Biomass pretreatment

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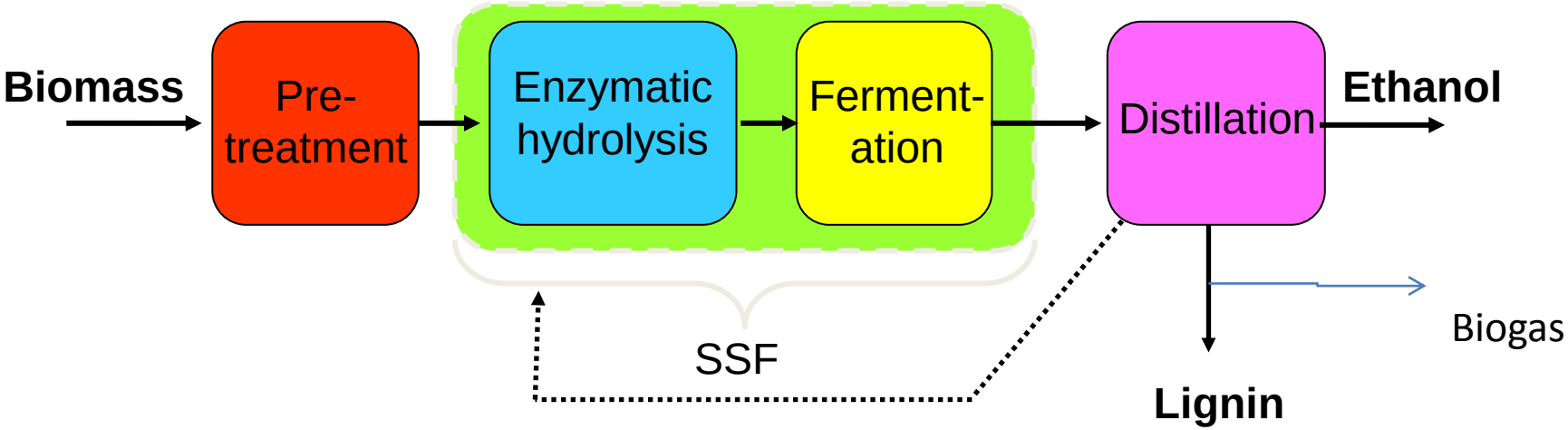
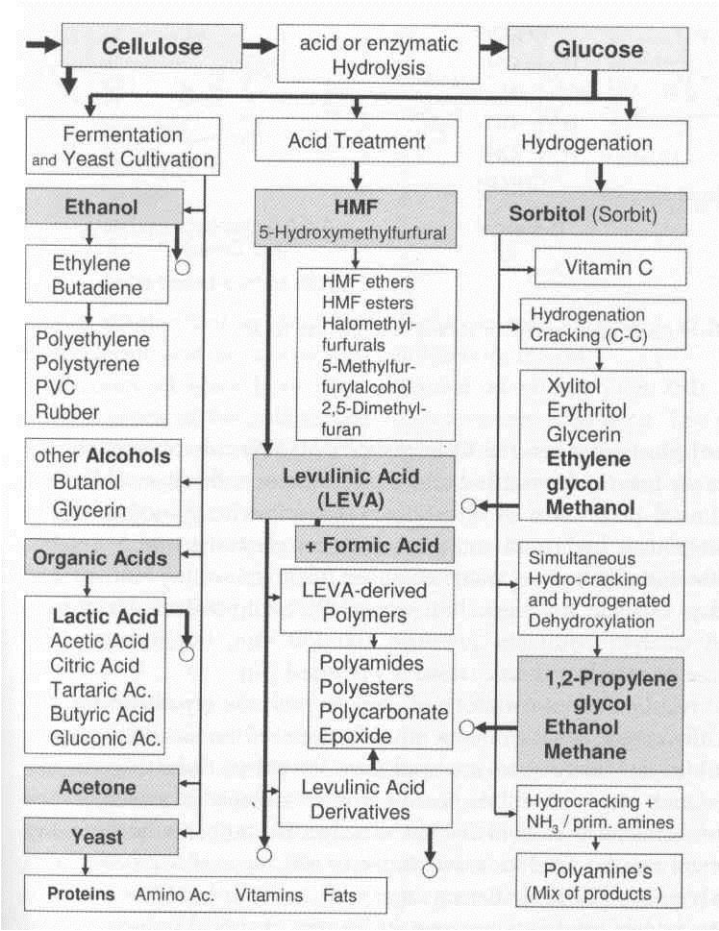
Research @ Chem Eng – Lund Examples

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



Biorefinery concept



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

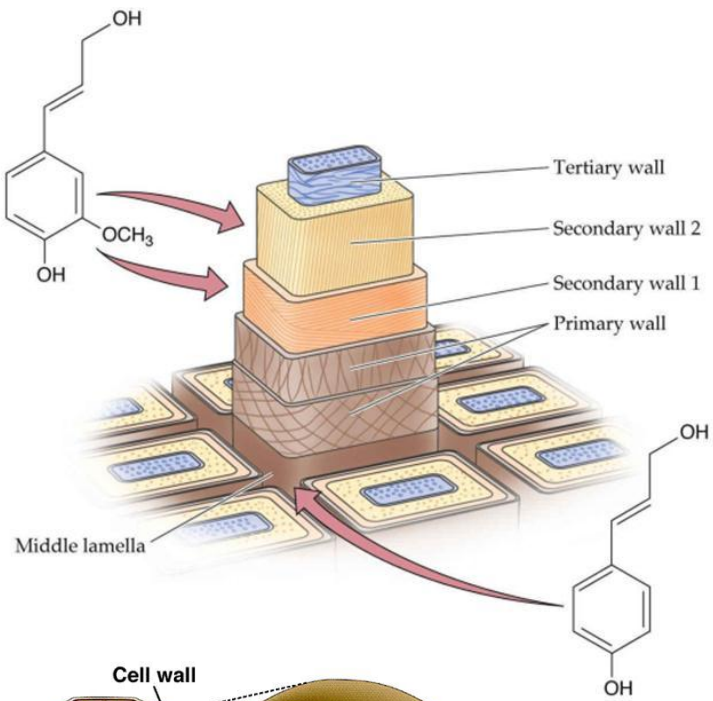
Pretreatment
What is THAT?

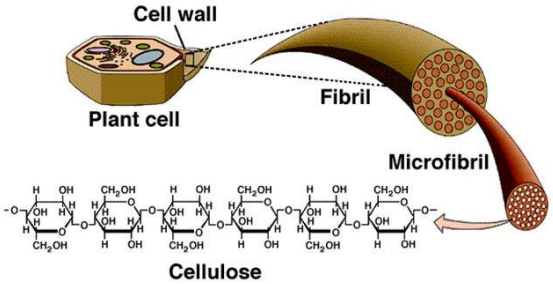
- Some kind of action before the treatment…
- Likely to be different for different raw materials and desired products

- 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)

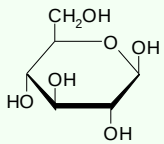
Lignocellulosic materials rather recalcitrant

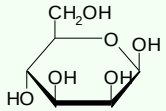
- Starchy materials mainly glucose units
  - Less severe conditions needed
- Cane mostly sucrose – extractable
- Avoid drying of the lignocellulosic materials: pore shrinking, limits diffusion etc.

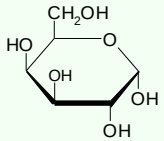


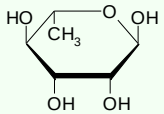


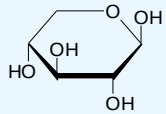
Products & By-products

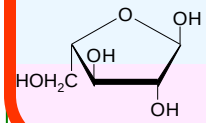

glucose

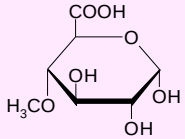

mannose

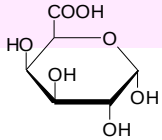

galactose


rhamnose


xylose

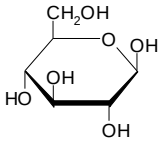

arabinose

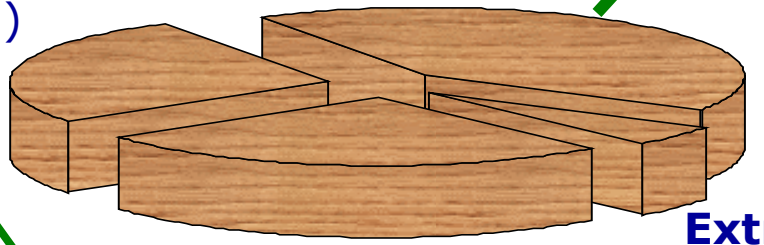

glucurono-pyranose


galacturono-pyranose

Hemicellulose
(20%)

Cellulose
(42%)

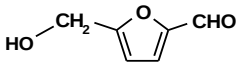

glucose



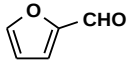
Extractives

Lignin
(21%)

FURALDEHYDES



HMF



furfural

ETHANOL

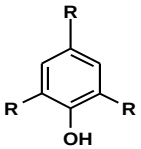
ALIPHATIC ACIDS

CH_3COOH
acetic acid

HCOOH
formic acid

$CH_3COCH_2CH_2COOH$
levulinic acid

PHENOLICS



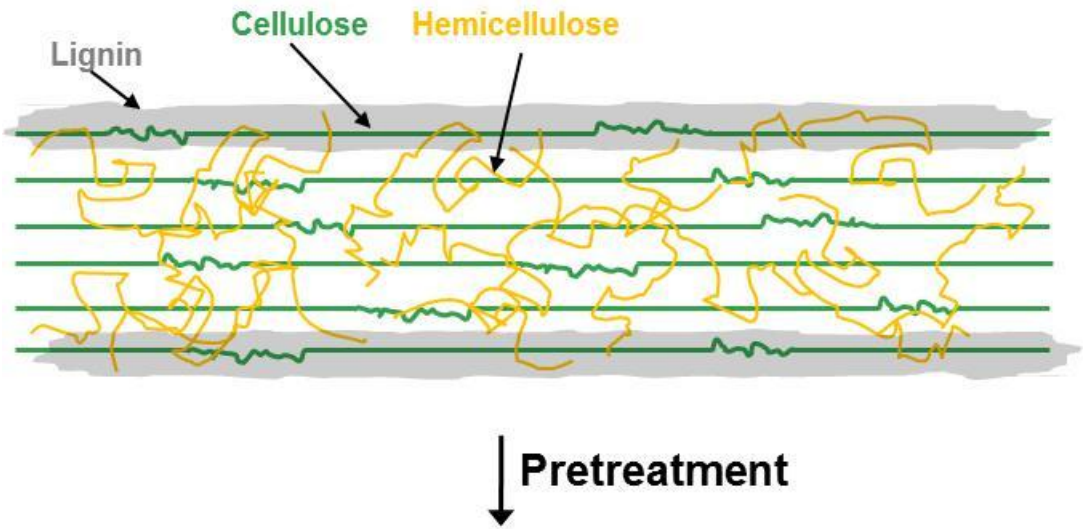
EXTRACTIVES
Terpenoids etc.

