Forbehandling af biomasse

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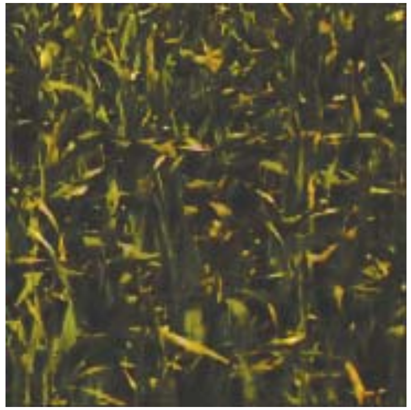
Præsentation

7. Maj 2013

Restabioasse fra Landbrug og Naturarealer til Biogasproduktion

Biomasses relevant for DK

- Manure – Today around 5-6% is used!
- The goal is to use 50% by year 2020
- Industrial wastes are very popular but limited
- Agricultural residues
  - Straw
  - Beet-tops
  - Garden-park wastes
  - Sea weed
- Energy crops
  - Maize
  - Grass
  - Beets



Substrate handling

Approx. size distr.:
1 +/- 0.8cm

Biomass sources

Plant material (99% of the worlds annual production of organic matter is plants, only 1% is of animal origin)

Energy crops (special crops cultivated for energy production purposes

- Agricultural residues

Organic matter in residue and wastes

Components of lignocellulose

- *Cellulose*:

  unbranched polymer of glucose

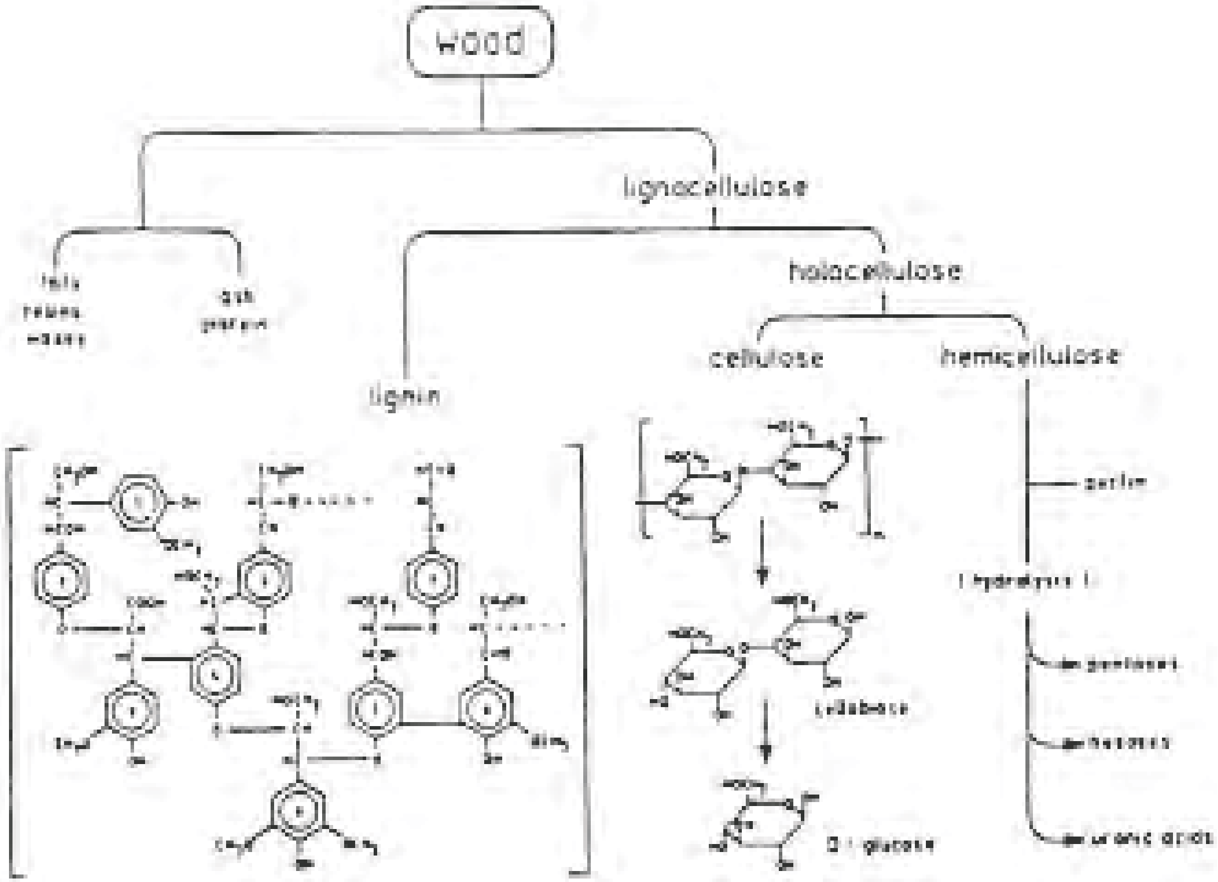
- *Hemicellulose*:

  branched polymer of various sugar units (*e.g.* xylose, mannose or glucose)

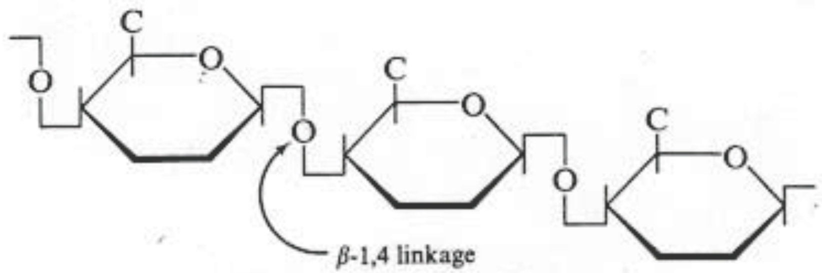
- *Lignin*:

