Development of a Lignocellulose Biorefinery for Production of 2nd Generation Biofuels and Chemicals

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Energy research Centre of the Netherlands

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Introduction

Energy research Centre of the Netherlands (ECN)

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  - Solar energy
  - Wind energy
  - Sustainable process technology
  - Policy studies

ECN

- Independent research institute
- 570 employees
- Locations:
  - Petten (HQ)
  - Amsterdam
  - Eindhoven
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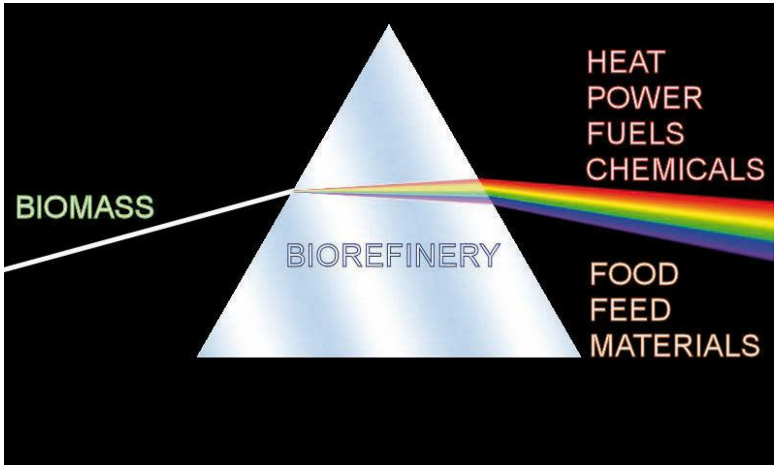
Biorefinery

"The sustainable processing of biomass into a spectrum of marketable products (food, feed, materials, chemicals) and energy (fuels, power, heat)"

(definition IEA Bioenergy task 42)

Various types of biorefineries depending on type of biomass:

→ lignocellulosic biomass.



Lignocellulosic Biomass

Lignocellulosic biomass:

- Hardwood: poplar, willow, ...
- Softwood: spruce, pine, ...
- Herbaceous: miscanthus, wheat straw, …

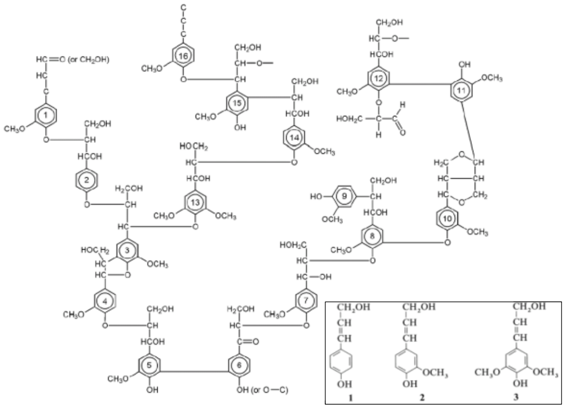
Available in form of:

- (Forestry / agricultural) residues.
- Energy crops.

Advantages compared to other types of biomass:

- Wide range of low cost feedstocks.
- No direct competition with food production.
- High CO_2 reduction of derived fuels and products.

Lignocellulose Constituents



Lignin (model)

Sugar polymers:

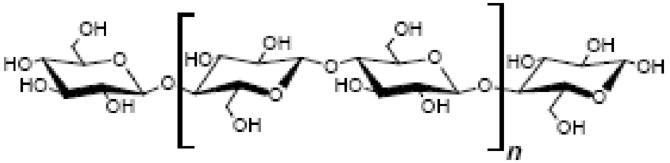
- Cellulose, linear polymer of glucose.
- Hemicellulose, branched copolymer of C5 and C6 sugars.

Lignin:

- Polymer of aromatic compounds.

Factors influencing composition, e.g.:

- Plant species.
- Part of plant (bark, stem, …).
- Location of cultivation.



Cellulose

Based on its chemical composition, lignocellulose potential feedstock for:

- Performance materials (cellulose, lignin).
- Sugar-based 2G biofuels (e.g., bioethanol) and chemicals (e.g., furans).
- Lignin derivatives.

