Biomass pretreatment

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Examples

- **Steam pretreatment** (water, acid or alkali)
- Fermentation of all sugars (incl. **Pentoses**)
- Ethanol, polymers & biogas
- Energy integration
- Integration with other processes

**Diagram:**
- Biomass → Pre-treatment → Enzymatic hydrolysis → Fermentation → Distillation → Ethanol
- SSF → Lignin
- Biogas
Biorefinery concept

- A selection of potential products from lignocellulose
- Ranging from bulk to high-value chemicals
- Important to maximize the yield from the starting material
  - Prepare the material for attack!
Pretreatment
What is THAT?

- Some kind of action before the treatment...
- Likely to be different for different raw materials and desired products

- Some steps also before pretreatment (Pre-pretreatment?)
- Washing/separation of inorganic matter, pebbles, etc.
- Size reduction (grinding, milling, crushing...)
- Separation of solubles (e.g., sucrose residues)
Lignocellulosic materials rather recalcitrant

- Starchy materials mainly glucose units
  - Less severe conditions needed
- Cane mostly sucrose – extractable
- Avoid drying of the lignocellulosic materials: pore shrinking, limits diffusion etc.
### Products & By-products

- **Cellulose** (42%)
- **Lignin** (21%)
- **Hemicellulose** (20%)
- **Extractives**

#### Sugars:
- Glucose
- Mannose
- Galactose
- Rhamnose
- Xylose
- Arabinose

#### Monosaccharides:
- Glucurono-pyranose
- Galacturono-pyranose

#### Polyols:
- Ethanol

#### Furan Derivatives:
- Furfural
- HMF

#### Aliphatic Acids:
- Acetic acid
- Formic acid
- Levulinic acid

#### Phenolics:
- Extractives
  - Terpenoids etc.

#### Fermentation Inhibitors:
- ETHANOL
- PHENOLICS
Pretreatment – desired features for fermentation

- Hydrolysis of hemicellulose
- High recovery of all carbohydrates
- High digestibility of the cellulose in enzymatic hydrolysis
- No or very limited amounts of sugar and lignin degradation products
  The pretreatment liquid should be possible to ferment without detoxification
- High solids concentration and high concentration of sugars
- Low energy demand or possible to re-use secondary heat
- Low capital and operational cost
Action of pretreatment

- Modification of the structure
- Increased surface area
- Increased pore sizes
- Partial hydrolysis of hemicellulose
Rough classification in terms of pH

- **Acid based methods**, i.e. at low pH using an acid (H2SO4, SO2, H3PO4, Acetic acid…))
  Results in hydrolysis of the hemicellulose (HC) to monomer sugars and minimize the need for hemicellulases

- **Methods working close to neutral conditions**
  e.g. steam pretreatment and hydrothermolysis
  Solubilise most of the HC (due to acetyl groups in HC → acetic acid)
  Do not usually result in total conversion to monomer sugars
  Requires hemicellulases acting on soluble oligomers of the HC

- **Alkaline methods**
  Leaves a part of the HC in the solid fraction
  (For ammonia fibre explosion, AFEX, almost all HC)
  Requires hemicellulases acting both on solid and dissolved HC
## Classification of pretreatment methods

<table>
<thead>
<tr>
<th>Physical methods</th>
<th>Chemical &amp; Physicochemicals</th>
<th>Biological</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Milling:</strong></td>
<td></td>
<td><strong>Fungi and actinomycetes</strong> (lignin peroxidase, manganese peroxidase, laccase...) White-rot &amp; Brown-rot fungi</td>
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<tr>
<td>- Ball milling</td>
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<td>- Two-roll milling</td>
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<tr>
<td>- Hammer milling</td>
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<tr>
<td><strong>Irradiation:</strong></td>
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<tr>
<td>- Gamma-ray irradiation</td>
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<td>- Electron-beam irradiation</td>
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<tr>
<td>- Microwave irradiation</td>
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<tr>
<td><strong>Others:</strong></td>
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<td></td>
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<tr>
<td>- Hydrothermal</td>
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<tr>
<td>- High pressure steaming</td>
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<tr>
<td>- Extrusion</td>
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<tr>
<td>- Pyrolysis</td>
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</tbody>
</table>