FERMENTATION INHIBITORS

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 (H_2SO_4, SO_2, H_3PO_4, Acetic acid…))
  Results in hydrolysis of the hemicellulose (HC) to monomer sugars and minimize the need for hemicellulases

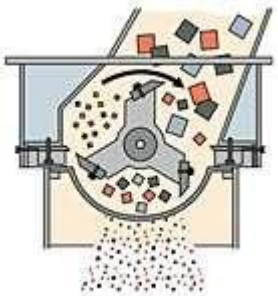
- **Methods working close to neutral conditions**
  e.g. steam pretreatment and hydrothermolysis
  Solubilise most of the HC (due to acetyl groups in HC → acetic acid)
  Do not usually result in total conversion to monomer sugars
  Requires hemicellulases acting on soluble oligomers of the HC

- **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

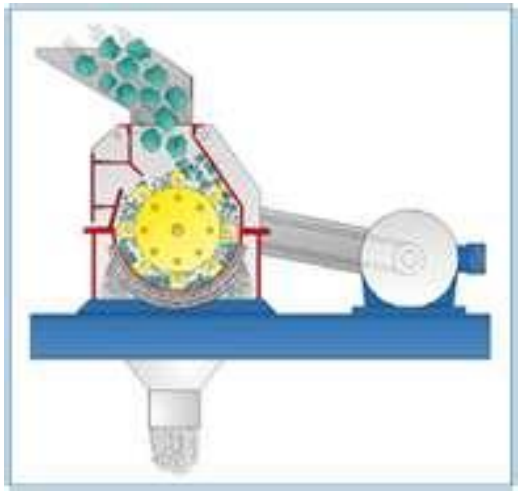
Classification of pretreatment methods

Physical methods	Chemical & Physicochemicals	Biological
Milling: - Ball milling - Two-roll milling - Hammer milling **Irradiation:** - Gamma-ray irradiation - Electron-beam irradiation - Microwave irradiation **Others:** - Hydrothermal - High pressure steaming - Extrusion - Pyrolysis	**”Explosion”:** - Steam, Ammonia, CO_2, SO_2 , 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**	**Fungi and actinomycetes** (lignin peroxidase, manganese peroxidase, laccase…) White-rot & Brown-rot fungi

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

Irradiation:

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

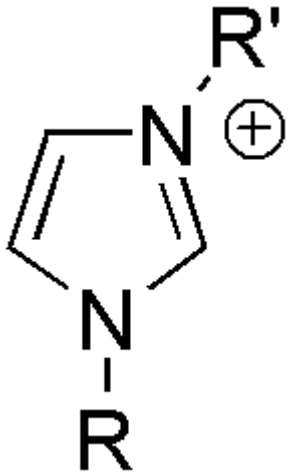
Ionic liquids (IL)

- 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 increaes
- More accessible carbohydrates

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

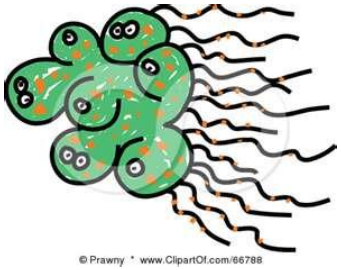
Organic solvents

- 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?

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

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

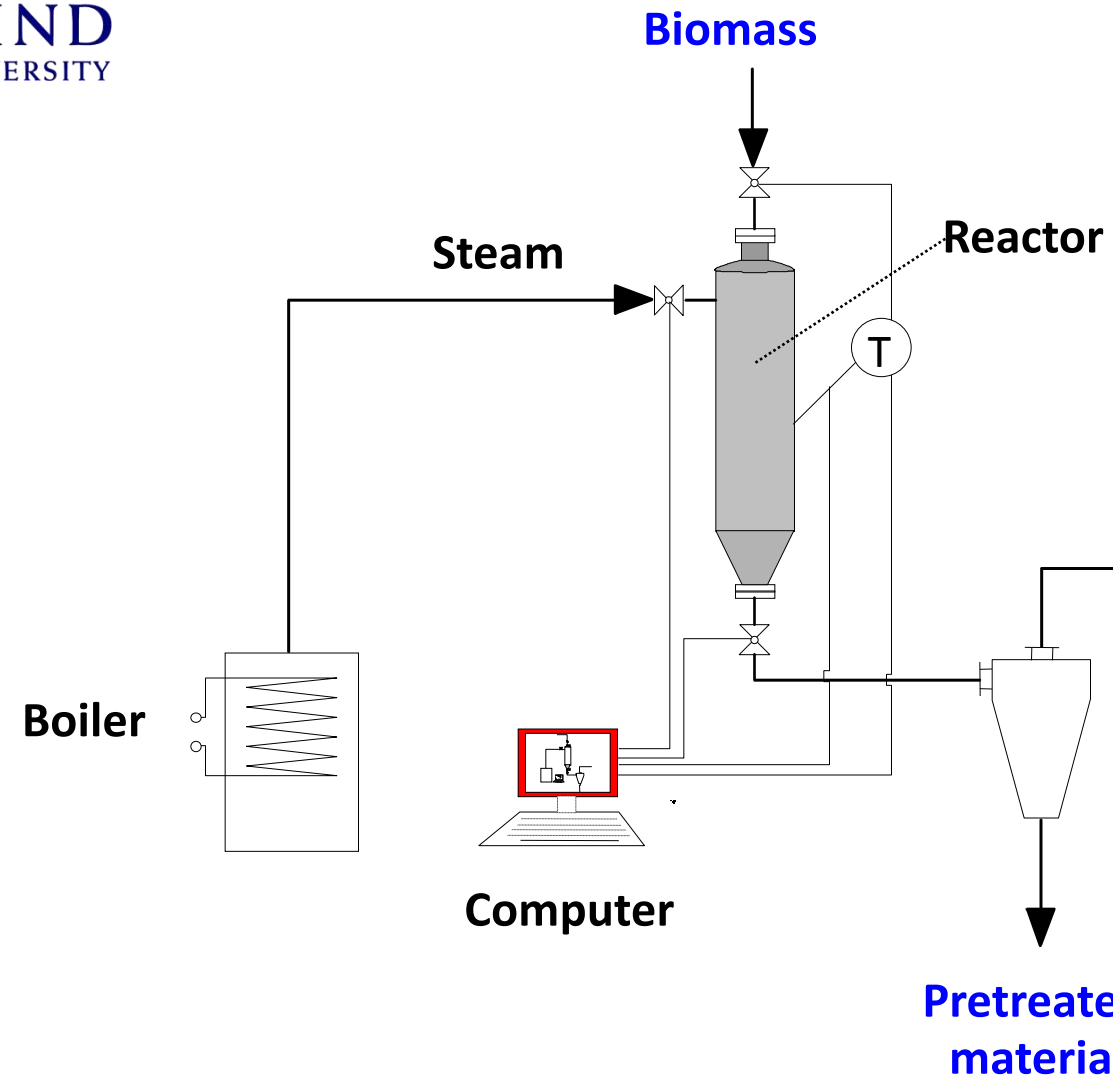
Dilute-acid pretreatment

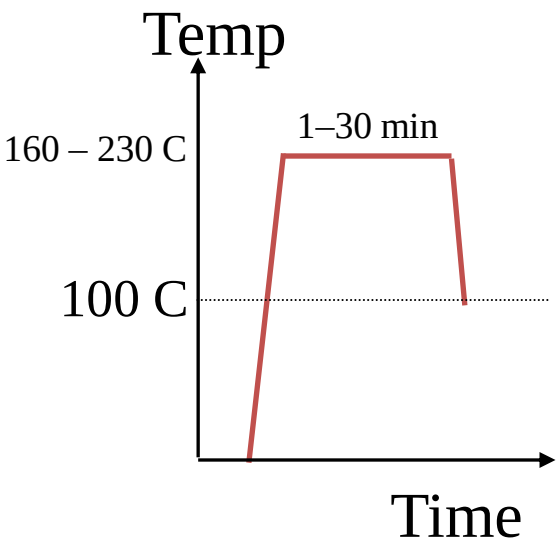
- Addition of an acid, e.g., H_2SO_4 H_3PO_4, SO_2, Hac, etc.
- Usually < 2%; commonly 0.2-0.5%
- Acid concentration depends on temperature & residence time