Cellulosic Fuels and Chemicals - Pretreatment

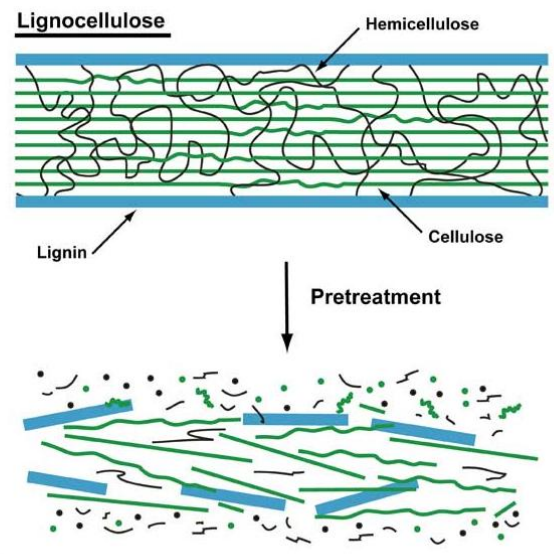
Hydrolysis of cellulose into glucose: enzymatic or chemocatalytic.

Direct enzymatic saccharification of lignocellulose not feasible:

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

Pretreatment: overcoming biomass ‘recalcitrance’ by e.g.:

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



Lignin

low volume - high value market 10000 €/t

- Potential feedstock for wide range of chemicals (aromatics!) and performance products.
- Valorisation lignin improves carbon footprint & economics lignocellulose biorefinery.