**”Explosion”:**
- Steam, Ammonia, CO₂, SO₂, Acids

**Alkali:**
- NaOH, NH₃, (NH₄)₂SO₃

**Acid:**
- Sulfuric, Hydrochloric & Phosphoric acids

**Gas:**
- ClO₂, NO₂, SO₂

**Oxidizing agents:**
- Hydrogen peroxide
- Wet oxidation
- Ozone

**Solvent extraction of lignin:**
- Ethanol-water extraction
- Benzene-water extraction
- Butanol-water extraction

**Organosolv/ Ionic liquids**
Chipping, milling, grinding

- Particle size reduction to some microns
- Increased surface area
- Some decrystallization occurs improving enzymatic hydrolysis

For enzymatic hydrolysis very small particles required

Very high energy requirements

Extrusion combined with chemicals and heat an option
Irradiation

- Gamma-ray irradiation
- Electron-beam irradiation
- Microwave irradiation (short penetration) requires a liquid (or a wet mtrl), dilute solutions resulting
- Expensive!
- Ultrasound?
Ionic liquids (IL)

- ILs are salts
  - A large organic cation
  - A small anion, usually inorganic
- Liquids at room temperature
- Typically range 80 – 130°C
- Chemically stable
- Disrupts bonds between cellulose, hemicellulose and lignin
- Low degradation to by-products

- How to recycle the IL?
  - High cost
  - Are they safe?

Examples

| 1-Ethyl-3-methylimidazolium chloride [EMIM]Cl |
| 1-Butyl-3-methylimidazolium bromide [BMIM]Br |
| 1-Butyl-3-methylimidazolium acetate [BMIM]Oac |
Hydrothermal process

- Main principle is cooking in liquid hot water generally at 150-210 °C, 5-15 min.
- Autohydrolysis may occur due to organic acids in the mtrl. (mainly acetic acid)
- Hydrates cellulose
- Small removal of lignin

- May result in dilute solutions
- Oligo- and polymeric form

- A variation of hydrothermolysis is the wet-oxidation procedure, where air or oxygen is added
- Lignin is oxidized causing loss

- Best suited for agricultural or hardwood
- No addition of chemicals
- Less requirements for neutralization
- Cheaper construction materials
- Applied in demo-scale by Inbicon (Denmark)
**Alkali**

- Treatment with alkaline solutions
  - Sodium hydroxide
  - Ammonia
  - Potassium hydroxide
  - Lime
  - ...

- Soaking in alkali causes pore swelling

- Internal surface area increases
- More accessible carbohydrates

- Most efficient for agricultural crop low in lignin
- More severe cooking for woody materials
Organic solvents

- Organosolv
  - Methanol
  - Ethanol
  - Acetone
  - Glycols
  - Phenols
- Small addition of mineral acids

- Dissolves lignin in the organic phase
- Recovery of solvent an absolute requirement:
  - Economics
  - Enviromental reasons
  - May be act inhibiting on organisms and enzymes
- Best for agricultural materials
- The Lignol process for fuel ethanol
  - Pilot plant in Vancouver
Biological pretreatment

- Pretreatment using microorganisms:
  - White-rot fungi breaks down lignin
  - Brown-rot fungi breaks down cellulose and hemicellulose
  - Slow process!
  - Loss of material
  - Works at ambient conditions
Physico-chemical methods

Methods that act both chemically and physically

A bit of a grey zone...

- Steam pretreatment (steam explosion)
- Ammonia-freeze explosion (AFEX)
- Hydrothermolysis?
- Wet-oxidation?

**Steam pretreatment**
- Similar to dilute-acid hydrolysis
  - Higher dry-matter content
  - 160-240°C, 1-20 min.
  - Rapid release of the pressure
  - Works well for many materials in general, also softwood
  - Small amount of acid catalyst
  - Inherent acids OK with many materials
  - Disruptive effect from "explosion" not that important

**AFEX**
- Operates at elevated pressure
- Liquid ammonia
- Around 100°C, 10-60 min
- Results in polymeric carbohydrates
- Interesting properties, such as water-holding capacity and gel-formation
- Best for agricultural materials
- High amounts of NH3, e.g., 1.1 kg/kg biomass
Dilute-acid pretreatment

- Addition of an acid, e.g., H2SO4, H3PO4, SO2, Hac, etc.
- Usually < 2%; commonly 0.2-0.5%
- Acid concentration depends on temperature & residence time

Is it pretreatment?
Or is it actually hydrolysis?
Or both?