  complex, cross-linked and 3-D aromatic polymer of phenylpropanoid

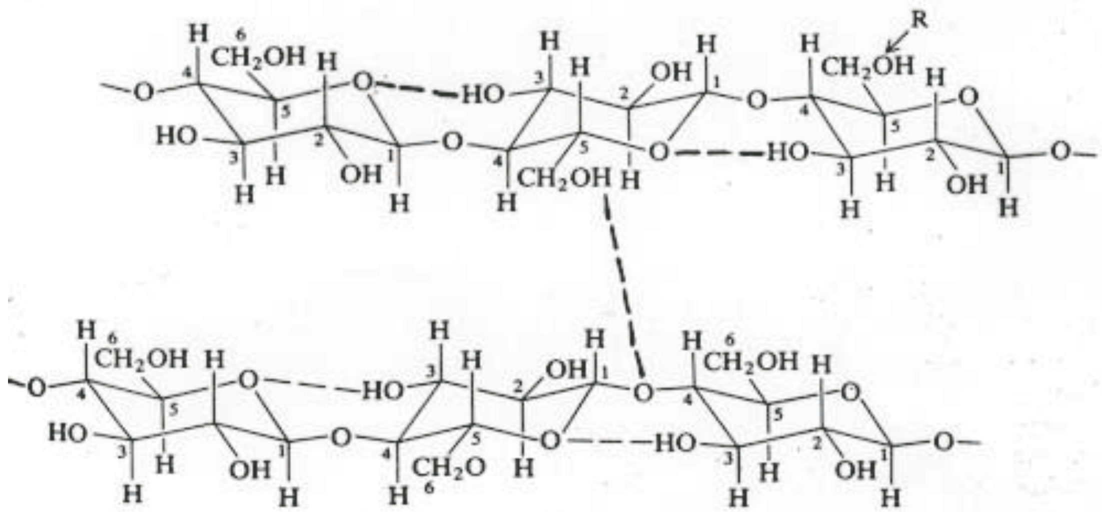
Plant cell wall contains sugars and lignin



Chemical structure of cellulose

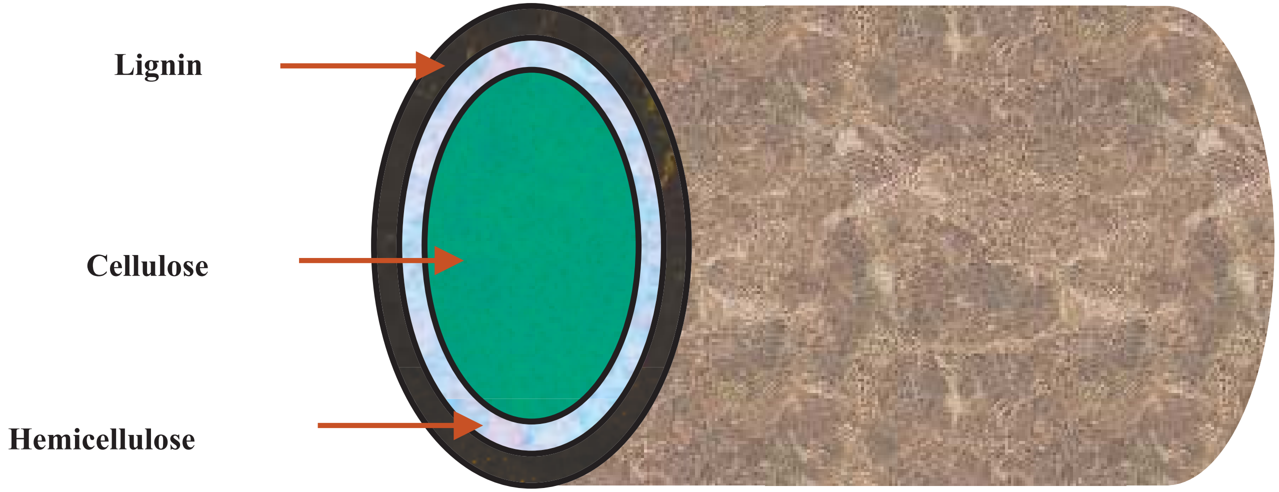


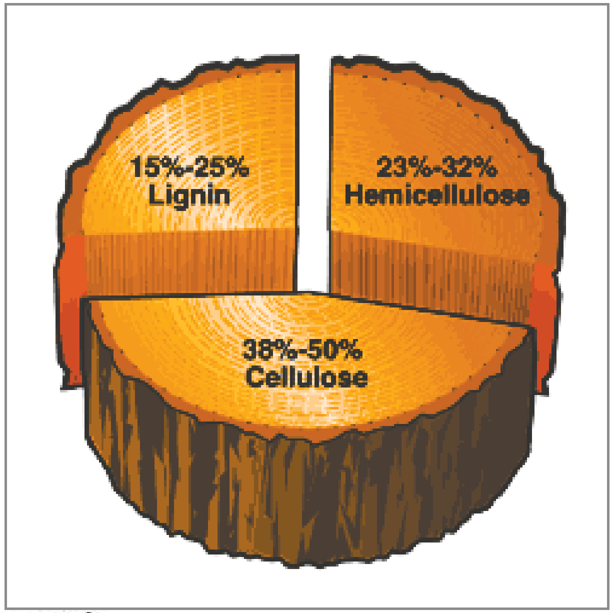
The glucose chain of cellulose



R is $-CH_3$, $-\underset{\underset{O}{\|}}{C}CH_3$, and $-CHCOONa$, respectively.