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

High DM: steam pretreatment
Low DM: hydrolysis

Steam pretreatment





Steam pretreatment unit

10 litre reactor

160 - 230 °C

Impregnation with H_2SO_4, SO_2 or alkali

Main purposes

Improve the enzymatic hydrolysis of cellulose

Hydrolysis of hemicellulose

Soaking

10 kg impregnation liquid per kg straw
Soak for 30 – 60 min

Press to 40% DM

Spraying

Spray acid to desired concentration and DM of straw

Mix for 10 – 30 min

Small amount of acid

Impregnation

Impregnated wood chips

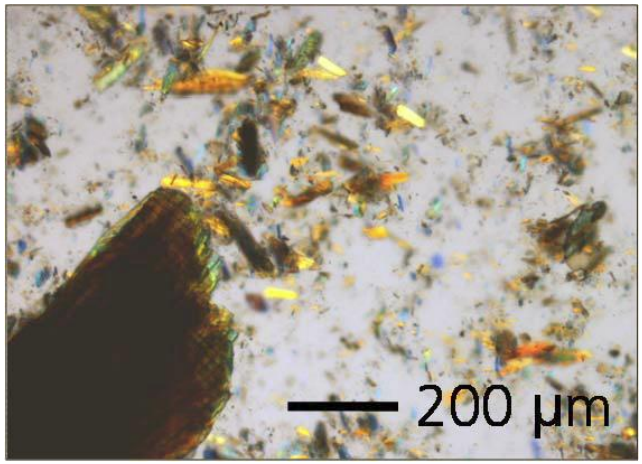
Steam pretreated
SO_2, 210 C, 5 min

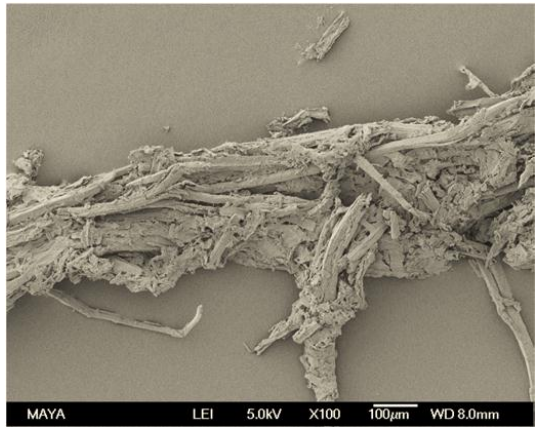
Contains potential inhibitors

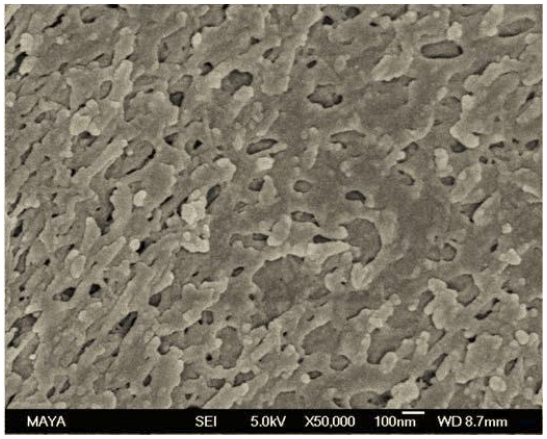
Extractives
Sugar degradation products e.g. Furans and acids
Lignin degradation products (phenolic compounds)

