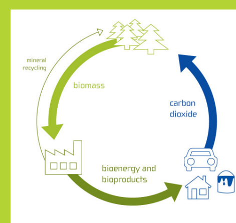
WP1 Advanced physical/chemical fractionation
Status & Progress of activities
WP Coordinator: Robert Bakker

Workshop of the EU FP6
Integrated Project BIOSYNERGY



EBCE, July 2nd 2009, Hamburg Germany

Overview

- Fractionation of lignocellulosic biomass
- Fractionation in BioSynergy
  - Goal
  - Processes, partners
- Focus on two routes
  - Modified Organosolv (ECN)
  - Mechanical/Alkaline Fractionation (A&F)
- Conclusions; Ongoing work

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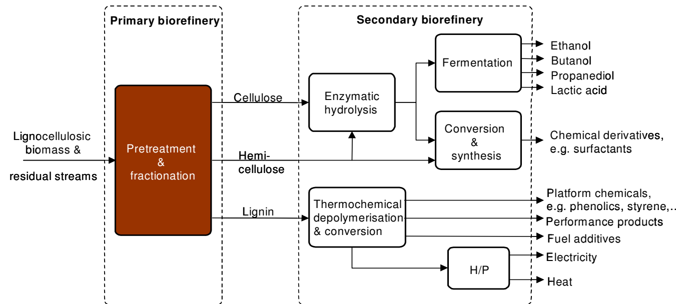
Fractionation of lignocellulosic biomass



Goals Fractionation:

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

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Objectives of Fractionation in Biosynergy

- To obtain a detailed overview of both available physical and chemical fractionation processes and of those currently being developed that are applicable in integrated thermochemical/ biochemical biorefinery processes.
- To design optimal enzyme systems for an efficient conversion of polymers from pre-treated raw materials into monomers.
- To develop methods for fractionation for lignocellulosic biomass into its composing components based on recently developed techniques.

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Advanced physical/chemical fractionation (WP1)

• Model feedstocks: straw, woods

Processes studied

• Mechanical/Alkaline fractionation (A&F)
• Ethanol/water Organosolv (ECN)
• Organic acid organosolv (Avidell process; ARD)
• Acid hydrolysis (Biorefinery.de)
• Reference technology: steam explosion (ABNT)
• Enzymatic hydrolysis

Ethanol/H2O Organosolv, ECN

Mech./alk pretreatment A&

Acid organosolv Pilot plant ARD

Partners: A&F, ABNT, ARD, Bioref, ECN, TUD

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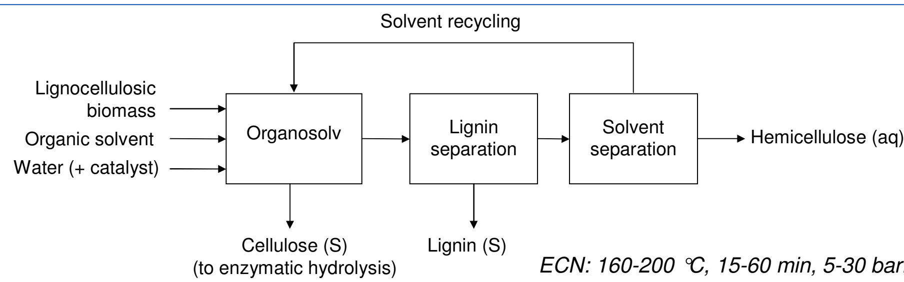
Benchmarks for evaluating Fractionation

- Delignification
- Lignin purity, quality
- Hemicellulose hydrolysis
- Enzymatic degradability of cellulose
- (Minimum) Formation of fermentation inhibitors
- Other factors e.g. operating and capital costs, chemical use, energy use, etc.

Organosolv process (ECN)



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?

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Biomass pre-treatment methods

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.

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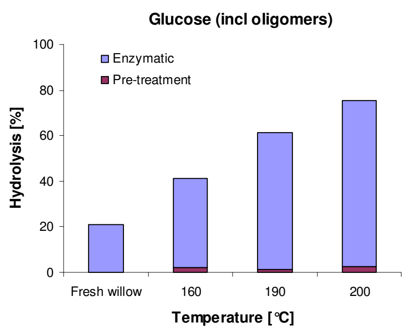
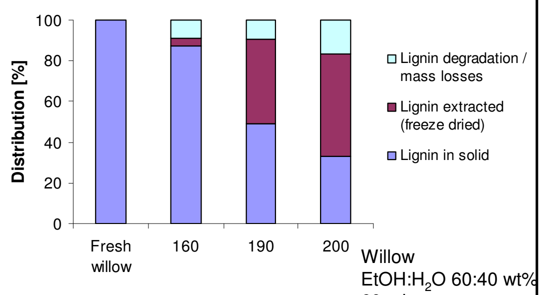
Reaction temperature





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

- 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.