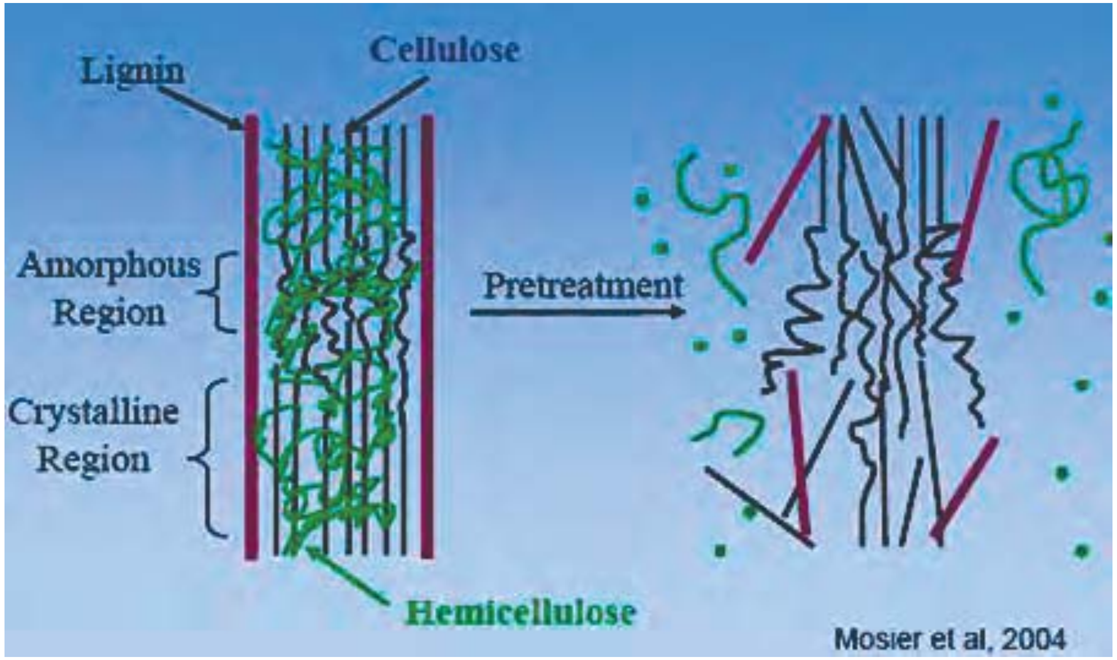
Structure of lignocellulosic material





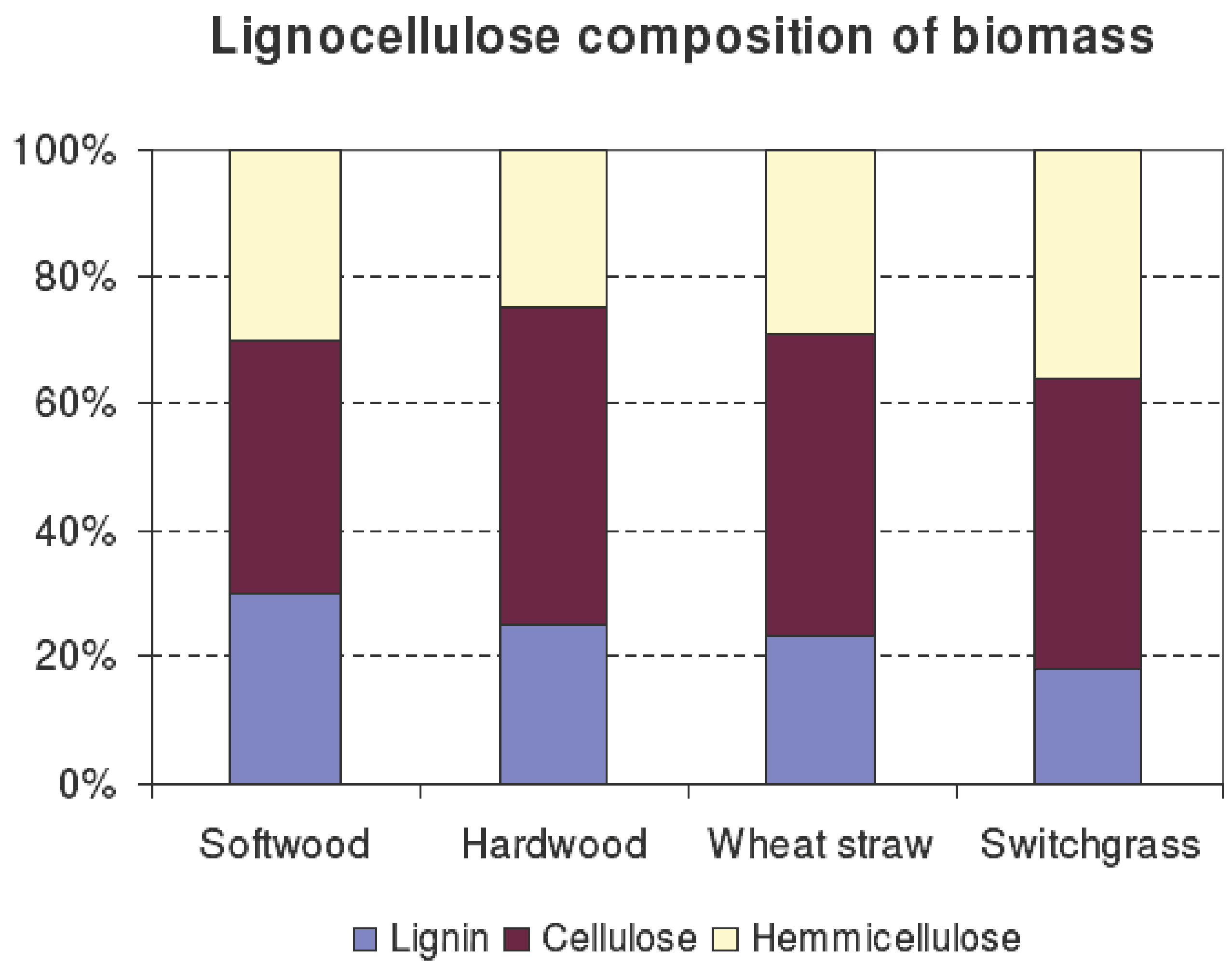
Pretreatment

- **The objectives are:**
  - To increase the surface area and porosity
  - Reduce the crystallinity of cellulose
  - To disrupt the heterogeneous structure of Lignocellulose



Effect of pretreatment on the Lignocellulosic Complex

Chemical Composition of Some Feedstocks



Composition of various lignocellulosic biomasses

Table 3 *Composition of different lignocellulosic materials used for fuel ethanol production*

	Cellulose (%) [a]	Hemicellulose (%) [a]	Lignin (%) [a]	Mannan (%) [a]	Galactan (%) [a]	Xylan (%) [a]	Araban (%) [a]
Hardwood							
alder	40.5		20.8	1.5	0.8	16.1	
aspen	43.2		16.0	2.2	0.5	15.1	
birch	40.7		19.1	1.7	0.7	20.0	
White oak	43.6		23.2	2.9	0.4	18.0	2.4
Willow	33.1		23.3	1.6	1.4	10.3	
Yellow popular	49.9		18.1	4.7	1.2	17.7	1.8
Softwood							
pine	42.4		24.7	11.8	1.9	4.7	1.6
spruce	41.6		25.7	11.5	2.0	4.7	
White cedar	41.0		30.7	8.0	1.4	10.0	1.2
Agricultural waste							
Bagasse	38.0	34.0	11.0				
Carnstalk	33.5	32.6	11.0	0	0.8	18.0	2.2
Corn cob	32	44.3	12.9			25.0	3.0
Sugar beet pulp	22	59[b]	2		5	2	21
Wheat straw	34.0	27.6	18.0	0	0.7	18.5	1.6
Others							
Municipal waste	76	13	11				
Energy grass	28.0	16.5	5..3		1.0	9.7	2.7