Scanning Electrone microscope Images

Steam pretreated spruce







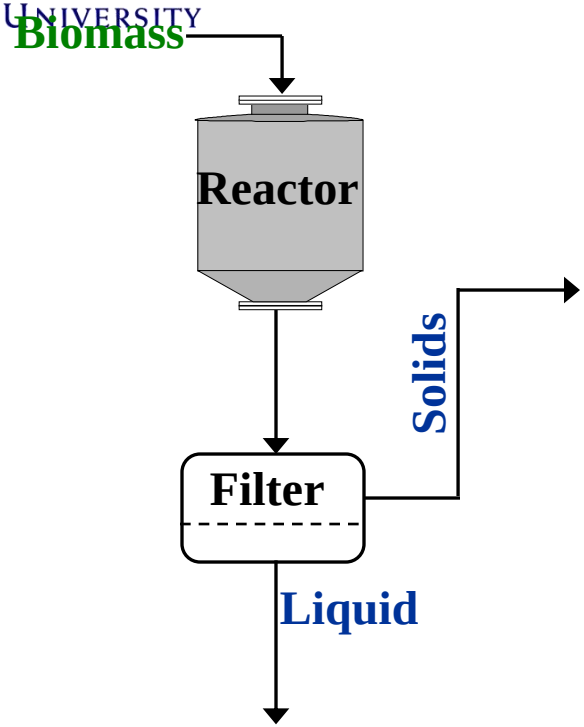
Wiman et al., unpublished

Impregnated material

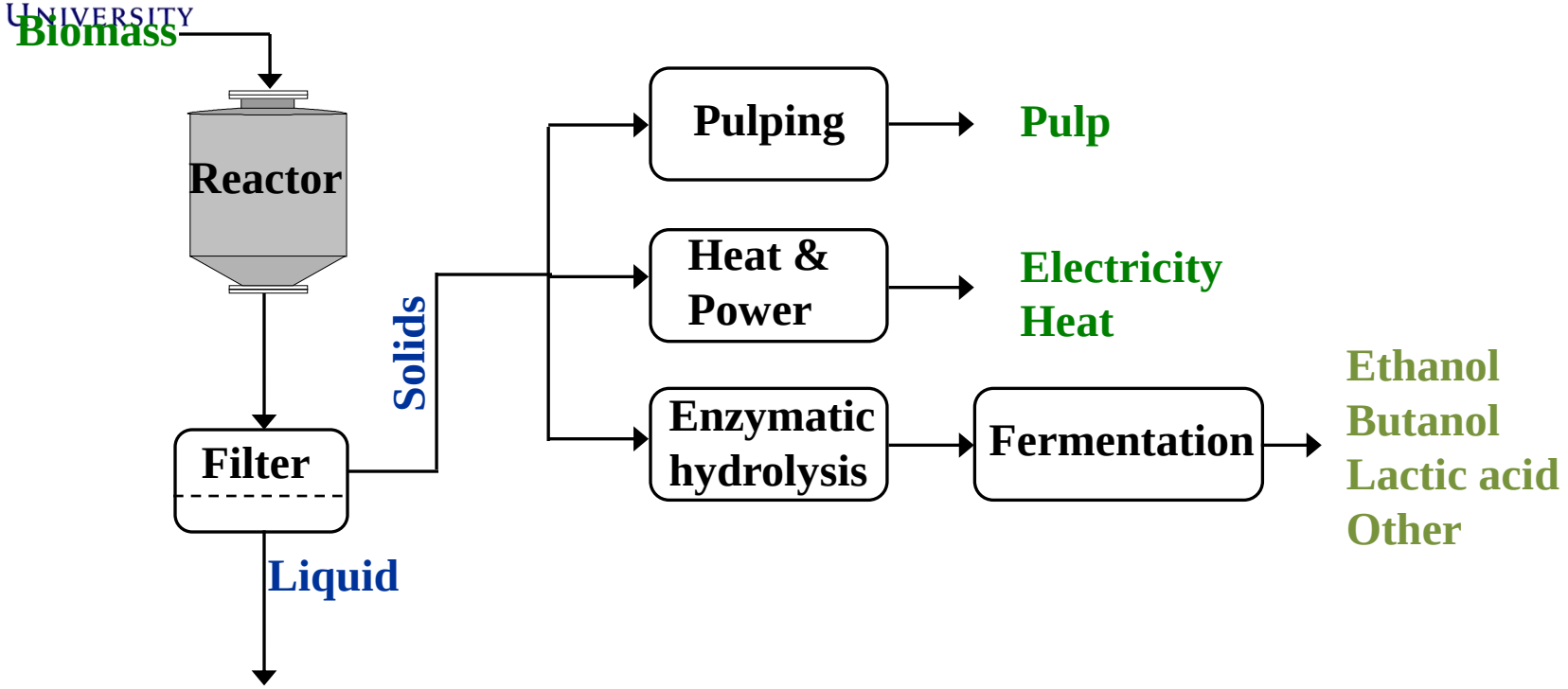
Straw

Steam pretreated
0.2 % H_2SO_4, 190 C, 10 min

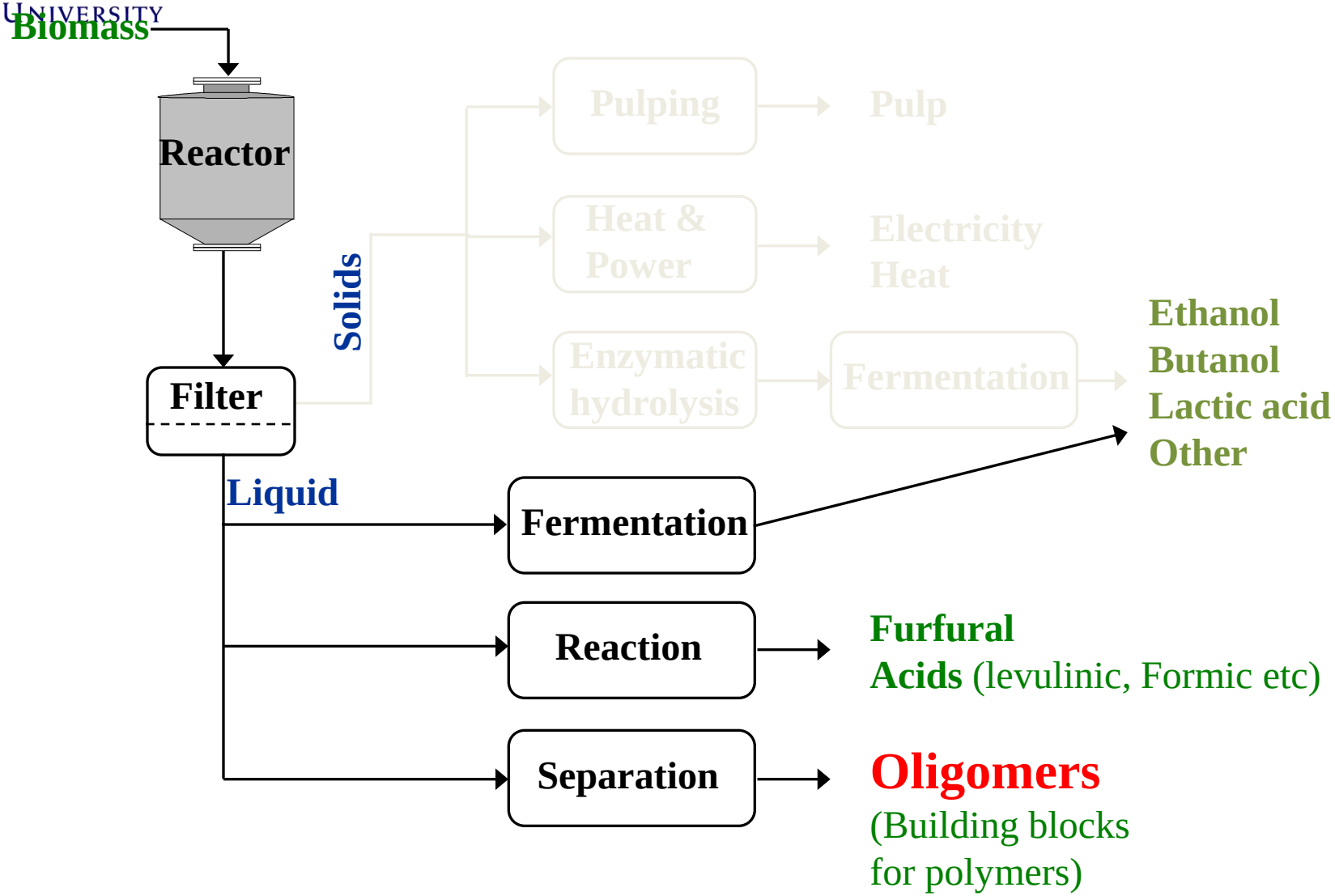
Conditions? Depend on purpose



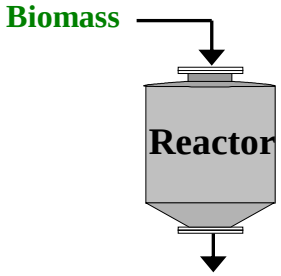
Conditions? Depend on purpose



Conditions? Depend on purpose



Assessment? Depends on purpose



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

Requires subsequent steps

- Enzymatic hydrolysis
- Fermentation
- SSF

Separation steps

Severity factor

$$Log(R_0) = Log[t * \exp[T - T_{ref} / 14.75]]$$

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

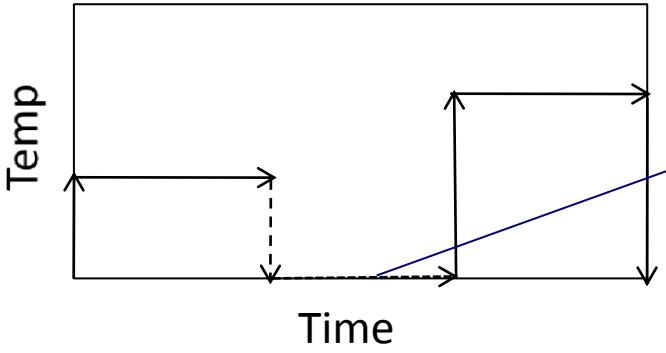
Low severity → **High severity**

Poor improvement of enzymatic hydrolysis!

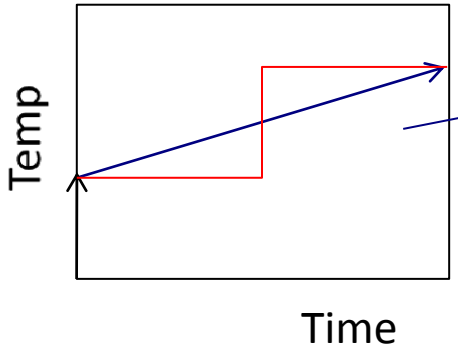
Formation of by-products inhibitory for fermentation!

Acid hydrolysis of pine

1st acid-hydrolysis step: 180-200 °C → 2nd acid-hydrolysis step: 200-225 °C



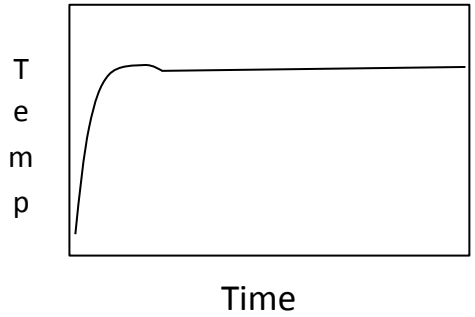
Traditional two-step hydrolysis: Cooling of substrate

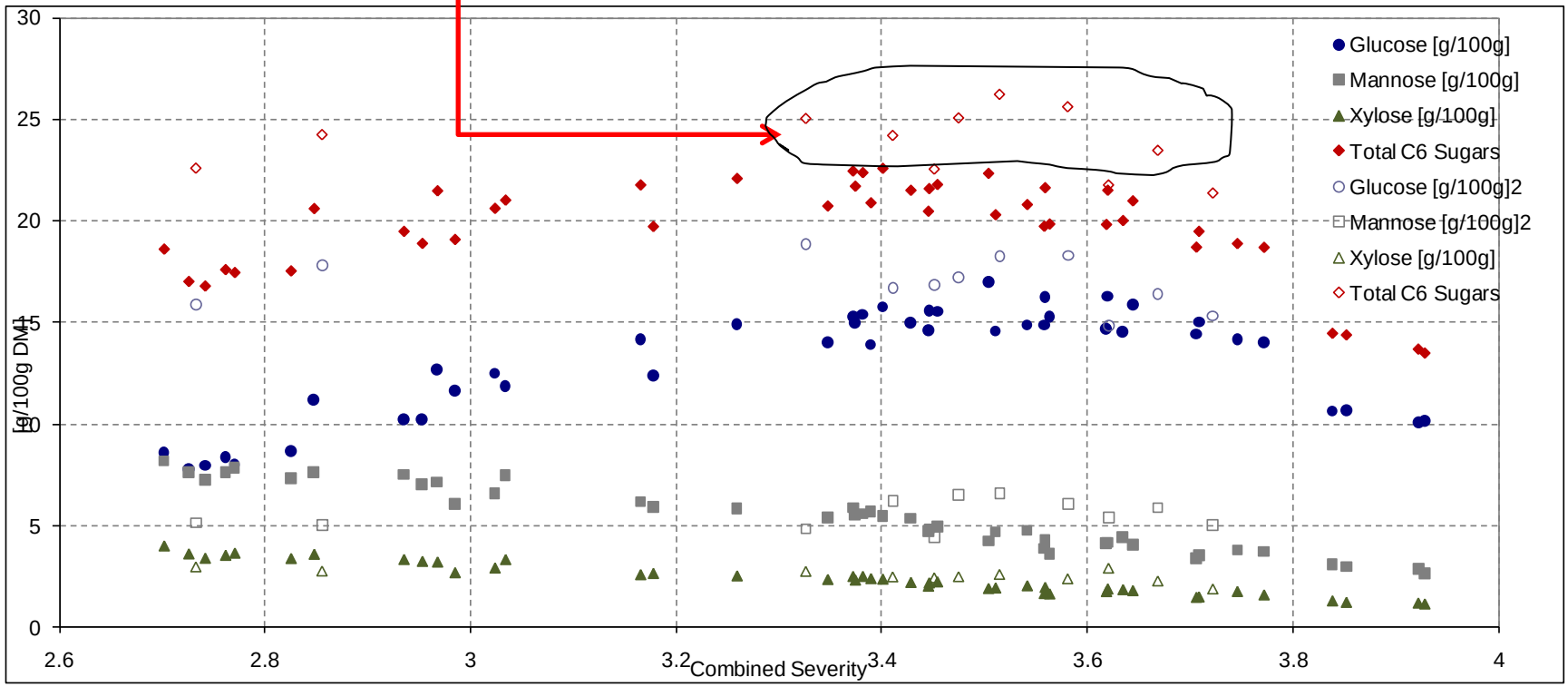


Consolidated two-step hydrolysis: Profile OR step-wise temperature change

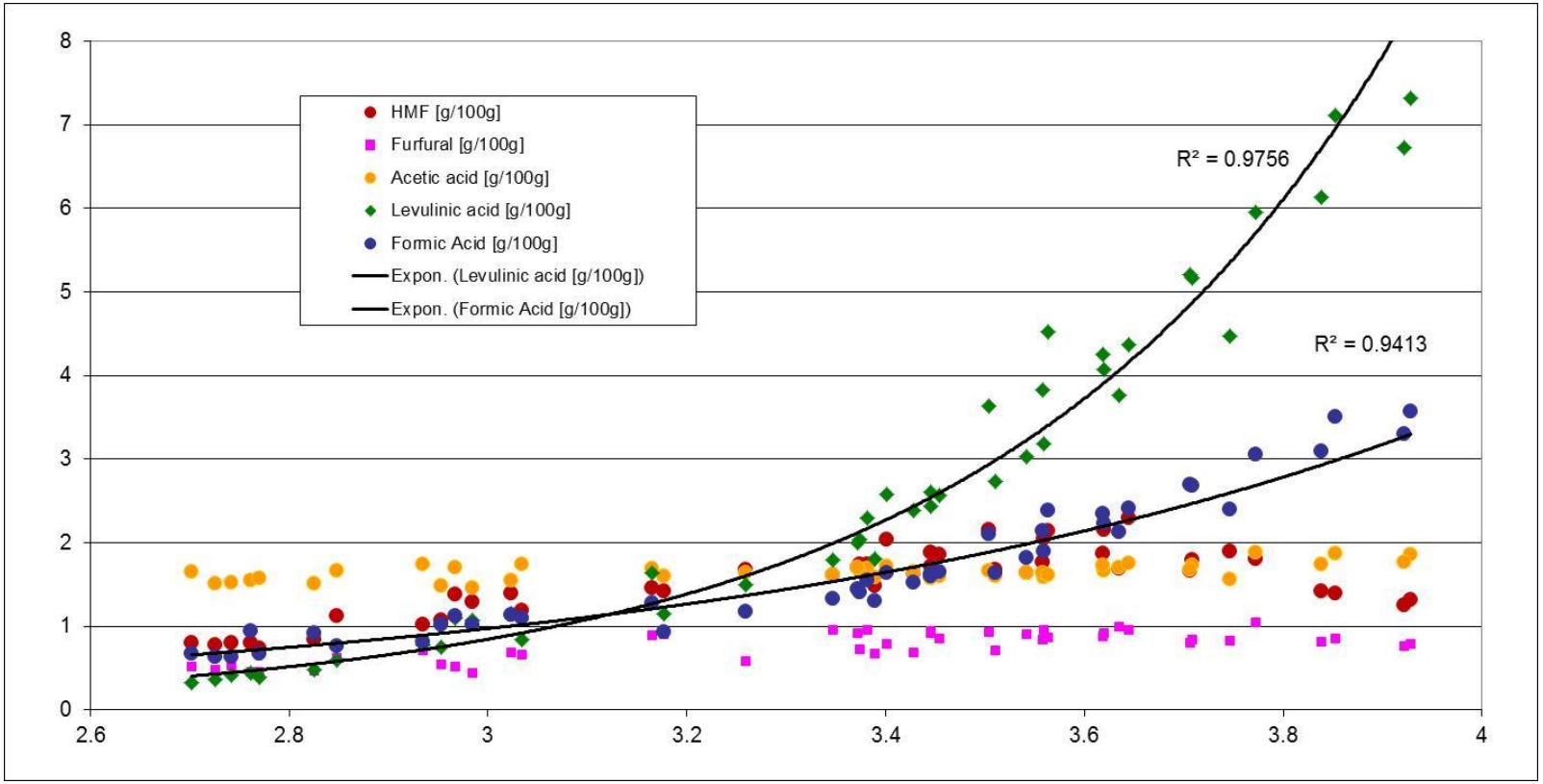
Improvement of temperature control in steam pretreatment