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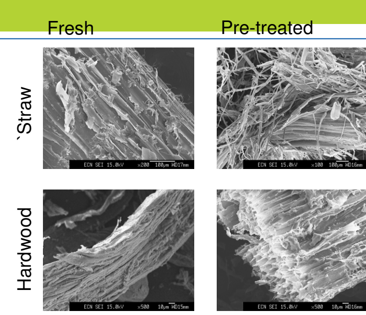
Types of biomass

- 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).



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)

ECN

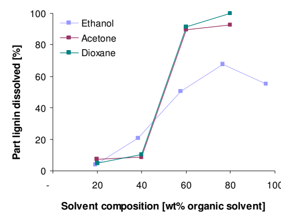
Lignin characterisation

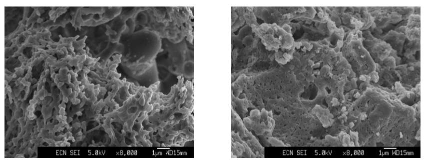
Lignin: light brown to black (compacted) powder.
Colour and structure dependent on process conditions organosolv, biomass type and contaminants.

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 ℃





Organosolv lignin

ECN

Conclusions Organosolv

- 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.

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Alkaline Fractionation (A&F)

- Common alkaline pretreatment routes
  - Base as catalyst (NaOH, $Ca(OH)_2$, ammonia); T<120 °C
  - Carried out under (close to) atmospheric conditions
  - Long reaction times (hours)
  - Need for chemical recycling

- Goal: Improving alkaline pretreatment
  - Apply milder process conditions
    - Less formation of degradation products (e.g. inhibitors)
    - Lower operational costs
  - Improve accessibility of sugars to enzymes
  - Obtain lignin of high purity

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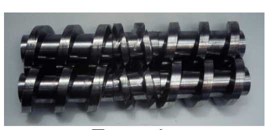
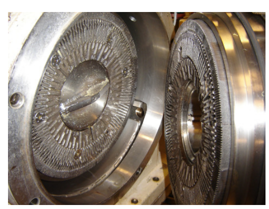
Combined mechanical/alkaline pretreatment

- Improve alkaline pretreatment by combination with mechanical action



Extrusion



Refining

- Focus: From wheat straw conversion to fermentable sugars, and lignin

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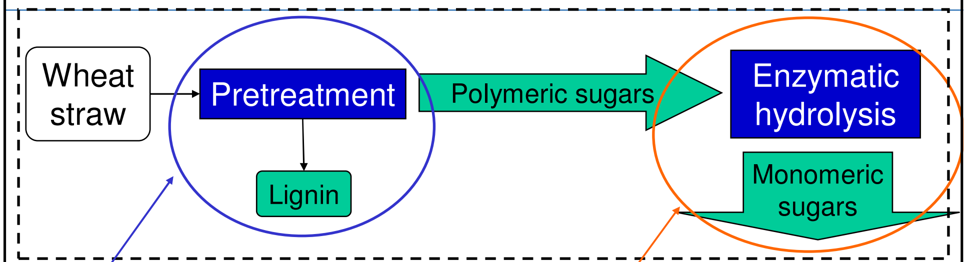
From wheat straw to fermentable sugars, lignin



- Fractionation efficiency
  - Properties of solid fraction (cellulose-rich)
    - Biochemical composition
  - Properties of liquid fraction
    - Sugars, organic acids and lignins in solution
    - Recovery of lignin
- **Enzymatic hydrolysis**
  - Conversion of solid fraction
    - Glucan to glucose
    - Xylan to xylose
  - Standard procedure
    - 50 °C, 120h
    - Excess of enzyme (GC220)

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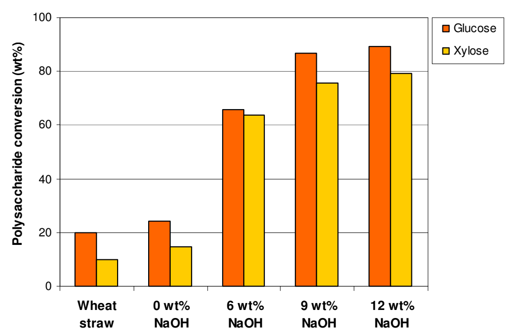
Enzymatic hydrolysis *Solid fraction*