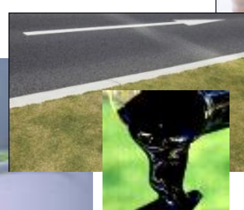
specialty chemicals

bio-plastics

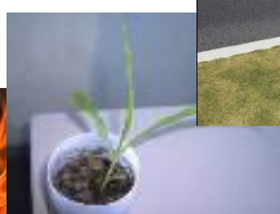
bio-resins for wood-adhesives


activated carbon, carbon-fibres and carbon-black

fuel-additives



bio-bitumen for asphalt



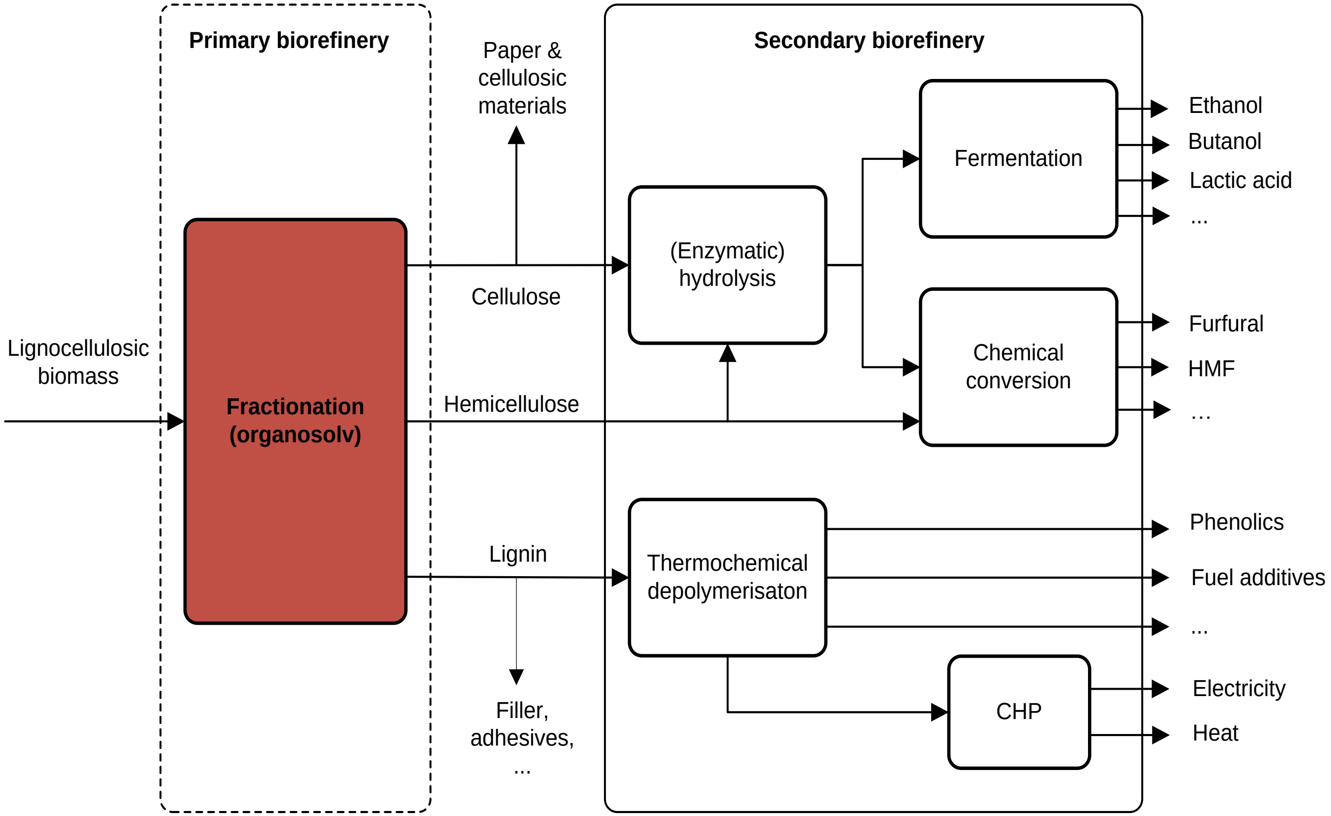
bio-char for soil improvement

bio-fuel for CHP

- No large-scale commercial market for lignin at the moment (in contrast to sugar derivatives).

high volume - low value market 100 €/t

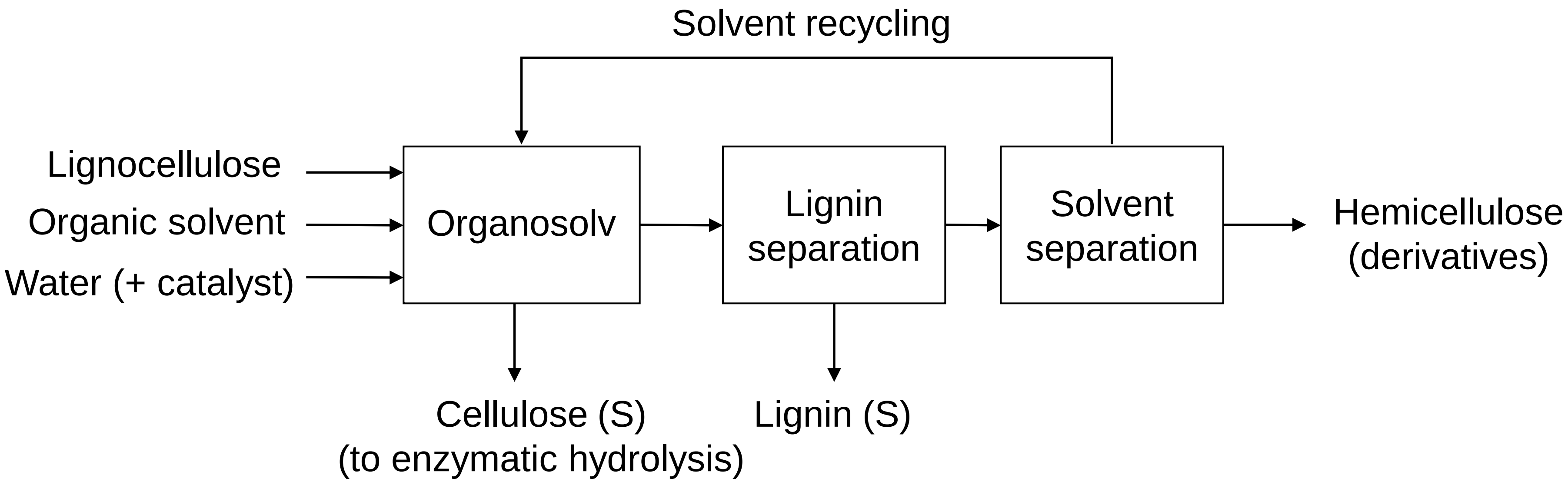
Lignocellulose Biorefinery



Why organosolv?

