The organosolv process for pretreatment and fractionation of lignocellulosic biomass for fermentation and lignin valorization

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The Organosolv Process for Pretreatment and Fractionation of Lignocellulosic Biomass for Fermentation and Lignin Valorization

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Contents

Introduction organosolv

- Biomass pretreatment for production second generation bioethanol
- Organosolv

Organosolv fractionation at ECN

- Experimental
  - Process conditions
  - Enzymatic cellulose hydrolysis
  - Lignin isolation & characterisation
- Process evaluation

Conclusions

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Lignocellulose Pretreatment

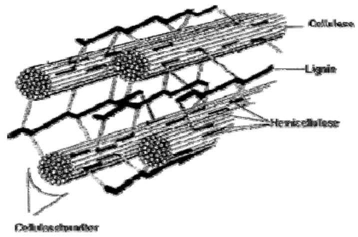
Production second generation bioethanol from lignocellulose:

1. Pretreatment.
2. Enzymatic hydrolysis cellulose to glucose.
3. Fermentation sugars to bioethanol.

Direct enzymatic saccharification of lignocellulose not feasible:

- Structural components strongly linked (physically & chemically).
- Cellulose protected against decay by lignin.
- Cellulose crystalline.
- …

→ Pretreatment required.



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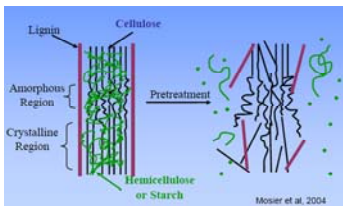
Functions Pretreatment

→ Pretreatment: overcoming nature's protection (biomass 'recalcitrance').

Enhancement enzymatic digestibility of cellulose to fermentable sugars:

- Removing hemicellulose and lignin to improve accessibility for hydrolytic enzymes.
- Removing / altering lignin to reduce non-productive cellulase binding.
- Reducing crystallinity of cellulose.
- Creating specific surface area.
- ….



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Pretreatment Processes

Several physical-chemical pretreatment routes under development.

Main pretreatment technologies at pilot/demo-scale:

- (Dilute) acid pretreatment
- Steam explosion

Routes effective for cellulose.

However:

- Lignin ends up in residue (with unconverted sugars, process chemicals, ash, etc).
- Residue generally only suitable for CHP.

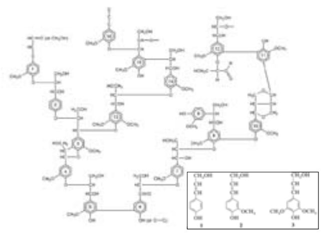
Alternative:

- Separation of lignin prior to enzymatic hydrolysis, while preserving the chemical structure of lignin → organosolv.

Lignin

Lignin:

- Polymeric network of aromatic compounds.
- Potential feedstock for wide range of chemicals and performance products.
- Renewable resource for aromatics!



Lignin (model)

Wood adhesives and resins

Lignocellulose biorefinery:

- No large-scale commercial market for lignin (derivatives) at the moment (in contrast to sugar derivatives).
- Valorisation lignin improves carbon footprint & economics lignocellulose biorefinery.

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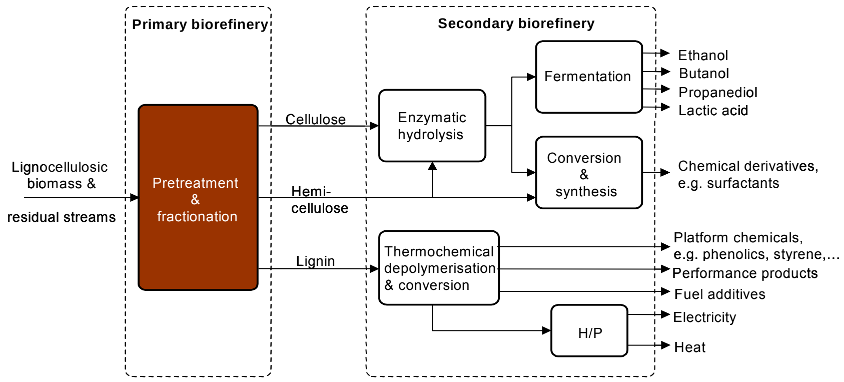
Lignocellulose Biorefinery