[a] The amount is given in % w w on dry matter basis

[b] Includes both the hemicellulose and the pectin

Purpose of pretreatment

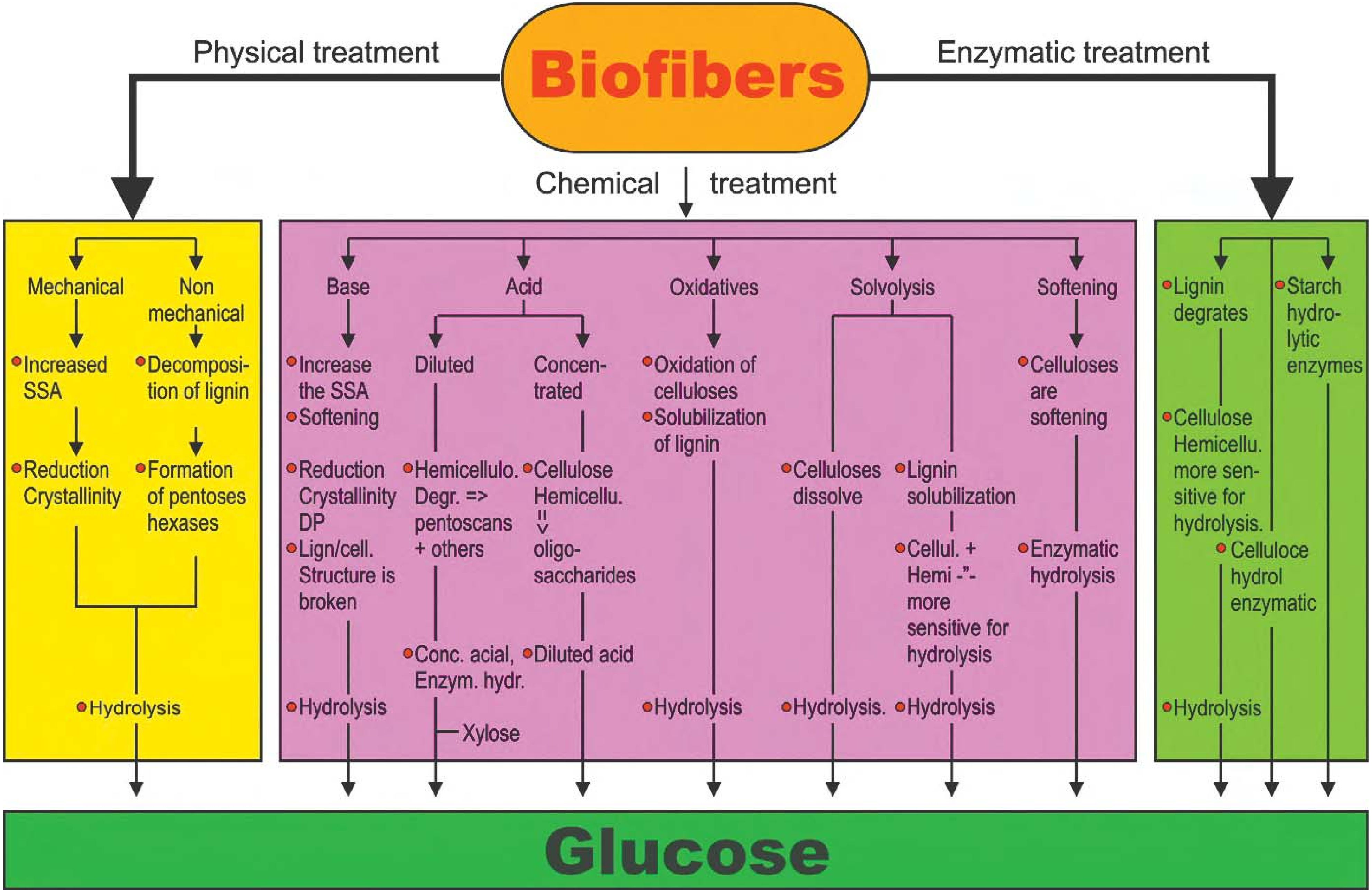
Un-treated biomass is rigged and smooth