- Fractionation of <u>all</u> major constituents in a sufficient quality for valorisation.
- Including extraction of high-quality lignin for production of chemicals.

Organosolv Process



- Solvents: ethanol, acetone, …
- Catalyst: H_2SO_4, ...
- Typical process conditions: 160-200 ºC, 30-120 min, mixture organic solvent-water.

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

Experimental Results

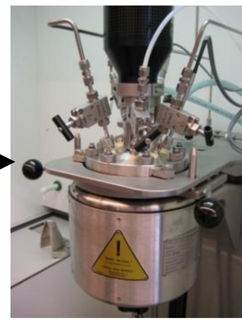
Experimental Set-up Organosolv Fractionation

Lignocellulose

Milling

Solvent / H_2O

Optional: catalyst



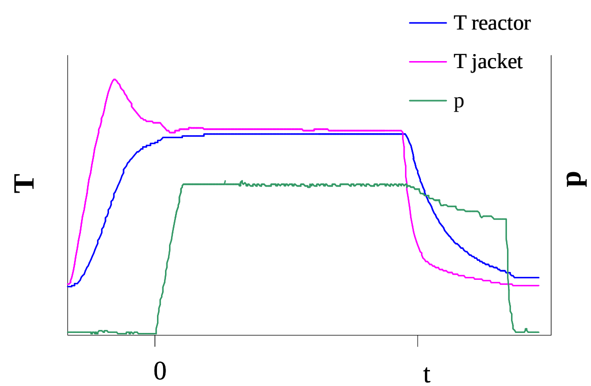
Volume: 0.5 / 2 / 20 ltr
Stirring
Temperature ↑