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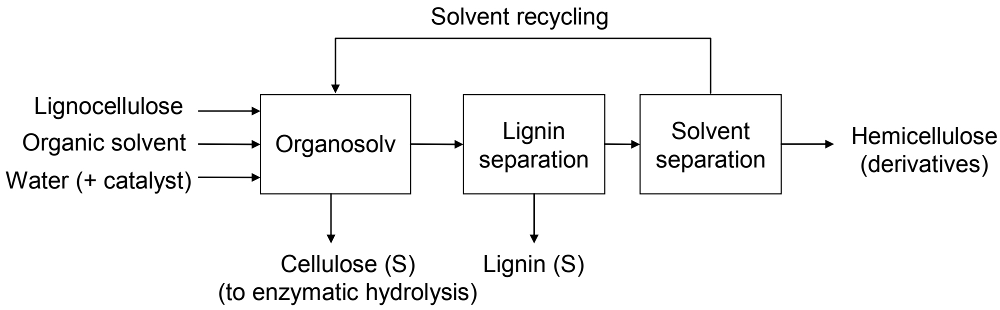
Organosolv Process



Many different organic solvents applied:

- Alcohols (methanol, ethanol, phenol, ethylene glycol…)
- Acetone
- Organic acids (formic, acetic, …)
- 1,4-Dioxane
- ….

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History Organosolv

Begin 20th century (analytics):

- Use organic solvent to separate wood components for analysis.

1970-90's (organosolv pulping):

- Organosolv as environmental-friendly alternative to Kraft pulping for paper making.
- Many different processes up to pilot-scale:
  - Alcell, ethanol-water pulping of wood (Canada).
  - Organocell, soda pulping with methanol (Germany).
  - ASAM, alkaline sulphite-anthraquinone-methanol (Germany).
  - Acetosolv, acetic acid based cooking (Germany).
  - Milox, formic acid and peroxyformic acid (Finland).
  - ….
- Extensive overview provided by E. Muurinen (2000), Organosolv pulping, PhD thesis, Oulu university, Finland.

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Organosolv Biorefinery Processes

Shift to organosolv as:

- Pre-treatment for second generation bioethanol.
- Primary biorefinery process.

Current developments:

- Organosolv biorefinery processes on pilot-scale.
  - Lignol (Canada), solvent = ethanol, feedstock = hardwood + softwood.
  - Chempolis (Finland), solvent = formic acid, feedstock = non-wood lignocellulose.
  - CIMV (France), solvent = mixture of formic & acetic acid, feedstock = wheat straw.
  - ….
- Many alternative routes under development at lab-scale.

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√ **Introduction on organosolv**

Organosolv fractionation at ECN

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Process Parameters

Parametric studies performed:

- Solvents: ethanol & acetone.
- Various lignocellulose feedstocks incl cereal straw.

Studied variables:

- Particle size
- Solvent mixture : solid ratio
- Solvent-water ratio ←
- Pretreatment severity: ←
  - Temperature
  - Reaction time
  - Acid catalysts such as H_2SO_4
- Stirring rate

→ Example: acetone-based organosolv on wheat straw (without catalyst).

Fresh wheat straw

After organosolv

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Experimental Set-up Organosolv Fractionation

Lignocellulose

Milling

Solvent / H_2O

Optional: catalyst

Volume: 0.5 / 2 ltr
Stirring
Temperature ↑

Filtration

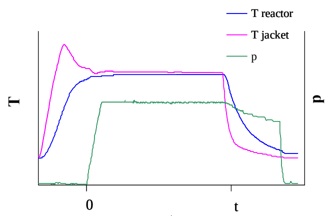
Washing

Solid residue

- Analysis composition
- Enzymatic hydrolysis

Filtrate

- Analysis sugars (monomeric + oligomeric)
- Analysis other compounds
- Lignin separation & analysis



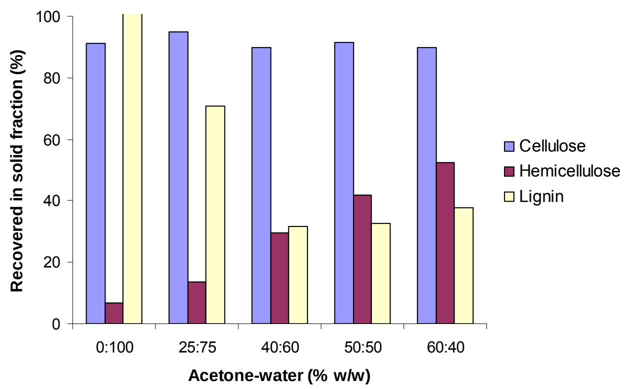
Acetone-Water Mixture

Fractionation:

- Organosolv fractionation effective.
- Cellulose recovery >90%.