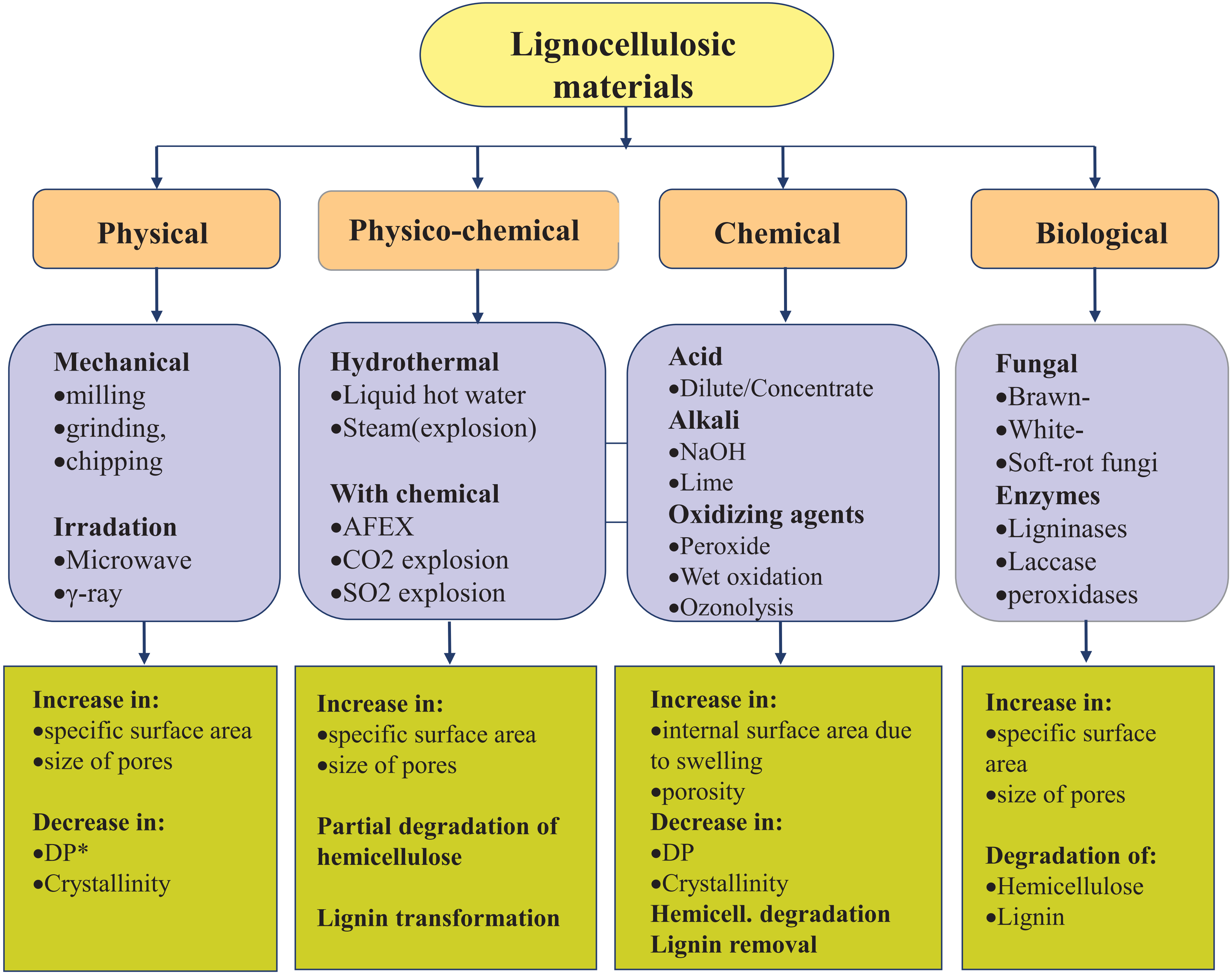
Polymers inaccessible for hydrolytic enzymes

- Cellulose, hemicellulose and lignin form a complex matrix

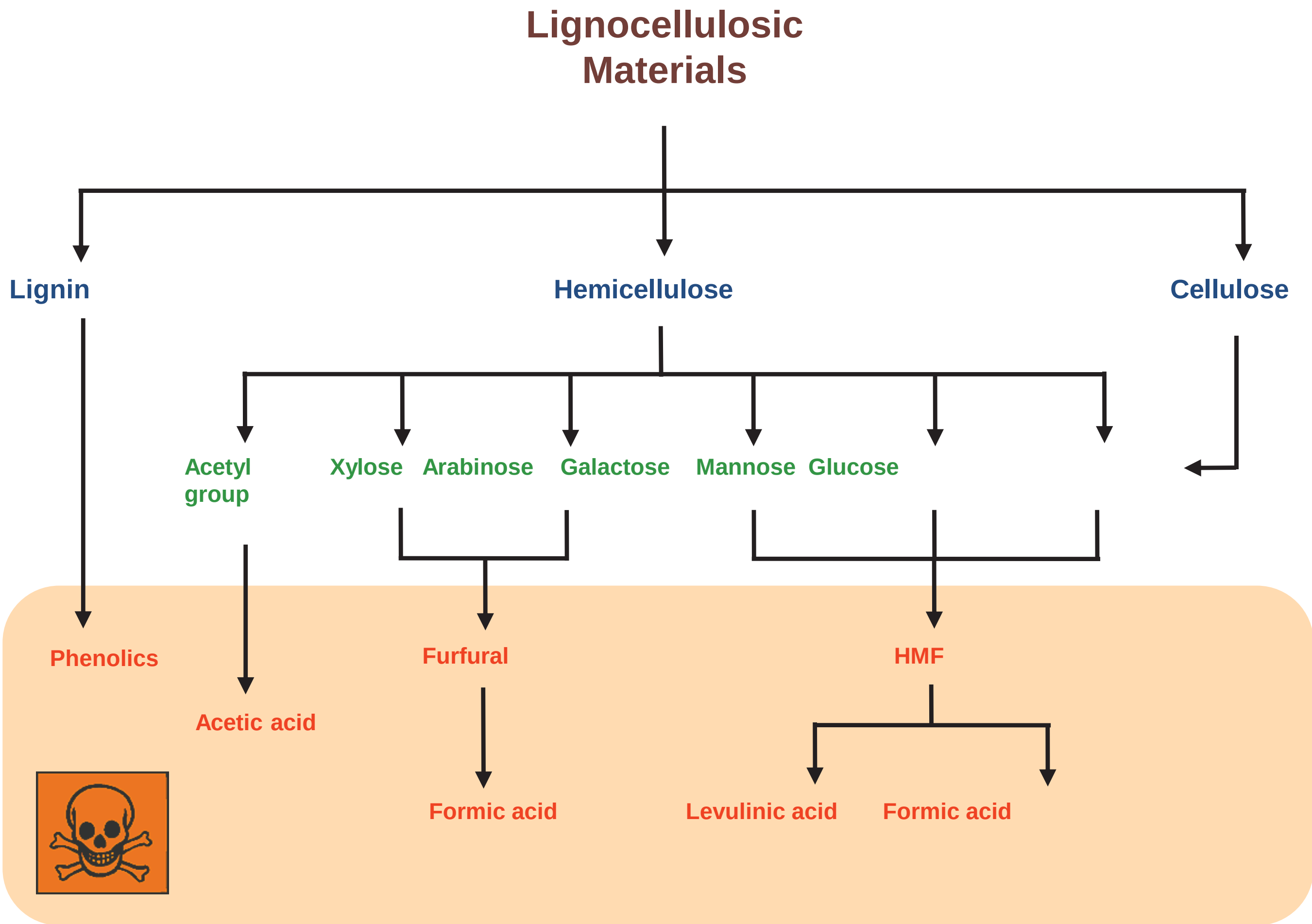
Pretreatment should:

- Increase of the surface area, better access of enzymes to carbohydrates
- Decrease cellulose crystallinity
- Degrade/disrupt/soften lignin structure
- Leave most of cellulose intact


Biofibers
Physical treatment
Enzymatic treatment
Chemical treatment
Mechanical
Non mechanical
Increased SSA
Decomposition of lignin
Reduction Crystallinity
Formation of pentoses hexases
Hydrolysis
Base
Acid
Oxidatives
Solvolysis
Softening
Increase the SSA
Softening
Diluted
Concentrated
Oxidation of celluloses
Solubilization of lignin
Celluloses are softening
Reduction Crystallinity DP
Lign/cell. Structure is broken
Hemicellulo. Degr. => pentoscans + others
Cellulose Hemicellu. => oligosaccharides
Celluloses dissolve
Lignin solubilization
Cellul. + Hemi -"- more sensitive for hydrolysis
Enzymatic hydrolysis
Conc. acial, Enzym. hydr.
Diluted acid
Xylose
Hydrolysis
Hydrolysis.
Lignin degrates
Starch hydrolytic enzymes
Cellulose Hemicellu. more sensitive for hydrolysis.
Celluloce hydrol enzymatic
Glucose


Lignocellulosic materials
Physical
Physico-chemical
Chemical
Biological
Mechanical
•milling
•grinding,
•chipping
Irradation
•Microwave
•γ-ray
Hydrothermal
•Liquid hot water
•Steam(explosion)
With chemical
•AFEX
•CO2 explosion
•SO2 explosion
Acid
•Dilute/Concentrate
Alkali
•NaOH
•Lime
Oxidizing agents
•Peroxide
•Wet oxidation
•Ozonolysis
Fungal
•Brawn-
•White-
•Soft-rot fungi
Enzymes
•Ligninases
•Laccase
•peroxidases
Increase in:
•specific surface area
•size of pores
Decrease in:
•DP*
•Crystallinity
Increase in:
•specific surface area
•size of pores
Partial degradation of hemicellulose
Lignin transformation
Increase in:
•internal surface area due to swelling
•porosity
Decrease in:
•DP
•Crystallinity
Hemicell. degradation
Lignin removal
Increase in:
•specific surface area
•size of pores
Degradation of:
•Hemicellulose
•Lignin

Formation of inhibitors



Enzymatic pretreatment

Enzymes for hydrolysis of the pretreated material

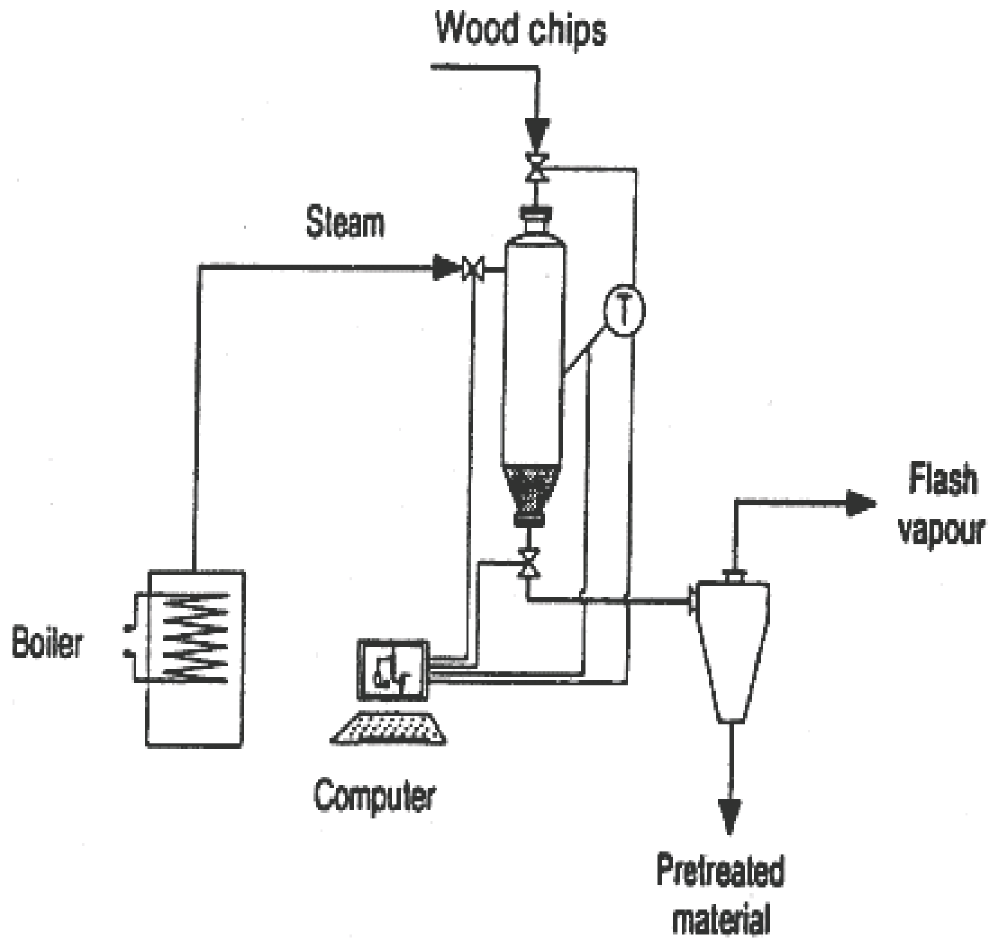
Examples of enzymes - Cellic® CTec2 (Novozymes) ; Accelerator (Dupont)

Mixing of enzymes with the pre-treated material

Example: The most common methods and corresponding conditions for pretreatment of wheat straw

Pretreatment technology	Procedure/Chemicals	Temp. (°C)	Reaction times	Solid loading (wt.%)
Dilute acid	0.5–5.0% H_2SO_4	120–180	5–60 min	5–30
Steam Explosion	saturated steam	160–230	5-30 min	<30
Alkaline peroxide	>0.25 g H_2O_2/g biomass, pH=11.5	25-35	3-24 h	<10
Wet oxidation (Alkaline)	6-12 bar O_2 pressure (+ 0.11 g Na_2CO_3/g biomass)	185-195	10-15 min	6
Lime	0.05–0.15 g $Ca(OH)_2$/g biomass	85-135 50-65	1–3 h 24 h	5–20