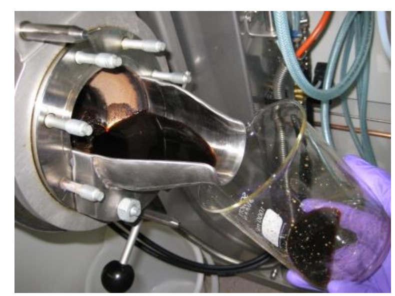
Filtration

Washing

Solid residue
- Analysis composition
- Enzymatic hydrolysis

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





Selection Lignocellulose Feedstocks

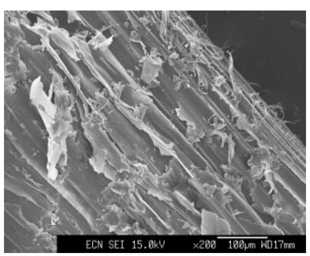
Effectiveness organosolv dependent on type of lignocellulosic biomass:

- Large variety of feedstocks tested.
- Optimum pretreatment conditions feedstock dependent.
- Organosolv less suitable for softwoods and dense hardwoods.
- Best results obtained for specific annual plants (straw) and hardwoods (willow, birch).

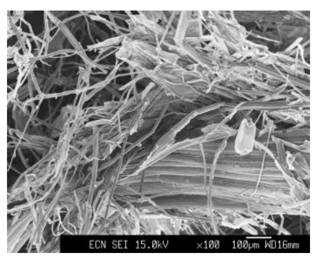
→ ECN process: primary focus on wheat straw.

Straw

Feedstock

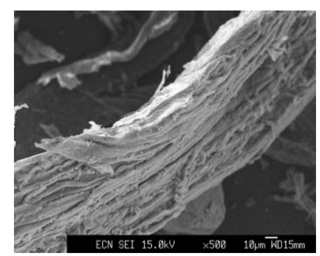


Pretreated

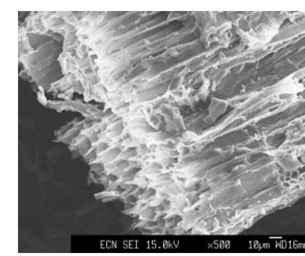


Willow

Feedstock



Pretreated



Process Parameters

Parametric optimisation studies:

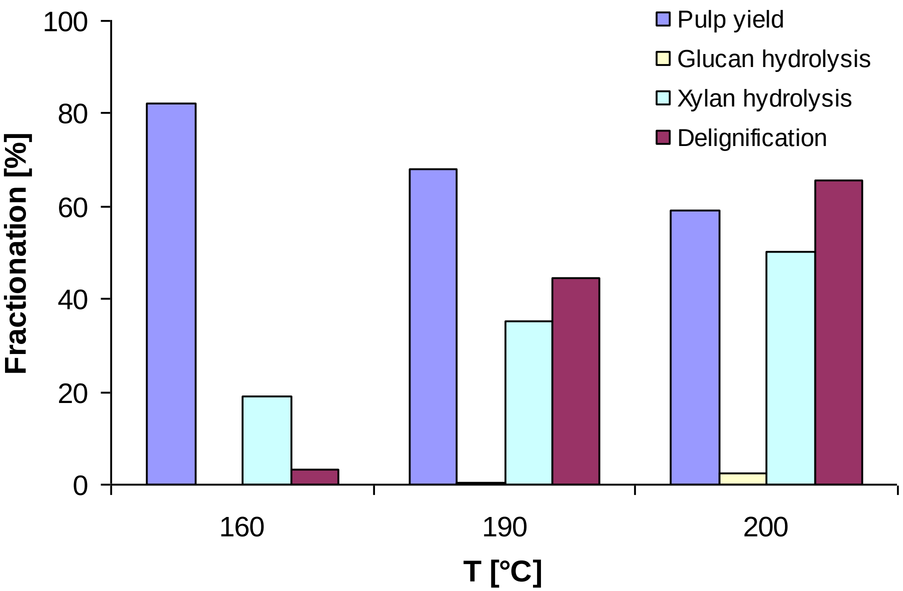
- Feedstocks: wheat straw & willow.
- Solvents: ethanol & acetone.
- Studied variables:
  - Particle size
  - Pretreatment severity: ←
    - Temperature
    - Reaction time
    - Acid catalysts such as H_2SO_4
  - Solvent mixture : solid ratio (L/S)
  - Solvent-water ratio ←
  - Stirring rate

