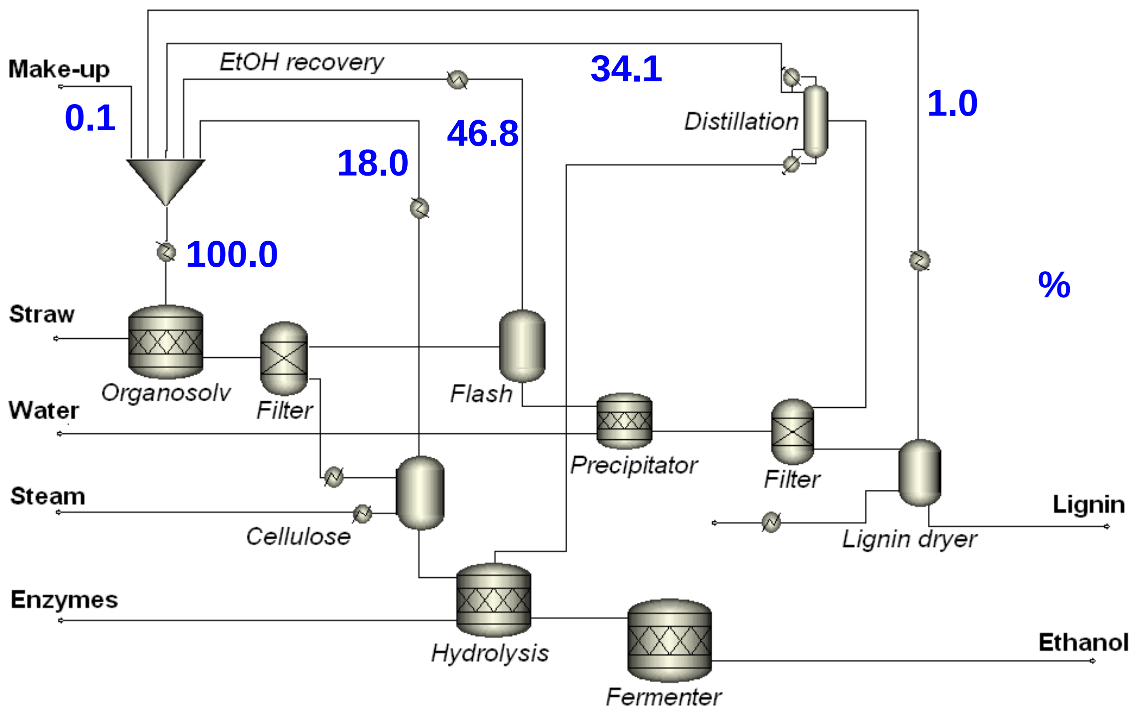
Recycling:

- 1 ton wheat straw → 0.32 ton EtOH (maximum).
- Solvent: 2.7 ton EtOH/ton straw.
- Recycling degree 99% → 8% EtOH production loss.
- Recycling degree >99% required!

Ethanol mass balance

- Recycling degree ethanol set at 99.9%.
- Separation and recycling of ethanol present in cellulose and lignin required!

- Solvent = product!
- Ethanol in cellulose and hemicellulose streams not directly lost.
- Recycling required to avoid product inhibition during fermentation.
- Recycling degree might be slightly lowered to save costs.



Energy consumption

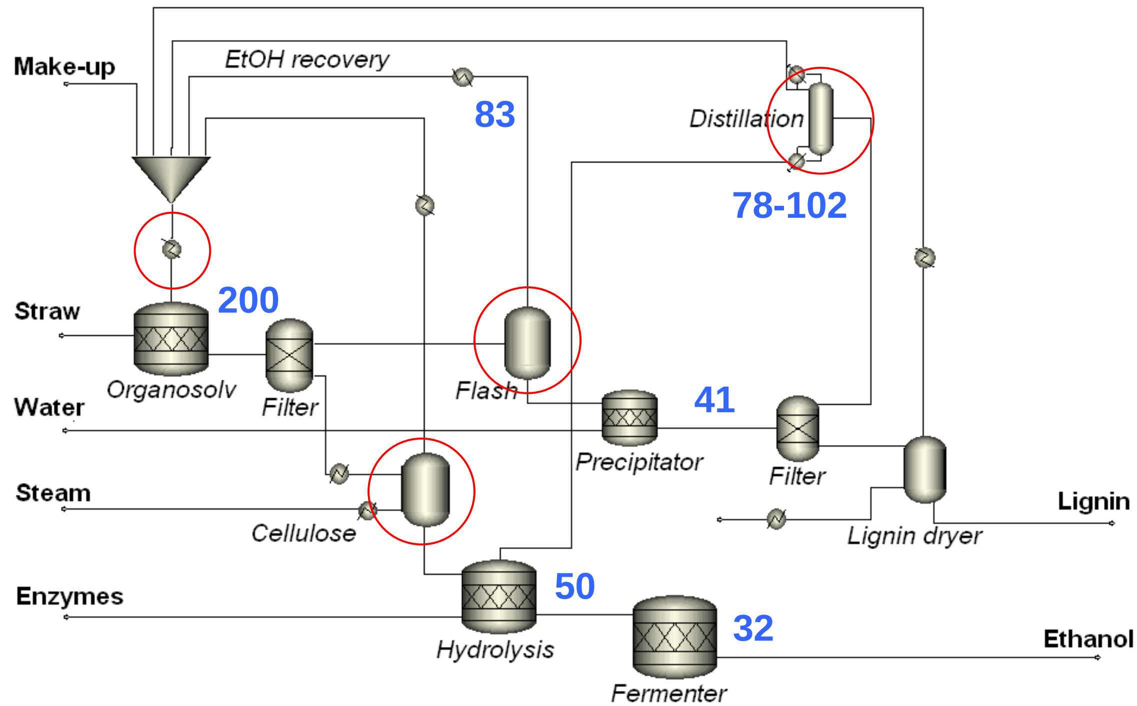
• Large differences in process temperatures.