Steam explosion



- 200 g wheat straw
- 200°C
- 20 bar
- 5 minutes
- Rapid pressure release

Hydrothermal pre-treatment of rapeseed straw

Solid fraction

Cellulose and lignin

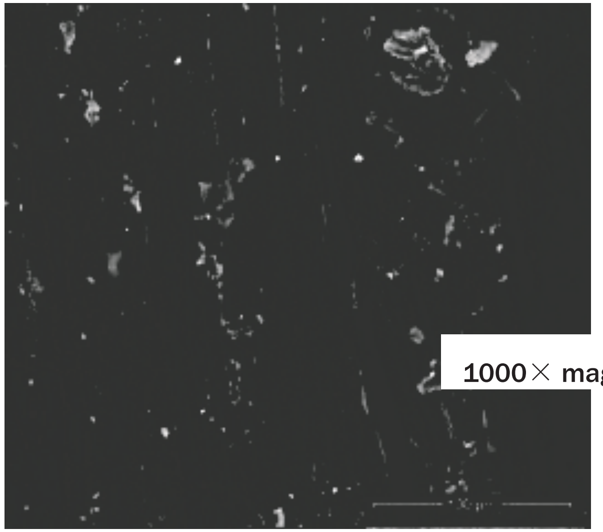
Liquid fraction

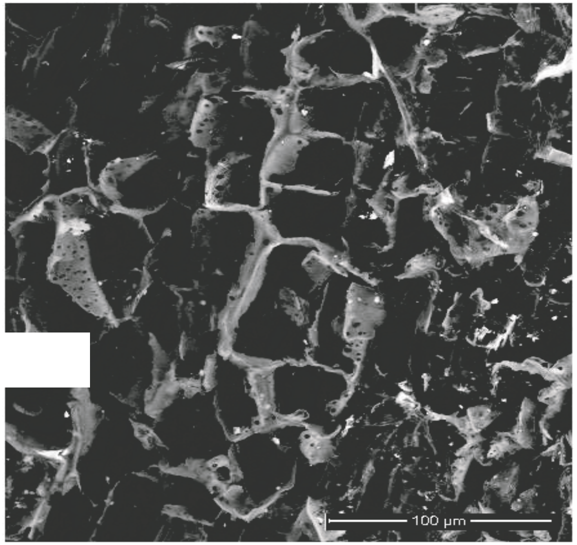
(inhibitors, hemicellulose,

and salts

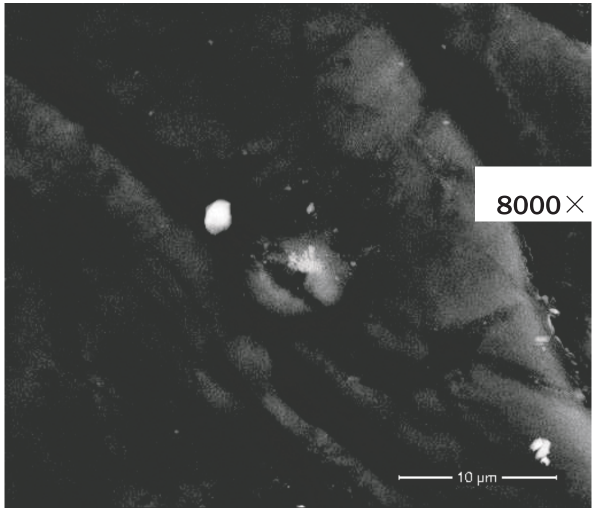
Liquid fraction (hydrolysate)		Solid fraction	
Characteristics	*Value*[a]	*Characteristics*	*Value*[b]
Glucose	1.5	Cellulose	53.9
Xylose	11.1	Xylan	8.8
Arabinose	1.5	Arabinan	0.3
Total hemicellulose	12.6	Total Hemicellulose	9.1
TS(g/l)	27.9	Klason lignin	24.2
VS(g/l)	25.6	Ash	2.9
		Residual	9.9

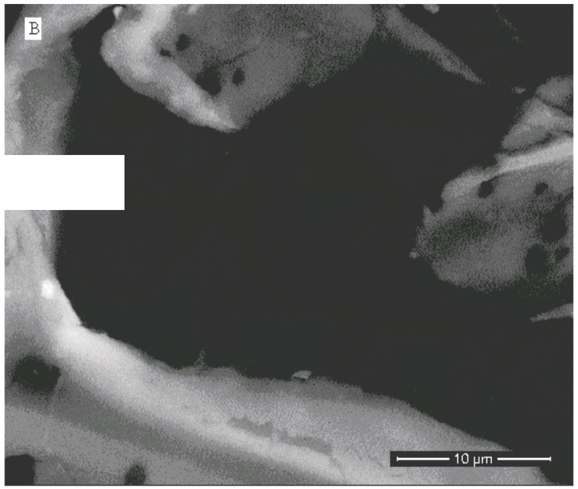
Physical effect of hydrothermal pretreatment





1000× magnification





8000× magnification

Untreated

Treated

Hydrothermal pretreatment of rapeseed straw

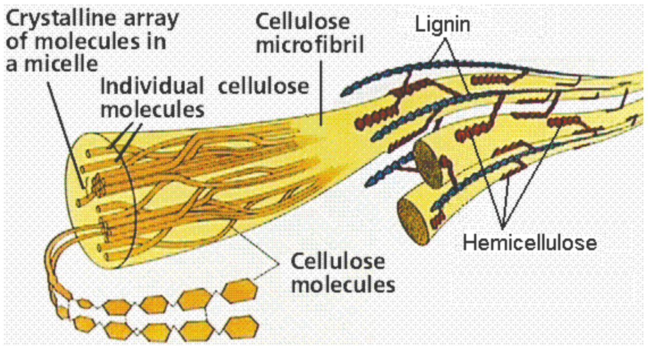
- Temperature (160, **180**, 190 ^{o}C)
- Reaction time (0, 5, 7.5, **10**, 15 min)
- Solid content (5, 10, 15, **20**, 30, 50%)
- Use of sulphuric acid as catalyst (0, 0.5, **1**%) → **70% Ethanol yield based on the solid phase alone**
- Mixing time of sulfuric acid

✓ **Maximization of sugar release (hemicellulose solubilization)**

✓ **Minimization of inhibitors formation (furfural, HMF)**

✓ **Maximization of ethanol production**

For more details: Lu X., Zhang Y., and Angelidaki (2009). Optimization of H2SO4-catalyzed hydrothermal pretreatment of rapeseed straw for bioconversion to ethanol: focusing on pretreatment at high solids content. *Bioresource Technol.* 100(23)3048-3053.