- Enhanced enzymatic degradability due to pretreatment
  - Structural changes of wheat straw (e.g. delignification)
  - Minimal formation of degradation products due to mild conditions

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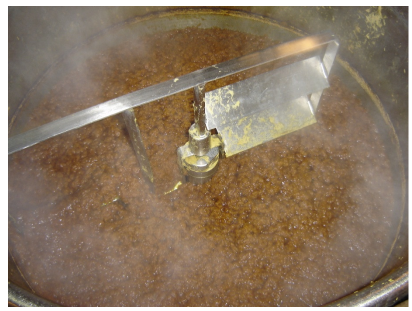
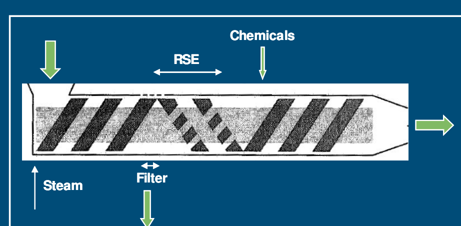
Base case

- Chopped wheat straw (1-2 cm)
- 9 wt% NaOH based on dry straw
- 4h at 90 ℃



Extrusion

1st Delignification
Whole wheat straw
6 wt% NaOH, 2h, 90℃



2nd Delignification
6 wt% NaOH, 2h, 90 ℃

- Transport of biomass to RSE (reversed screw element)
  - Accumulation and compression of material
  - High compression and shear forces
  - Material is dry and absorbs added chemicals very well (e.g. NaOH)
- Shortening of fibres and fibrillation

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Refining

1st Delignification
Chopped wheat straw
6 wt% NaOH, 2h, 90 °C

2nd Delignification
6 wt% NaOH, 2h, 90°C

- Shear and compression forces
  - Increase of surface area
  - Shortening of fibres and fibrillation
  - Homogeneous, clean fibres

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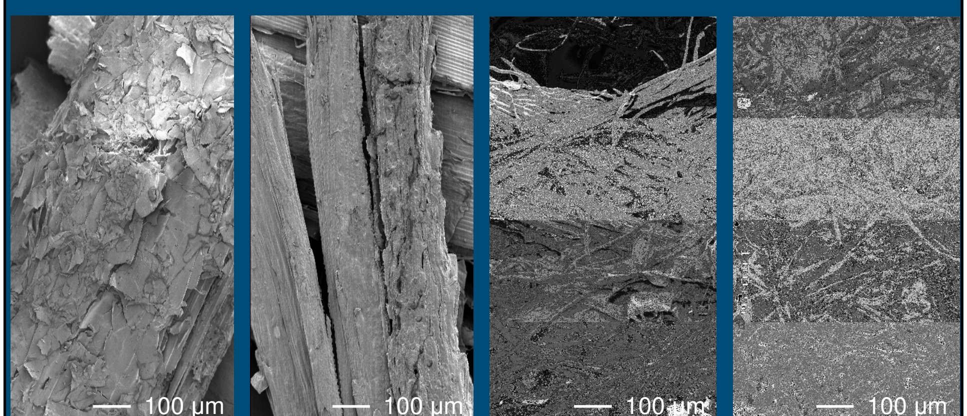
Scanning Electron Microscopy



Wheat straw | Base case | Extrusion | Refining

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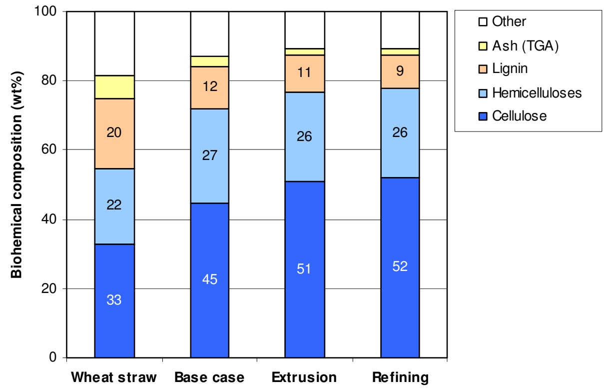
Fractionation efficiency — *Solid fraction*



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Fractionation efficiency

	Base case	Extrusion	Refining
Yield solid fraction	70-75%	60-65%	60-65%
Delignification	40-50%	70-80%	70-80%
Sugars in liquid fraction	<10%	20-30%	20-30%