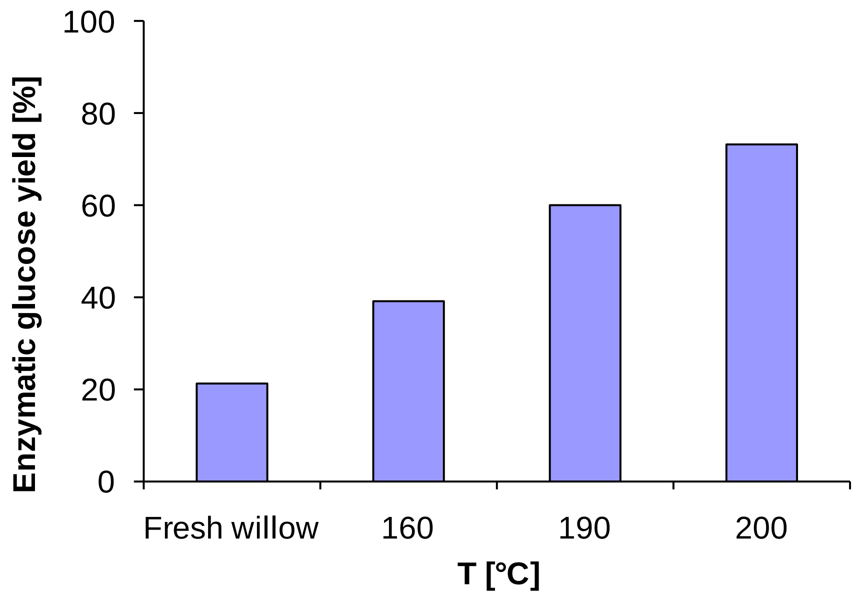
Wheat straw

After organosolv

Process Temperature

Willow
EtOH:H_2O 60:40 wt%
60 min

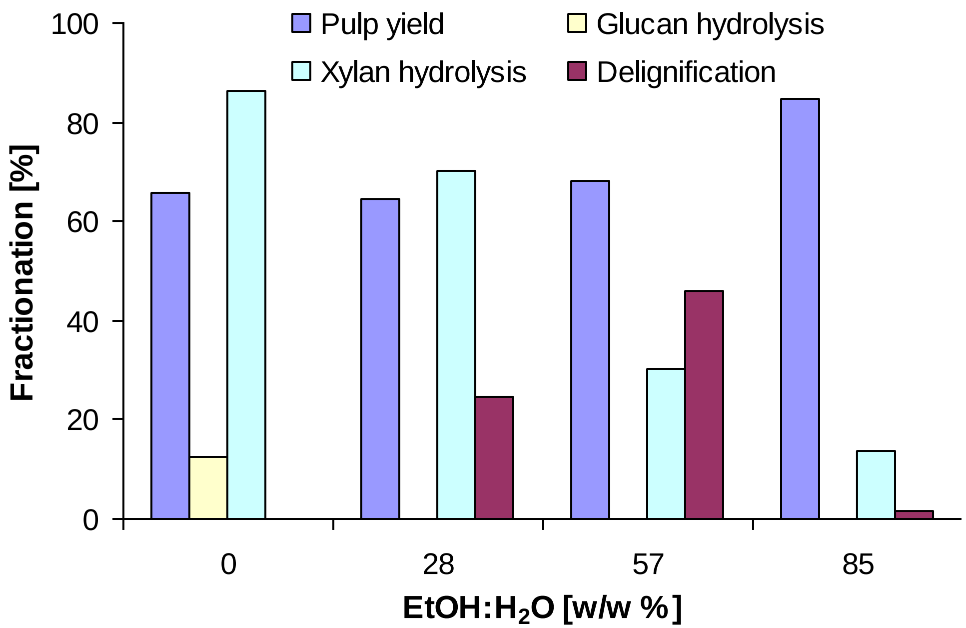


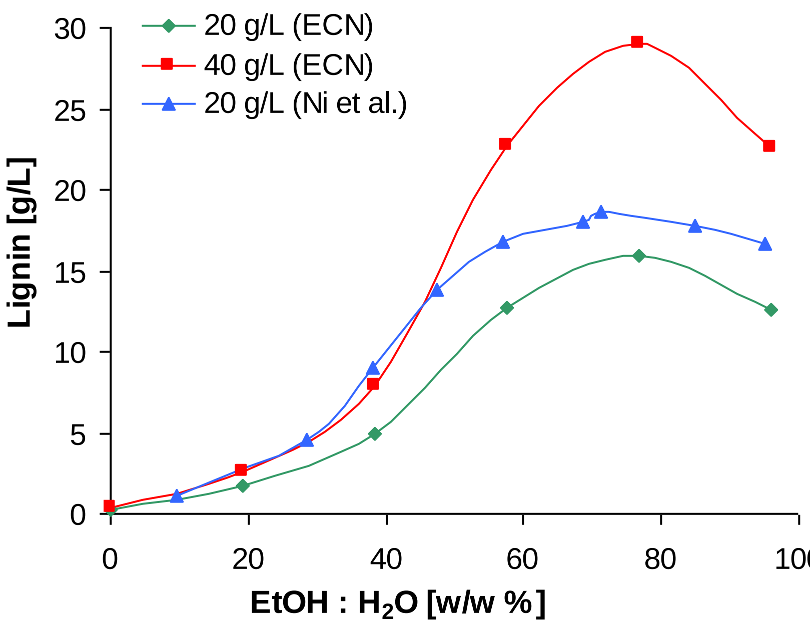


Effect temperature:

- Increase lignin extraction and hemicellulose hydrolysis.
- Above 200 ºC, cellulose hydrolysis and degradation of sugars during pre-treatment.
- Strong enhancement enzymatic cellulose hydrolysis.