Pretreatments applied on digested manure for biogas production

- **Physical**
  - Mechanical
  - Decompression explosion
  - Thermal
- **Chemical**
  - NaOH
  - NH_4OH
  - Base combinations
- **Microbiologic**
- **Enzymatic**

Effect of the different treatments on the biodegradability achieved from cattle manure

Treatment		Biodegr. incr. (%)
Maceration	< 0.35 mm	20
Maceration	2 mm	16
Decompression explosion		17
NaOH	20 g/kgVS	13
NaOH	40 g/kgVS	20
NH_4OH	< 20 g/kgVS	0
NH_4OH	40 g/kgVS	-
$NaOH:KOH:Ca(OH)_2$	40 g/kgVS	20

Common pretreatments

Dilute acid (high temp. + pressure, short time)

Removes hemicellulose, alters lignin structure

Alkaline (low temp, no pressure, long time)

Removes lignin and some hemicellulose

Oxidative (H_2O_2, low temp, no pressure, long time)

Removes lignin and hemicellulose

Jerusalem artichoke

- **Lignocellulosic biomass**
  - Above ground
- **Root vegetables (tubers)**
  - Underground
  - Up to 20% w.w. is sugars
- **Grow up to 3m tall**
- **Cultivated by SLU at Alnarp, Sweden**
- **Plants harvested on three occasions**
  - September, October and December

Example of different pretreatment for biogas production

Using strong oxidizer (e.g. H_2O_2)

Up to 80% lignin degradation into many products

Aromatic aldehydes

Carboxylic acids

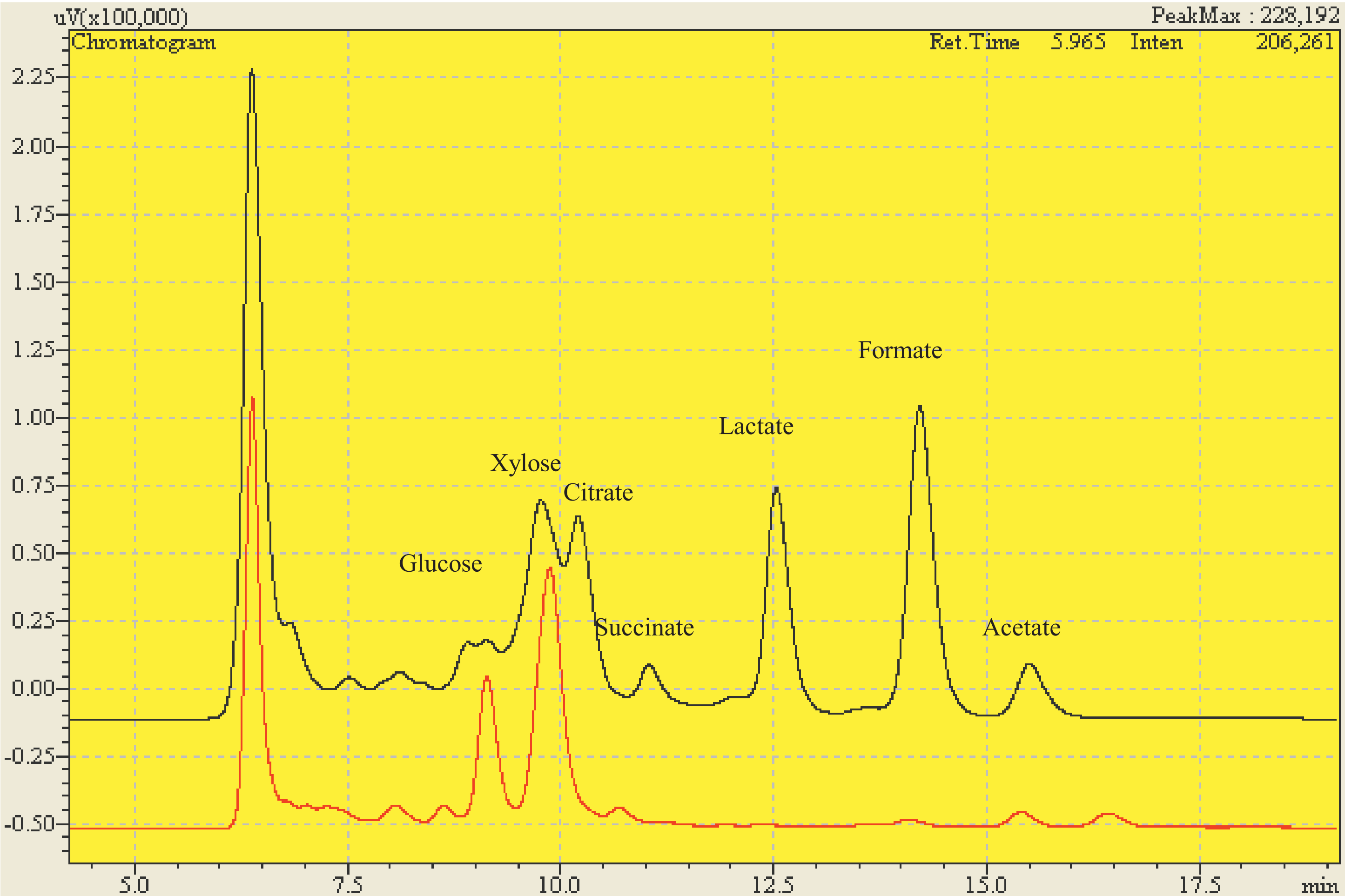
Could favor anaerobic digestion of lignin

Sulfuric acid potentially causes problems

Sulfate reducing bacteria compete w. methanogenes

Solid material post pretreatment

Lignin degradation products in liquid



Black = H2O2 hydrolysate

Red = H2SO4 hydrolysate

Conclusions

Pretreatments have the aim in releasing the sugars from the lignocellulosic structure

Pretreatment is not always needed

Enzymes are existing in a biogas reactor

The pretreatments should be cheap and simple