High DM: steam pretreatment
Low DM: hydrolysis
Steam pretreatment

Biomass

Steam

Reactor

Temp

100 C

160 – 230 C

1–30 min

Time

Boiler

Computer

Flash-vapour

Pretreated material
Steam pretreatment unit

10 litre reactor
160 - 230 °C
Impregnation with H₂SO₄, SO₂ or alkali

Main purposes
Improve the enzymatic hydrolysis of cellulose
Hydrolysis of hemicellulose
10 kg impregnation liquid per kg straw
Soak for 30 – 60 min

Press to 40% DM
Spray acid to desired concentration and DM of straw
Mix for 10 – 30 min
Small amount of acid
Impregnation

Impregnated wood chips

Steam pretreated
SO$_2$, 210°C, 5 min

Contains potential inhibitors

Extractives
Sugar degradation products e.g. Furans and acids
Lignin degradation products (phenolic compounds)
Scanning Electron microscope Images

Steam pretreated spruce

Wiman et al., unpublished
Impregnated material

Straw

Steam pretreated
0.2 % H$_2$SO$_4$, 190 C, 10 min
Conditions? Depend on purpose
Conditions? Depend on purpose
Conditions? Depend on purpose

Biomass

Reactor

Filter

Solids

Liquid

Fermentation

Reaction

Separation

Pulping → Pulp

Heat & Power → Electricity

Enzymatic hydrolysis → Fermentation

- Ethanol
- Butanol
- Lactic acid
- Other

Furfural

Acids (levulinic, Formic etc)

Oligomers (Building blocks for polymers)
Example:
Fermentation of all carbohydrates
  Yield of sugars
  Concentration of sugars/product
  Fermentability

Example:
Oligomers as building blocks
  Molecular weight distribution
  Structure (side groups etc)
  Purity
  etc

Assessment? Depends on purpose

Requires subsequent steps
  Enzymatic hydrolysis
  Fermentation
  SSF
  Separation steps
Severity factor

\[ \log(R_0) = \log[t \times \exp(T - T_{\text{ref}}/14.75)] \]

The severity factor is a pseudo-first-order reaction that combines the treatment temperature (T) and residence time (t) in one value and provides an approximate indication of the treatment conditions.

- Severity increases with:
  - Temperature
  - Residence time
  - Acid concentration

Low severity

- Poor improvement of enzymatic hydrolysis!

High severity

- Formation of by-products inhibitory for fermentation!
Acid hydrolysis of pine

1st acid-hydrolysis step: 180-200 °C

2nd acid-hydrolysis step: 200-225 °C

Traditional two-step hydrolysis: Cooling of substrate

Consolidated two-step hydrolysis: Profile OR step-wise temperature change
Improvement of temperature control in steam pretreatment

Control by pressure: Fast, requires pT-data

![Graph showing temperature control](image)

- **Glucose [g/100g]**
- **Mannose [g/100g]**
- **Xylose [g/100g]**
- **Total C6 Sugars**

![Graph legend](image)
By-products after dilute-acid hydrolysis
Combined pretreatment and enzymatic hydrolysis of Barley Husk
Combined pretreatment and enzymatic hydrolysis of Barley Husk

0.3 g/l HMF
1 g/l Furfural
3 g/l Acetic acid

Rather low in inhibiting compounds
Microwave pretreatment

- Microwave oven
- Rotor
- Shell
- Control unit
- Treatment vessel
Continuous pretreatment reactor
Sekab E-technology
Extraction of hemicellulose from barley husks

Steam explosion

Filtration - LAROX filter press

Concentration using UF
Extraction of Arabinoxylan from Barley husks
Screening with microwave oven

Impregnation with water (pH 6.5)
Res. time: 5 min

Temperature: 200°C
Res. time: 5 min

Alexandra Andersson, Henrik Stålbrand
Biochemistry, LU
Autohydrolysis \textit{(barley husks)}

15-20\% yield is possible to achieve without removing the acetyl groups or significantly decreasing the molecular mass

### Microwave irradiation

- **Molecular mass (kDa)**
- **Yield (\%)**
- **Mw**
- **Severity factor**

### Steam pretreatment

- **Xylan yield (\%)**
- **Severity factor**
Steam pretreatment with NaOH

25-35% yield possible to reach when using modest concentrations of NaOH
If pH decreases, the molceular mass decreases
Which condition is optimal?