Acetone:water ratio:

- Strong influence on hemicellulose hydrolysis & delignification.
- Optimisation dependent on product revenues.

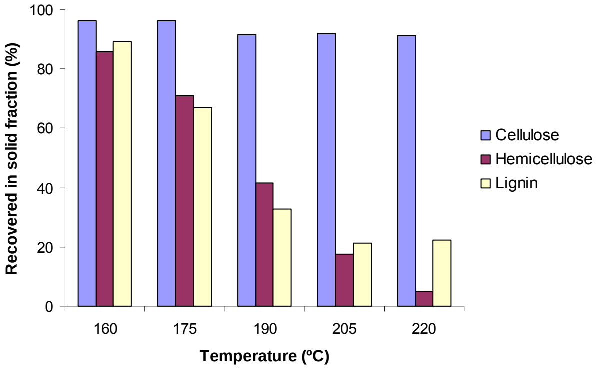


Huijgen et al. (2010), Pretreatment and fractionation of wheat straw by an acetone-based organosolv process, submitted.

Pretreatment Severity

Fractionation improves with pretreatment severity (temperature & time).

Maximum severity limited by:
- Decrease cellulose recovery.
- Degradation reactions → product loss & inhibiting effect on fermentation.



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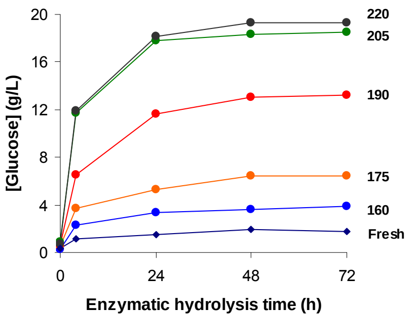
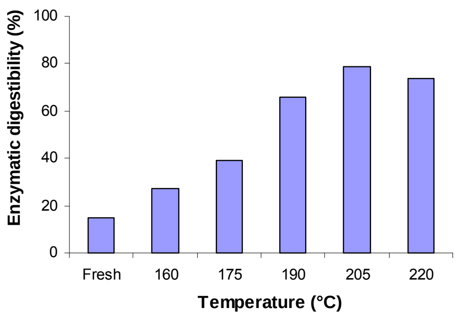
Enzymatic Cellulose Hydrolysis

Organosolv effective pretreatment process:
- Strong enhancement enzymatic cellulose hydrolysis (>10x).
- Enzymatic digestibility at optimised conditions → ~90%.





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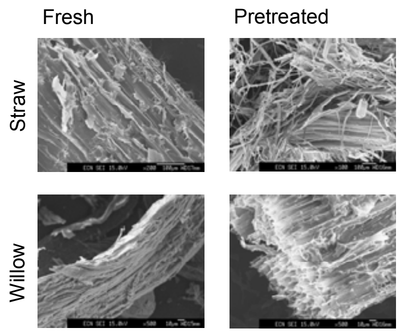
Feedstocks

Effectiveness organosolv dependent on type of lignocellulosic biomass:

- Organosolv less effective for softwoods and (more dense) hardwoods.
- More severe pretreatment conditions or use of catalyst required.
- Organosolv especially suitable for straws.



Biomass	Xylan hydrolysis (%)	Delignification (%)	Enzymatic digestibility (% cellulose feedstock)
Barley straw	80	57	92
Wheat straw	76	59	88
Willow	50	64	71
Olive tree	44	50	53
Poplar	28		39
Spruce		33	

200 °C
EtOH-H_2O 60:40% w/w

Lignin Isolation & Characterisation

160, 180, 200, 220 °C

Lignin isolation:

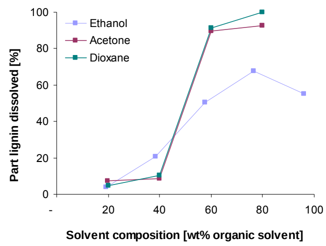
- Insoluble in H_2O, soluble in ethanol & acetone.
- Precipitation lignin from organosolv liquor.
- Lignin isolation efficiency >90%.

Lignin appearance:

- Light brown to black (compacted) powder.
- Colour and structure dependent on process conditions organosolv, biomass type and contaminants.

Lignin purity:

- High purity (>90 wt%, up to 96% for wheat straw derived lignin without additional processing).
- Main contaminant oligomeric xylose (hemicellulose).
- Lignin sulphur and ash free (max 0.1 wt% S).