- Extrusion and refining comparable results
- Higher degree of delignification accompanied by loss of sugars by hydrolysis

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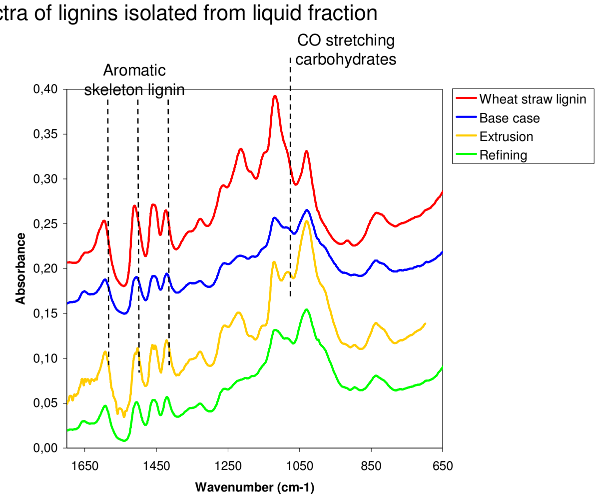
Lignin Quality *Liquid fraction*

IR-spectra of lignins isolated from liquid fraction



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Conclusions Alkaline Fractionation

- Alkaline fractionation excellent for
  - Delignification (40-50%)
  - Improvement of enzymatic degradability of cellulose and hemicellulose (from 20 to 70-80%)
- Added value of extrusion or refining:
  - More delignification (70-80%)
  - Further improvement of enzymatic degradability (from 20 to 100%)
- Economic feasibility of combined mechanical/alkaline pretreatment depends on value of lignin produced

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Enzymatic Hydrolysis (WP1)

- Tests with commercially available enzymes on BIOSYNERGY cellulose fractions by A&F, Bioref, ARD
- Target ABNT: Developing tailor-made enzyme mixture able to hydrolyse substrates at costs < 0,02 €/l ethanol
  - High productivity strains (>100 g protein per liter broth)
  - Increased effective activity (dosages< 5mg protein/g glucan entering hydrolysis)
  - Developing a host able to produce the required enzyme mixture for the ethanol production process at industrial scale
  - Developing the enzyme mixture processing and manufacturing technology using the selected host

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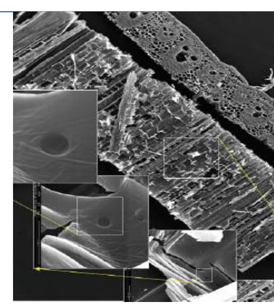
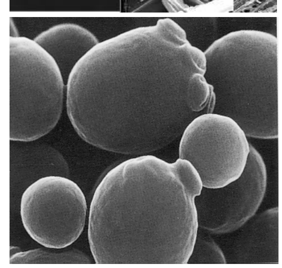
Enzymatic Hydrolysis (WP1)

Progress ABNT to date

- Selection of base enzyme cocktail for setting up process conditions.
- Expression and purification of selected enzymes from the cocktail.
- Enzyme supplementation studies.
- Cost reduction fermentation media.
- Conceptual design on-site enzyme production plant.





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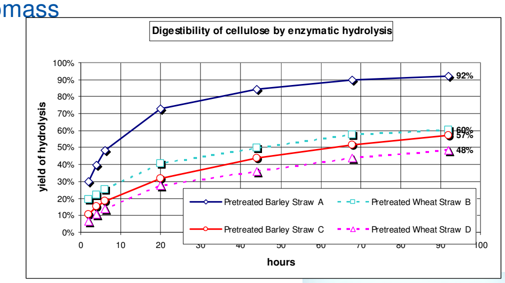
Preliminary conclusions Fractionation

- All fractionation routes lead to considerable fractionation of lignocellulose into separate C5, C6 and lignin components. No clear "winner".
- For cellulose degradability and hemicellulose hydrolysis there is variation in the effect of fractionation on biomass



- Fractionation techniques can and should be optimised towards the desired application of the fractionised products
  - Hemicellulose hydrolysis for further processing of C5
  - High enzymatic degradability of the cellulose fraction
  - Recovery of a high quality lignin stream

Lignin products from Modified Organosolv Fractionation (ECN)

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Ongoing work

- Assessment of operating + capital costs for fractionation routes on a similar basis
  - Comparison with base case (steam explosion)
- Integrating fractionation into Biorefinery concepts
- Application tests with fractionised products
- Upscaling selected Technologies

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This work was performed in the context of:

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SIXTH FRAMEWORK PROGRAMME