• Major energy consumers:

- Ethanol separation for recycling.
- Heating feed + recycle stream.

• Heat flows significant compared to energy content ethanol produced.

→ Next step: heat integration.



Temperatures (°C)

Conclusions

- Ethanol-based organosolv able to fractionate lignocellulosic biomass.
- Enzymatic hydrolysis cellulose improved substantially.
- Efficient separation of high-quality lignin.
- Characterization lignin: promising properties for conversion to chemicals.
- Recycling organic solvent and heat integration crucial process elements.

Future research

- Development continuous organosolv reactor.
- Solvent integrity and recycling.
- Lignin conversion tests.
- Further development process simulations:
  - Heat integration organosolv plant.
  - Investment and operating costs.

ECN

Thank you for your attention!

More information:
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www.ecn.nl/bkm/

This work is in part performed in the context of:

BIOSYNERGY

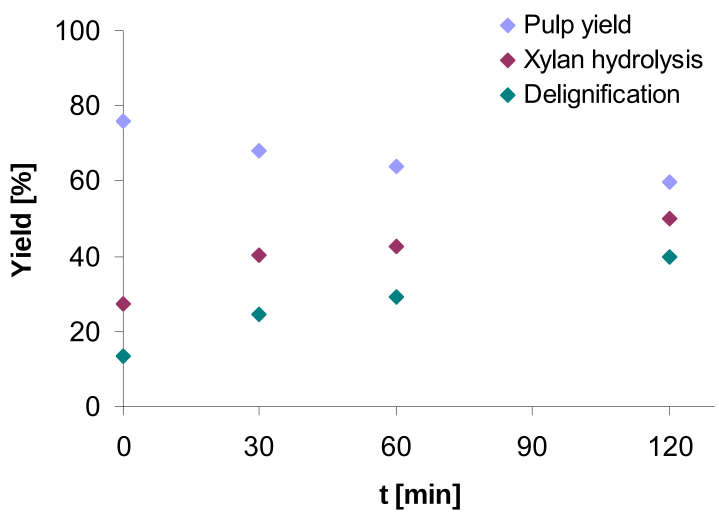
SIXTH FRAMEWORK PROGRAMME

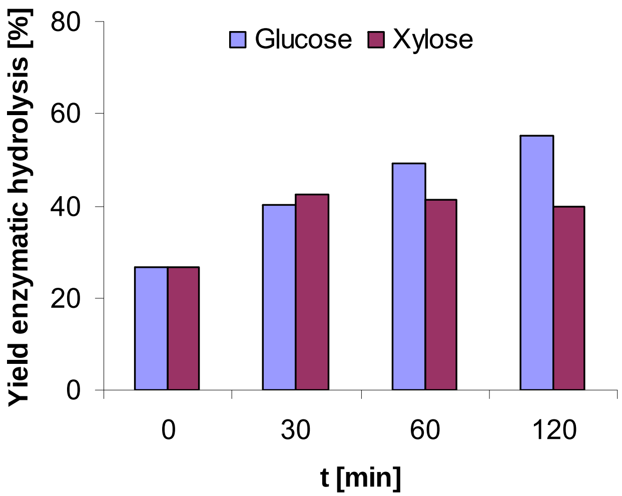
LignoValue

SenterNovem EOS-LT

See also other BioSynergy presentations by Gianluca Marcotullio (session 6B) and Paulien Harmsen (session 7B).

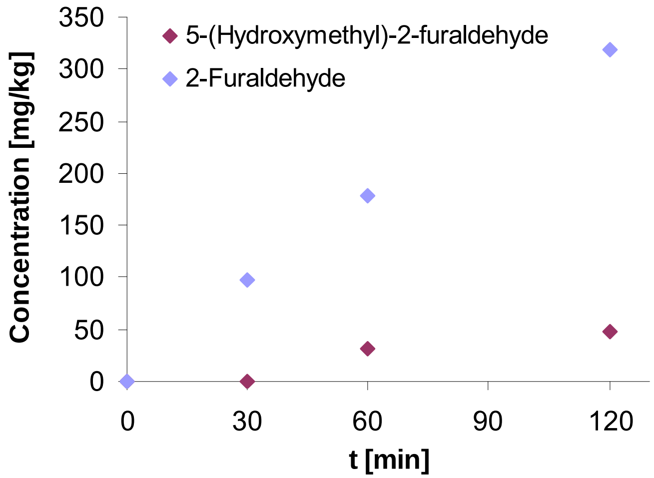
Kinetics – reaction time





Willow 180 °C

EtOH:H_2O 60:40 wt% No catalyst



- Increasing fractionation and pre-treatment with time.
- Increasing sugar degradation with time.
- Optimal reaction time requires economic optimization.

Recycling organic solvent

- Simplified calculation:

  1 ton straw → 0.36 ton glucan

  0.22 ton xylan } 0.32 ton EtOH (theoretical maximum)

  0.22 ton lignin

- Solvent mixture: 2.7 ton ethanol / ton wheat straw processed
  (L/S = 5 L/kg and ethanol : water = 60:40 (w/w))
- Compare maximum ethanol production : solvent in organosolv process
  → factor ~8!
- Recycling degree of 99%
  → 0.027 ton solvent loss or ~8% of EtOH produced!
- Recycling factor should be high, >99%.