Control by pressure: Fast, requires pT-data

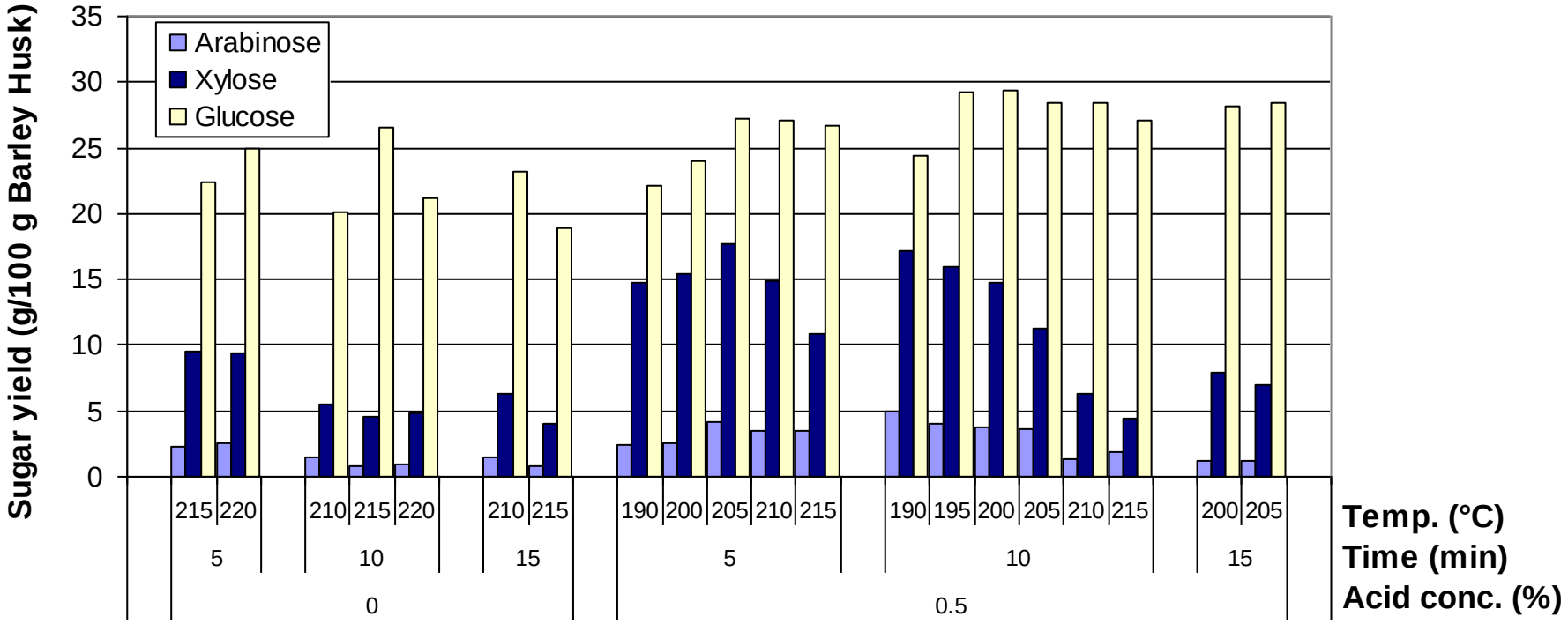




By-products after dilute-acid hydrolysis



Combined pretreatment and enzymatic hydrolysis of Barley Husk



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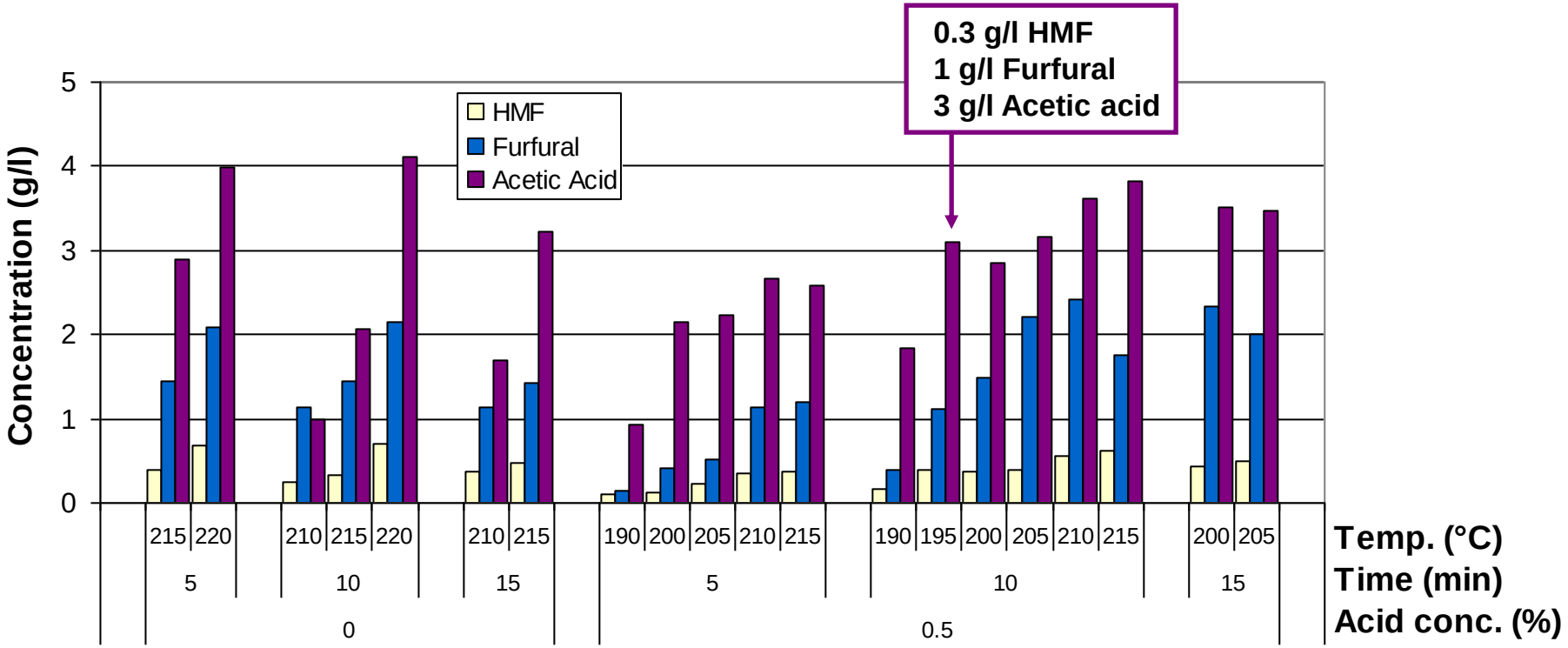
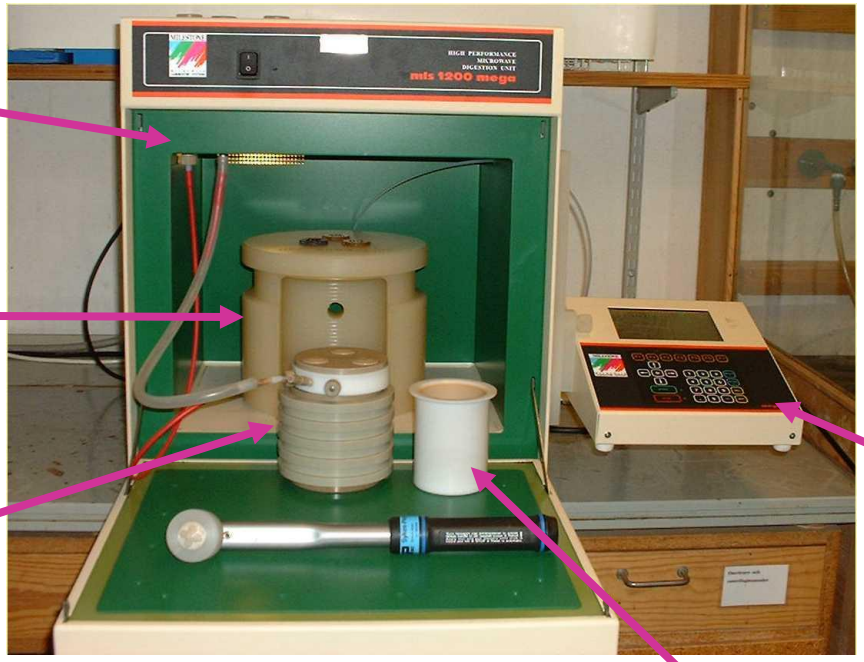


Rather low in inhibiting compounds

Microwave pretreatment



Microwave oven

Rotor

Shell

Control unit

Treatment vessel

Continuous pretreatment reactor
Sekab E-technology

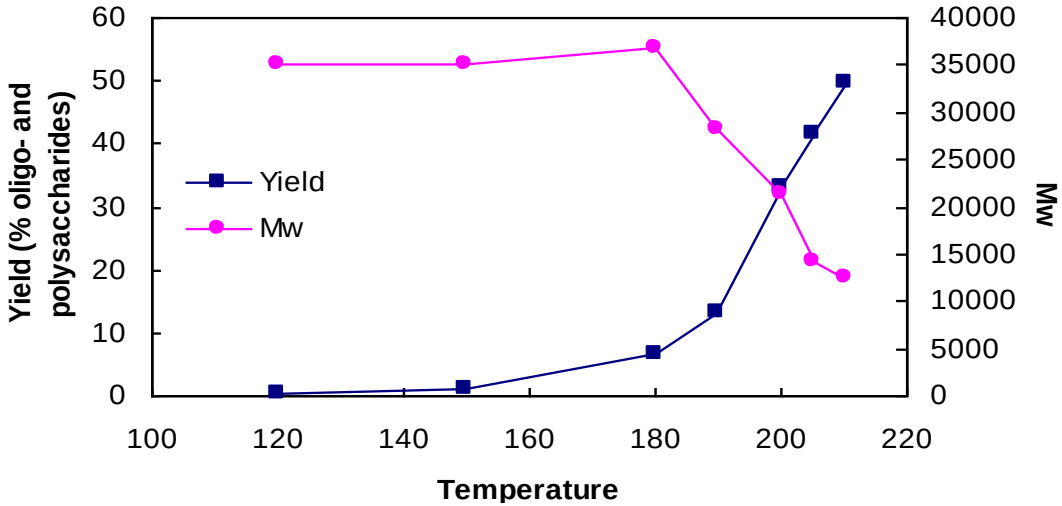
Extraction of hemicellulose from barley husks