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Lignin Characterisation - II

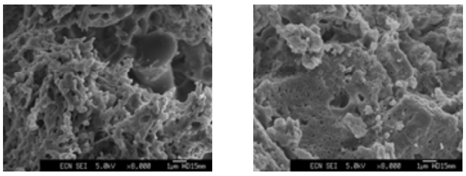
Molecular weight:

- Low mean molecular weight (2000-3500) compared to other types of lignins.
- Relatively narrow distribution.

^{31}P-NMR:

- Identification of functional groups.
- SGH type lignins in different ratios depending on feedstock.

→ Organosolv lignin promising properties for valorisation (relative to other types of lignin).



Organosolv lignin

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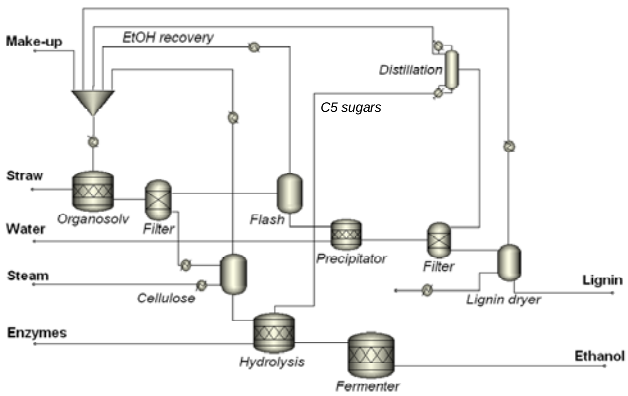
Simulation Organosolv Process

Process design in ASPEN:

- Determination of streams and energy consumption.
- Feedstock: wheat straw.
- Process: 200 °C, 60 min, EtOH:H_2O 60:40, 5 L/kg straw.
- Preliminary results.



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Recycling Ethanol

Importance recycling:

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

Simulations:

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

Benefits using ethanol as solvent:

- 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.

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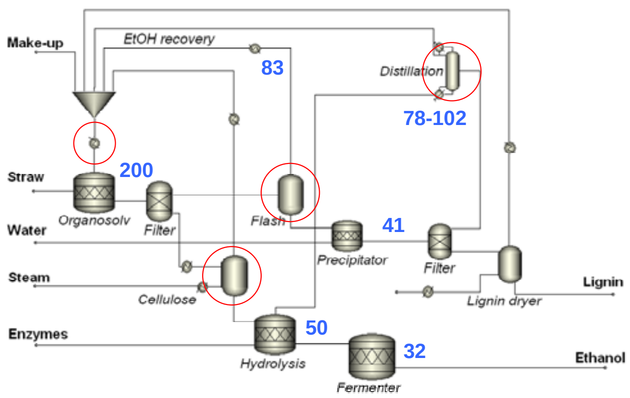
Energy Consumption

Major energy consumers:

- Ethanol separation for recycling.
- Large differences in process temperatures → heating.

Heat flows significant compared to energy content ethanol produced.



→ Next step:

- Improved process lay-out including direct recycling of liquor.

Temperatures (°C)

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Recycling Organosolv Liquor

Wheat straw pulping in ethanol.

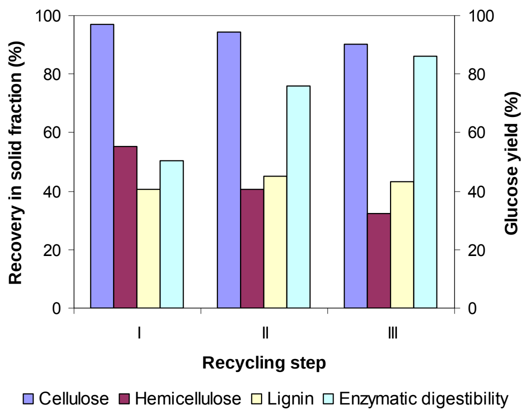
pH decrease due to recycling acetic acid.

Benefits recycling:

- Improvement hemicellulose hydrolysis.
- Substantial increase enzymatic hydrolysis.

On the other hand:

- Increase degradation hemicellulose sugars.
- Slight decrease cellulose recovery.



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Conclusions

Conclusions:

- Organosolv able to fractionate lignocellulose.
- Enzymatic hydrolysis cellulose improved substantially (up to ~90% for wheat straw).
- Organosolv particularly effective for straw.
- Successful isolation of lignin with high purity (>90%).
- Lignin promising properties for production of chemicals and performance products.
- Recycling organic solvent crucial process element.

Future plans:

- Development continuous organosolv reactor.
- Lignin conversion tests.
- Solvent integrity and recycling.
- Investment and operating costs.

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Thank you for your attention!

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LignoValue

Agentschap NL EOS-LT

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