**Only water**
- Acetyl groups remains
- No costs for chemicals
- Lower maximum yield

**With NaOH**
- Higher maximum yield
- De-Acetylation occurs
- Chemical costs
Test procedure – effect of pretreated slurry on enzymatic hydrolysis

I. Influence of various concentrations of the prehydrolysate

II. Whole slurry after pretreatment

III. Influence of fermentation of the prehydrolysate

IV. Influence of addition of various substances

In some cases, addition of e.g. nutrients, ethanol, glycerol or sugar solution

Tengborg et al Enzyme & Microbial Technol (2001)
Effect of pretreated slurry on enzymatic hydrolysis at low enzyme dosage

Cellulose (% conversion)

Time (h)

0% prehydrolysate
20% prehydrolysate
60% prehydrolysate
80% prehydrolysate
100% prehydrolysate
sugar solution
Whole slurry after pretreatment
washed

Tengborg et al Enzyme & Microbial Technol (2001)
Two-step steam pretreatment

Pretreatment step 1

180-190°C
Low severity

Hemi in liquid

Pretreatment step 2

210°C
High severity

High enzymatic digestibility
Two-step pretreatment of spruce (Yields of some sugars)
Improved One-step pretreatment of spruce

- Two-step dilute acid pretreatment
- Step-wise increase between two temperatures
- Linear increase in temperature

Temperature: 190 - 226 °C
Total residence time: 5 - 12 min
2.5% (w/w) SO₂

Pretreatment of wheat straw (Xylose yield)

Overall yield of xylose (g/100g dry straw)

<table>
<thead>
<tr>
<th>Pretreatment conditions</th>
<th>Overall yield of xylose</th>
</tr>
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<tbody>
<tr>
<td>190°C, 2 min</td>
<td>18.5</td>
</tr>
<tr>
<td>190°C, 5 min</td>
<td>17.0</td>
</tr>
<tr>
<td>190°C, 10 min</td>
<td>15.5</td>
</tr>
<tr>
<td>200°C, 2 min</td>
<td>14.0</td>
</tr>
<tr>
<td>200°C, 5 min</td>
<td>12.5</td>
</tr>
<tr>
<td>200°C, 10 min</td>
<td>11.0</td>
</tr>
<tr>
<td>210°C, 2 min</td>
<td>9.5</td>
</tr>
<tr>
<td>210°C, 5 min</td>
<td>8.0</td>
</tr>
<tr>
<td>210°C, 10 min</td>
<td>6.5</td>
</tr>
</tbody>
</table>

Maximum theoretical

Pretreatment of straw (Glucose yield)

Enzymatic hydrolysis
Maximum theoretical

Overall yield of glucose (g/100g dry straw)

Pretreatment conditions

Finally...

• Several pretreatment methods available
  High sugar yields for agricultural residues

• Dilute acid pretreatment /steam pretreatment
  High sugar yields for most biomass

• Several pilot/demo plants using pretreatment are in operation
  • Abengoa – Salamanca (E)
  • Chemtex – Tortona (I)
  • Inbicon – Kalundborg (DK)
  • SEKAB – Örnsköldsvik (S)
• Assessment of pretreatment difficult
  - Process configuration
  - Process conditions (the whole process)
  - Type of catalyst (affects downstream)
  - Impregnation method
  - Type of enzymes (and dosage)
  - Type of fermentation organism

• Technical-economical evaluation of the whole integrated process
Building for Demo scale Pretreatment Unit

Bottom of reactor
Research/pilot plant

- Two-steps dilute acid- and enzymatic hydrolysis
- Capacity: 2 tons of dry substance per 24 hours
- Complete plant with recirculation of process streams
- Investment 22 million Euro
- Inauguration: May 26 2004

Plan

Demo plant 2010/11
Industrial scale 2014
Problems in pilot plant (deposits)
Problems in pilot plant (leakage)