Steam explosion

Filtration - LAROX filter press

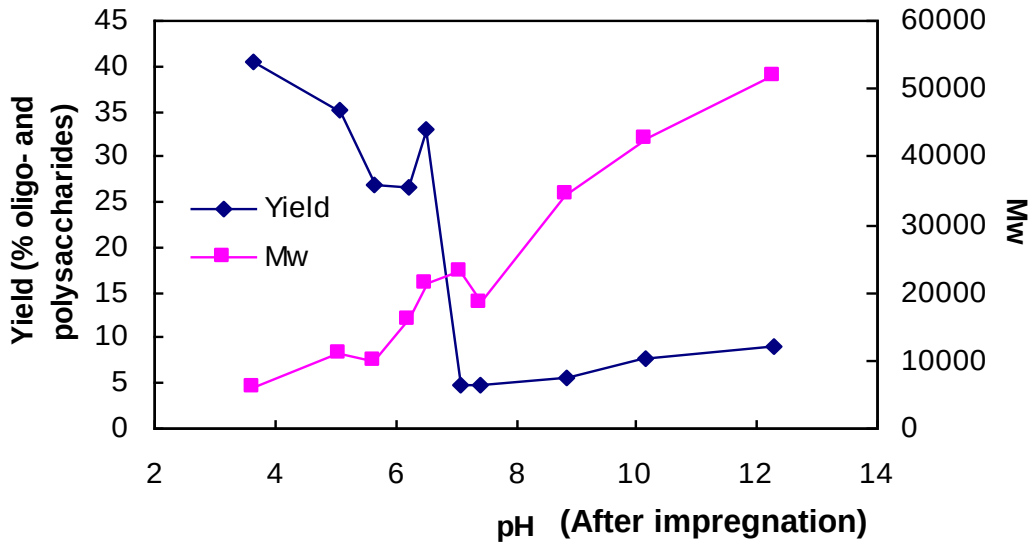
Concentration using UF

Extraction of Arabinoxylan from Barley husks
Screening with microwave oven



Impregnation with water (pH 6,5)

Res. time: 5 min

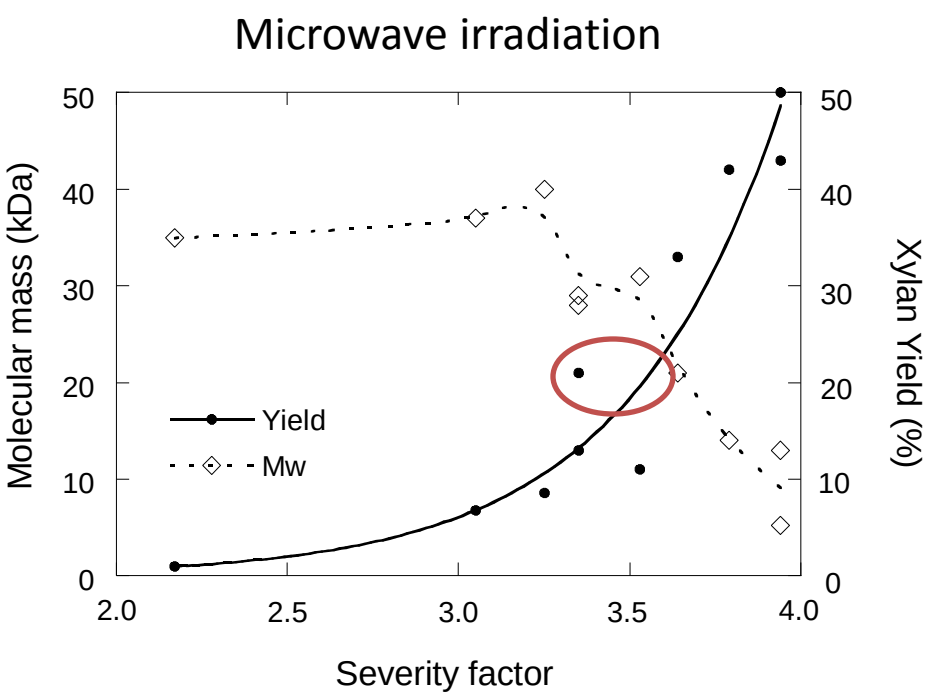


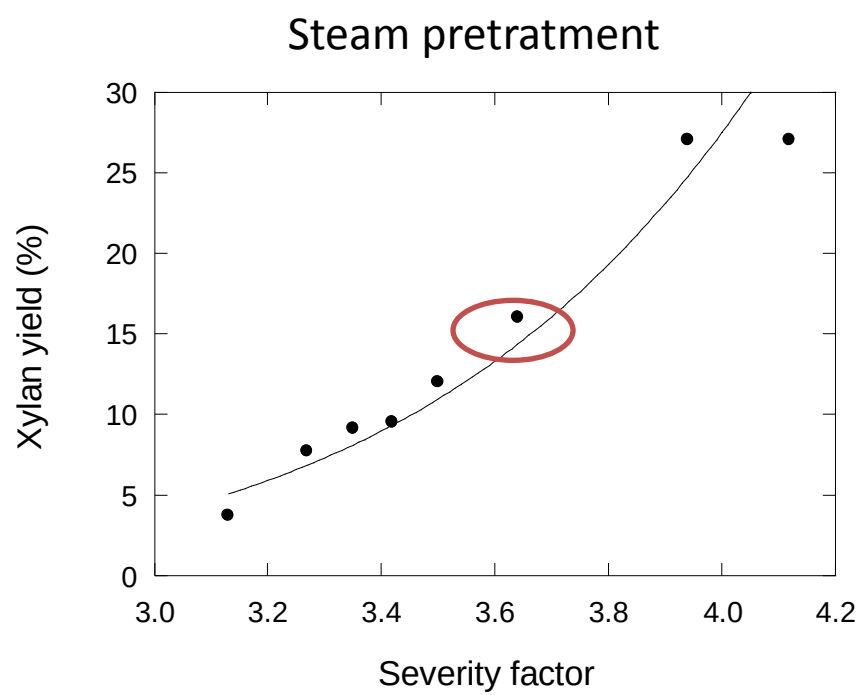
Temperature: 200°C

Res. time: 5 min

Alexandra Andersson, Henrik Stålbrand
Biochemistry, LU

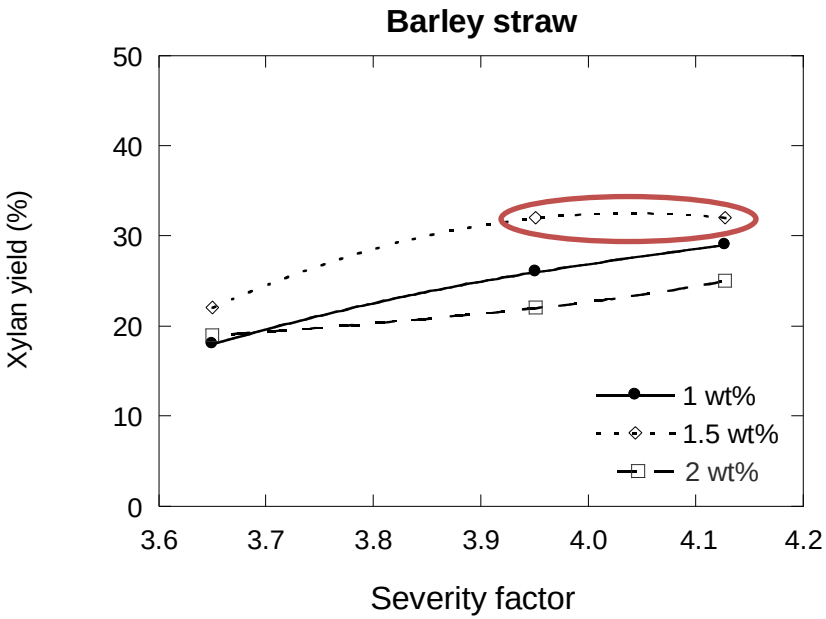
Autohydrolysis *(barley husks)*

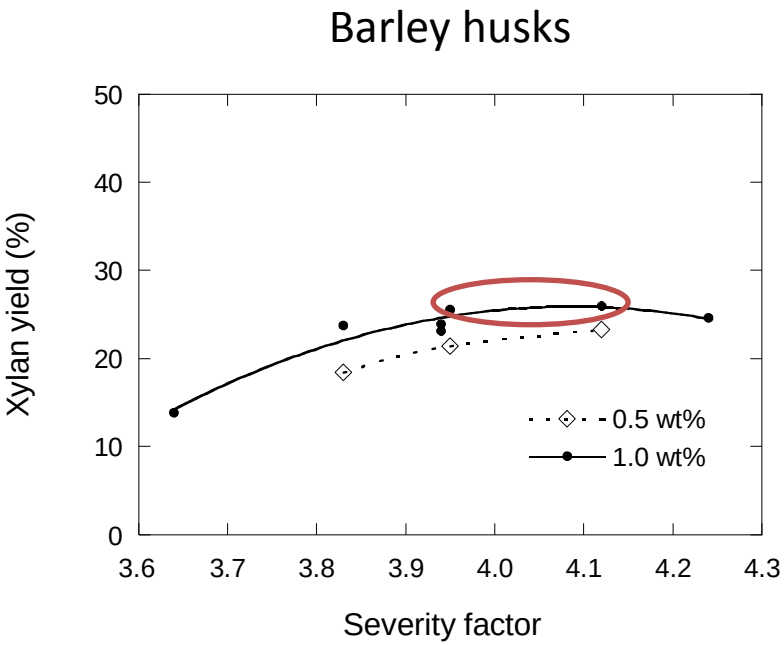


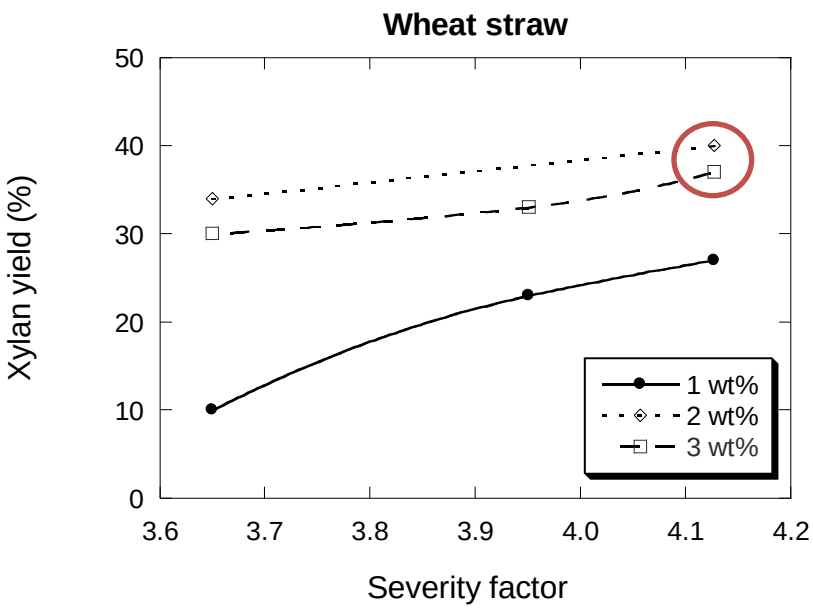


15-20% yield is possible to acchieve without removing the acetyl groups or significantly decreasing the molecular mass