Solvent-Water Ratio: Fractionation

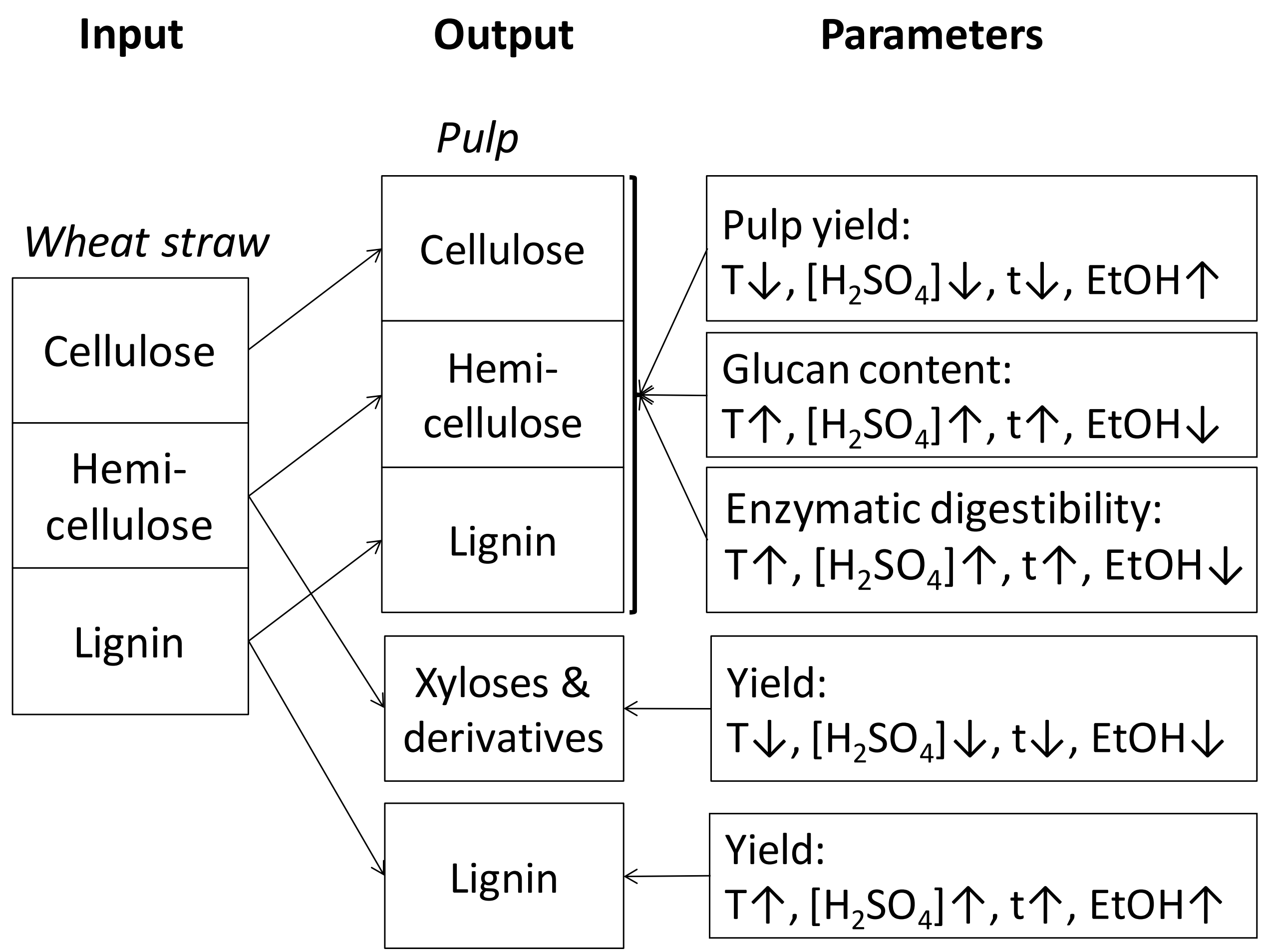




Willow
190 °C
60 min
No catalyst

- Ethanol major influence on delignification and hemicellulose hydrolysis.
- Optimum EtOH-H_2O ratio for delignification (~60 wt% EtOH).
- Solubility of lignin (fragments) dependent on solvent mixture composition.

Process-Product Scheme



Wildschut et al. (2011) Ethanol-based organosolv of wheat straw: process optimization and process product relations, EBC-19, Berlin, Germany.

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Optimisation

- Optimisation towards different products possible.
- Example from published results: enzymatic digestibility.
  - High enzymatic digestibility achieved in all cases.
  - Two main optima: autocatalytic and catalytic.

Feedstock	T (C)	Solvent (% w/w)	Catalyst	Enzymatic digestibility (%)
Wheat straw [1]	205	50% acetone	Auto	80
Wheat straw [4]	210	50% EtOH	Auto	86
Olive tree [2]	210	43% EtOH	Auto	90
Wheat straw [3]	190	60% EtOH	HCl (20 mM)	99
Wheat straw [4]	190	60% EtOH	H_2SO_4 (30 mM)	89
Willow [3]	190	60% EtOH	H_2SO_4 (10 mM)	87

1. Huijgen et al. (2010) Pretreatment and fractionation of wheat straw..., Ind Eng Chem Res, 49/20, 10132-10140.
2. Diaz et al. (2011) Organosolv pretreatment of olive tree biomass for fermentable sugars, Holzforschung, 65(2), 177-183.
3. Huijgen et al. (2011) Catalytic organosolv fractionation of willow wood and wheat straw..., J Chem Technol Biotechnol, 86(11), 1428-1438.
4. Wildschut et al. (2011) Ethanol-based organosolv of wheat straw: process optimization and process product relations, EBC-19, Berlin, Germany.

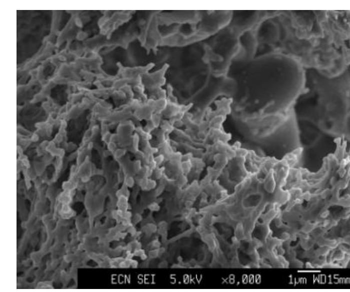
Lignin Isolation & Characterisation

Lignin isolation:

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

Lignin characteristics:

- Light brown to black (compacted) powder.
- High purity (>90 wt%).
  - Main contaminant oligomeric xylose (hemicellulose).
  - Lignin sulphur and ash free (max 0.1 wt% S).
- Molecular weight (relative to other types of lignins):
  - Low average (2000-3500 g/mol).
  - Narrow distribution.



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

Process Evaluation

References:

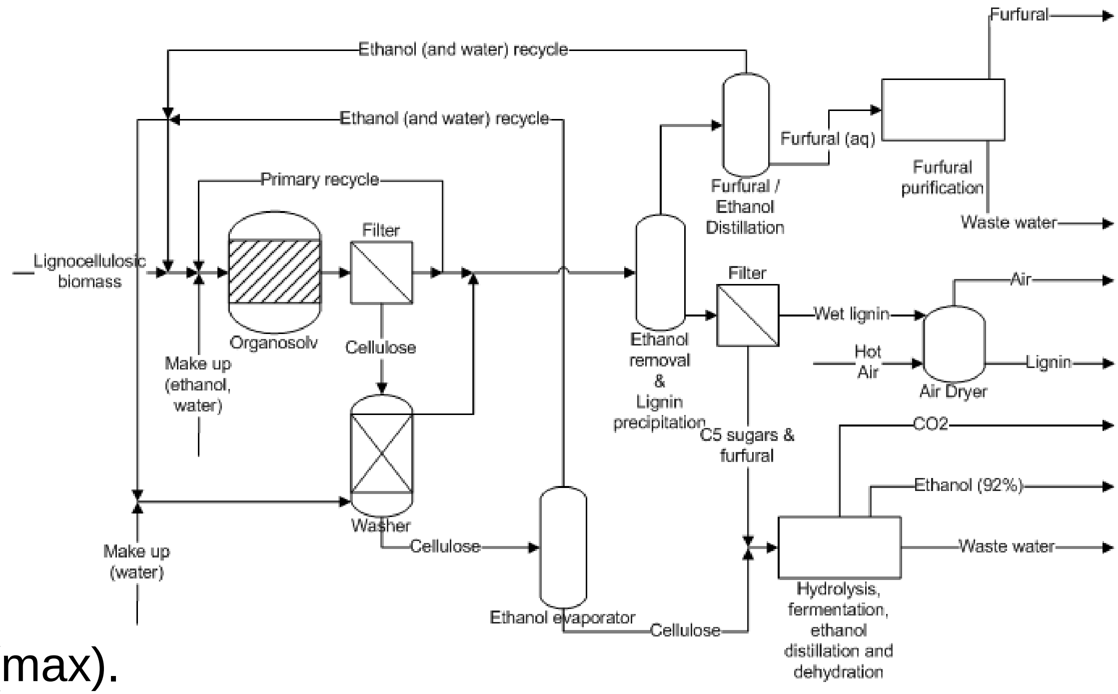
Van der Linden et al. (2011) Conceptual Process Design of an Organosolv-based Wheat Straw Biorefinery for Co-Production of Bioethanol, Furfural and Lignin, 7th International Conference on Renewable Resources & Biorefineries, Bruges, Belgium.

Van der Linden et al. (2011) Process Evaluation of an Organosolv-based Wheat Straw Biorefinery for Co-Production of Bioethanol, Furfural and Lignin, 19th International Symposium on Alcohol Fuels, Verona, Italy.

System Evaluation Organosolv Process

Process design in ASPEN:

- Feedstock: wheat straw.
- Products: bioethanol, lignin, and furfural.
- Process: 200 °C, 60% w/w EtOH, 5 L/kg straw.



Recycling:

- 1 ton straw → 0.32 ton EtOH (max).
- Solvent: 2.7 ton EtOH/ton straw.
- Recycling degree ethanol set at 99.9%.
- Recycling of ethanol present in adhering moisture solids required!

Mass Balance (kg/kg straw)

- Straw to products: 52% wt.
- Energy efficiency straw to products: 66% (LHV based).

IN	
Straw	1.00
Ethanol	0.004
Water	2.17
Total	3.17

OUT	
Ethanol	0.22
Furfural	0.06
Lignin	0.19
Waste water	2.33
CO_2	0.19
Water vapor	0.18
Total	3.17

Energy Consumption (MJ/kg straw)

- Heat integration is essential.
- Energy consumption: ~20% of LHV of straw.
- Option: anaerobic digestion & combustion of residues.

	Heating	Cooling
Ethanol recycling from liquor	3.4	2.6
Ethanol recycling from pulp	0.9	0.6
Ethanol product distillation	1.0	0.6
Other	1.8	2.8
Total before heat integration	7.1	6.6
Total after heat integration	3.3	2.9

Economic Evaluation - Base Case

- Scale:
  - 140 kton/yr straw (dw)
  - Straw from a 50 km radius
- 8000 hrs of operation / yr
- Price index: 2010
- Location: EU
- General surcharge factors used.

	Price (€/ton)	M€/yr
Ethanol	750	24.1
Furfural	625	5.7
Lignin	500	11.6
Income		41.4
Straw	60	9.3
Ethanol	750	0.4
Utilities		4.7
Maintenance		6.0
Other		13.5
OPEX		34.0
Total fixed capital (M€)		60
Pay-back time (yr)		8

Economic Evaluation - Sensitivity Analysis

- Largest uncertainty in cost evaluation in investment (organosolv reactor).
- Economy strongly dependent on feedstock price and lignin value.

	Straw price (€/ton)	Payback time (yr)
Base case	60	8.2
Straw price +33%	80	14.3

	Lignin price (€/ton)	Payback time (yr)
Base case	500	8.2
Lignin price +50%	750	4.6

Conclusions

Experimental:

- Process optimisation performed for hardwoods and straws.
- Enzymatic hydrolysis cellulose improved substantially (up to ~90%).
- Successful isolation of lignin with high purity (>90%).

Process evaluation:

- Recycling organic solvent crucial (conceptually and energetically feasible).
- Product values crucial for economy of organosolv biorefinery.

Ongoing and Future Work

- Lignin (derivatives) application tests with industrial partners.
- Development bench-scale continuous organosolv reactor.

→ Looking for partners for further technology development & commercialisation.

0.1 L

0.5 & 2 L (2007)

20 L (2010)

→ ?

Thank you for your attention!

More information:

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