Steam pretreatment with NaOH

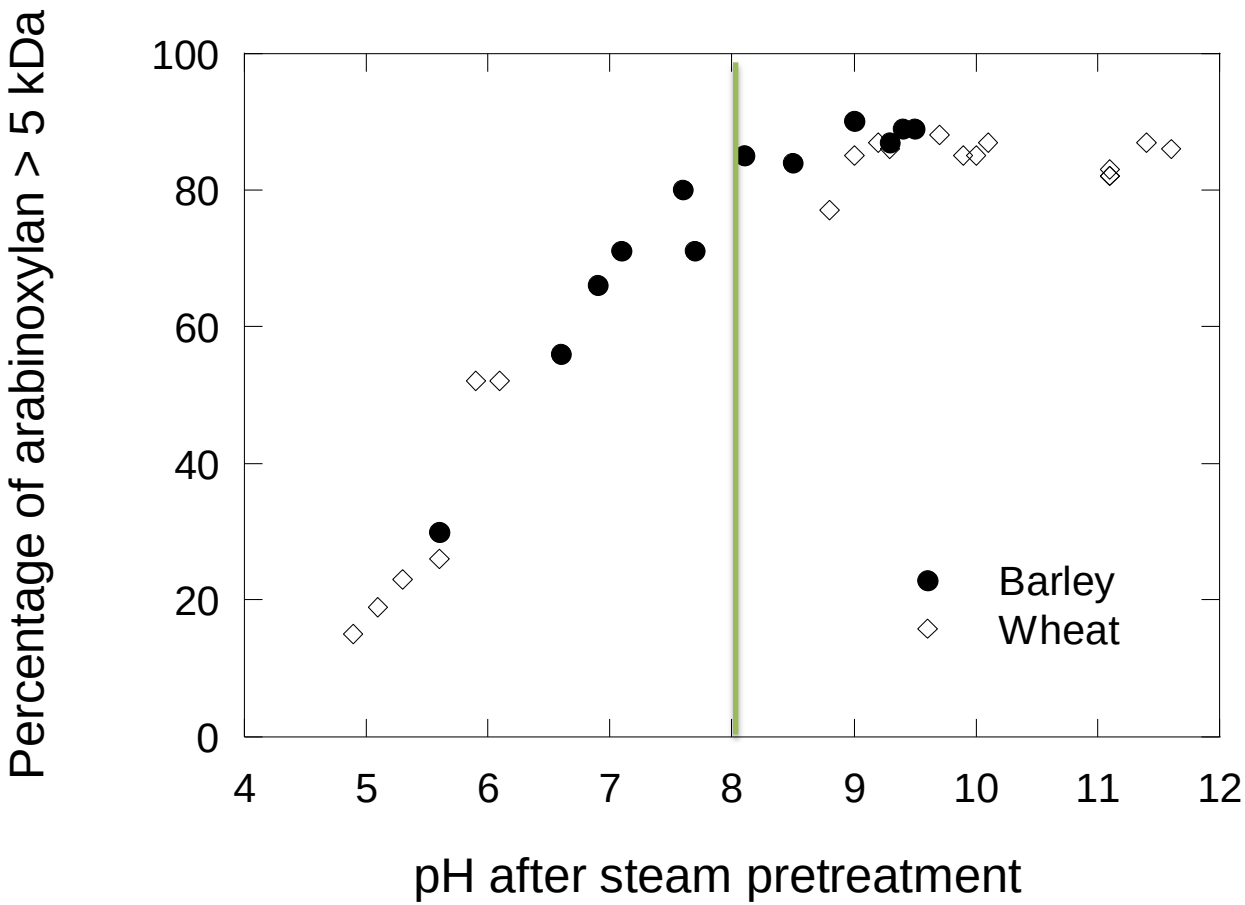






25-35% yield possible to reach when using modest concentrations of NaOH

If pH decreases, the molceular mass decreases



Which condition is optimal?

Only water

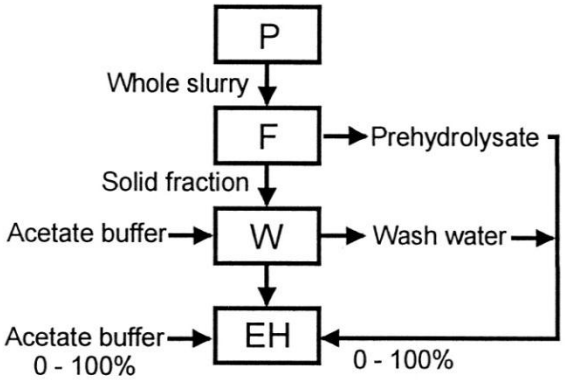
- Acetyl groups remains
- No costs for chemicals
- Lower maximum yield

With NaOH

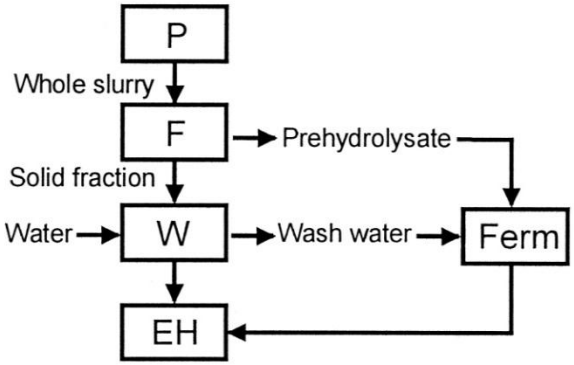
- Higher maximum yield
- De-Acetylation occurs
- Chemical costs

Test procedure – effect of pretreated slurry on enzymatic hydrolysis

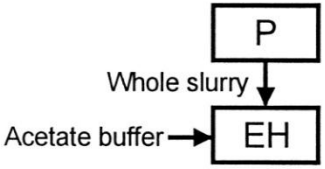
I. Influence of various concentrations of the prehydrolysate



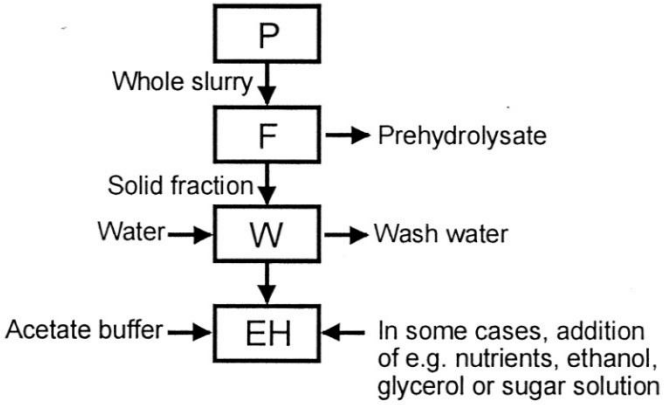
III. Influence of fermentation of the prehydrolysate



II. Whole slurry after pretreatment

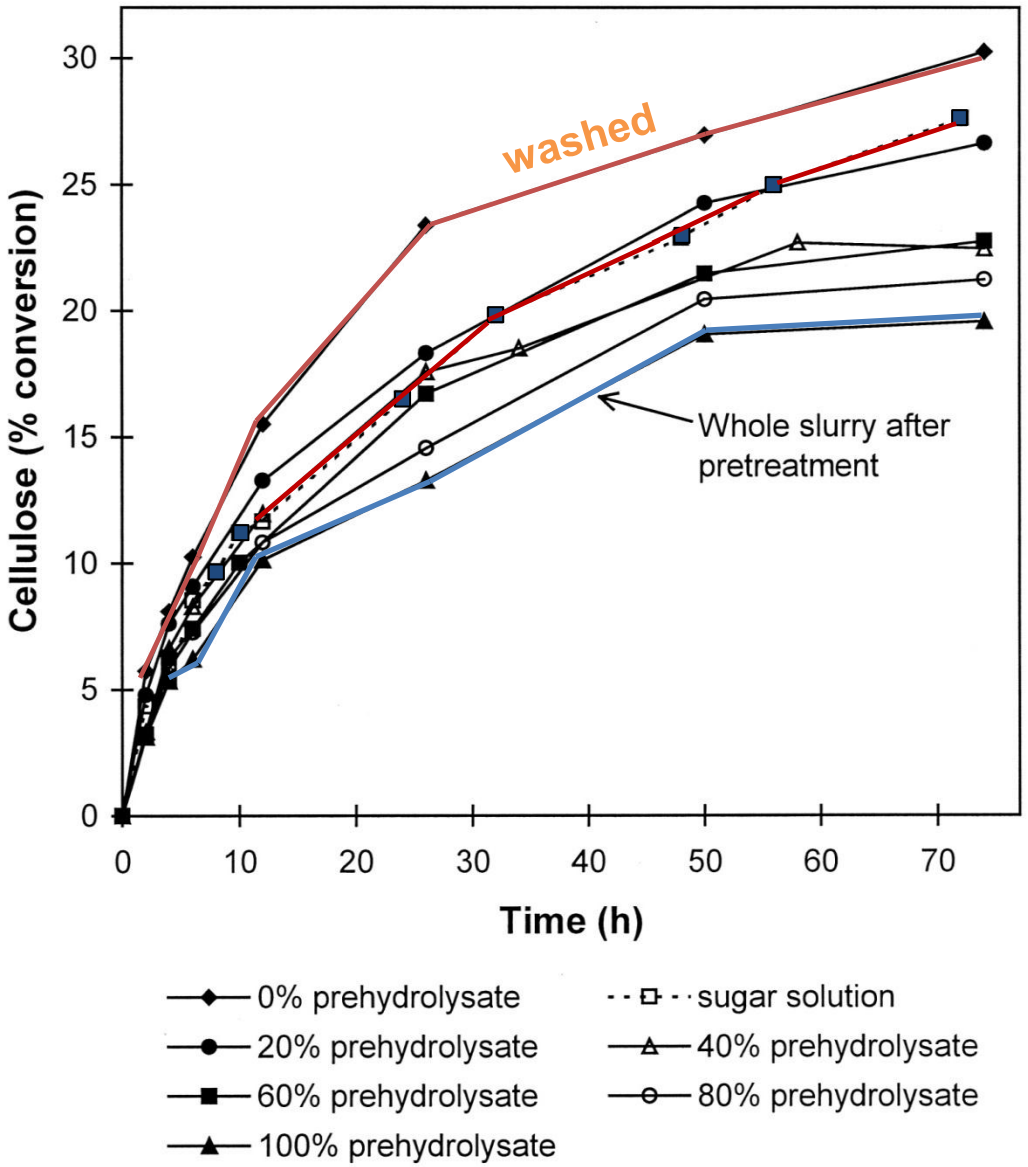


IV. Influence of addition of various substances



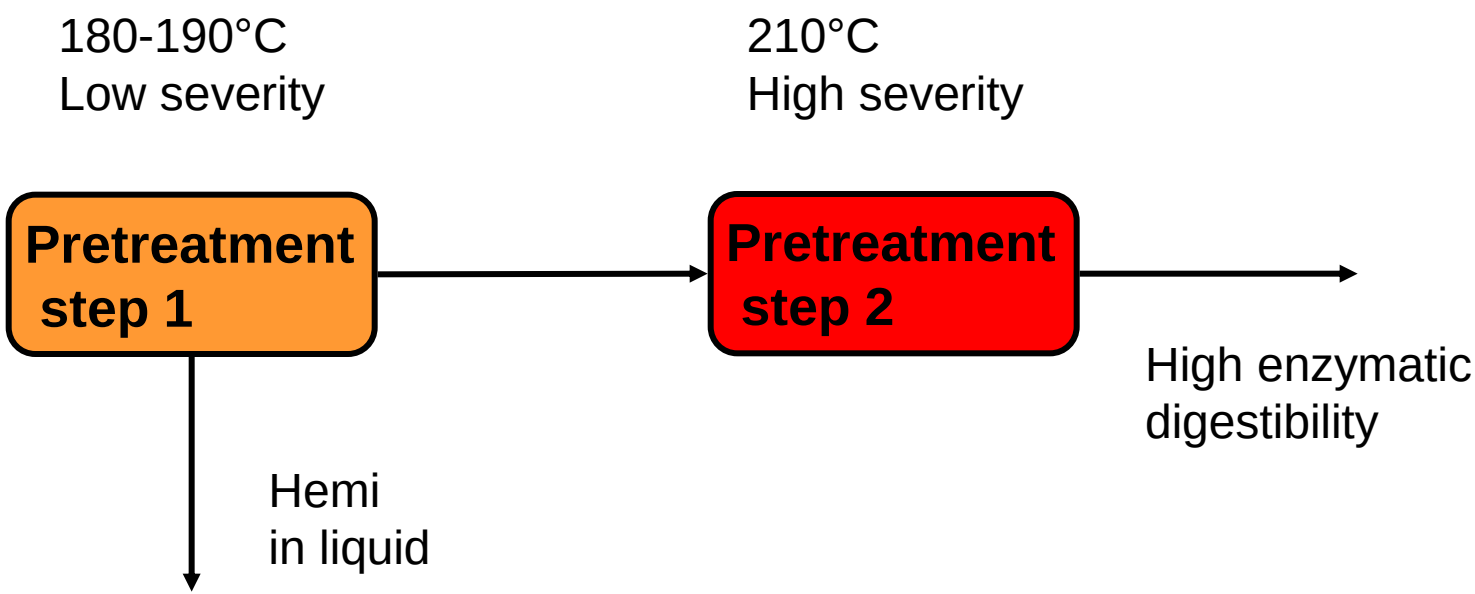
Tengborg et al Enzyme & Microbial Technol (2001)

Effect of pretreated slurry on enzymatic hydrolysis at low enzyme dosage

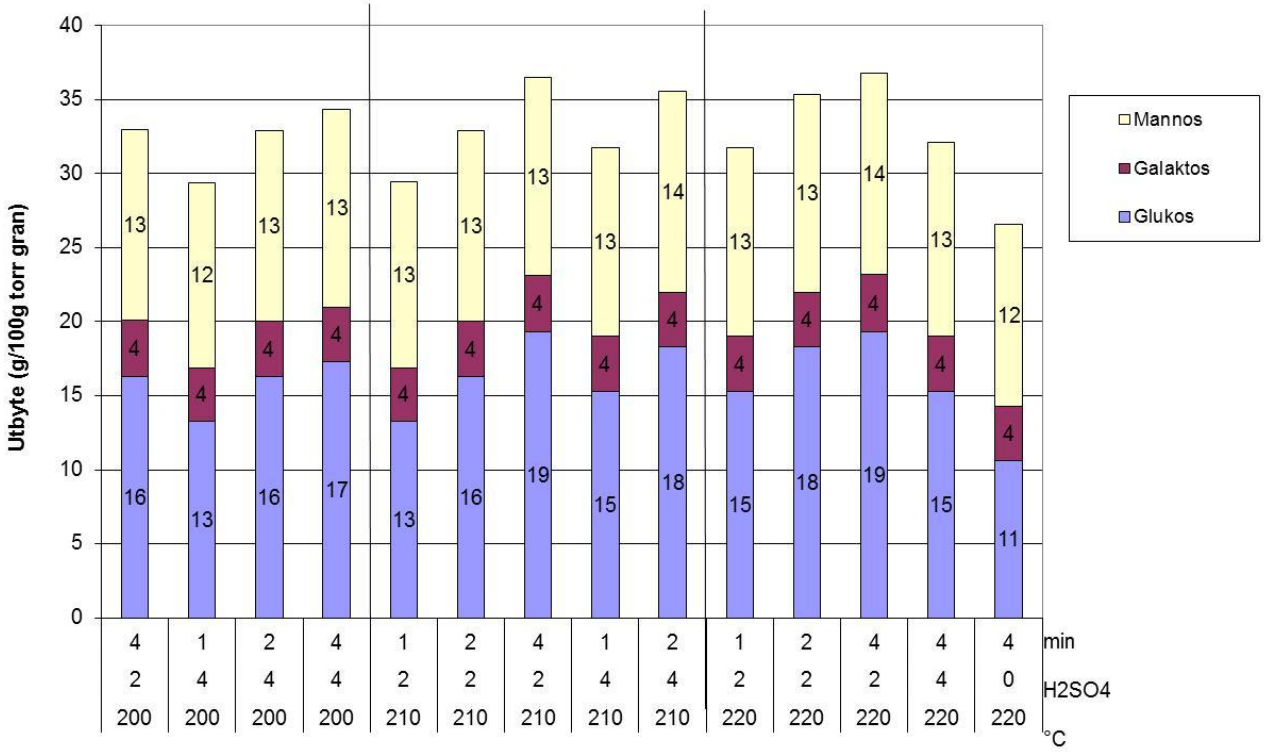


Tengborg et al Enzyme & Microbial Technol (2001)

Two-step steam pretreatment

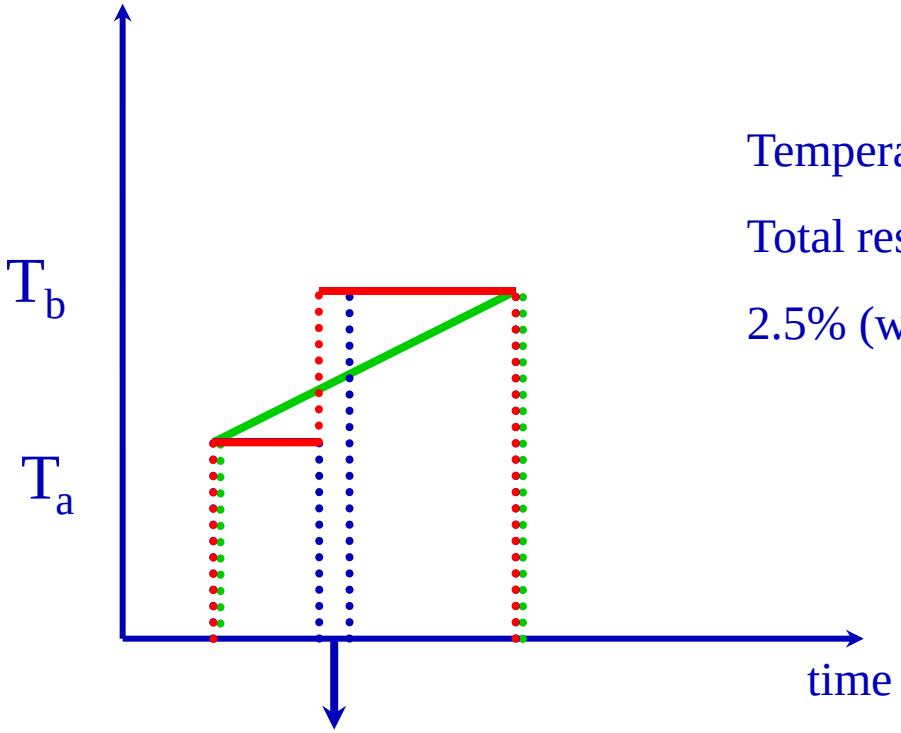


Two-step pretreatment of spruce (Yields of some sugars)



Improved One-step pretreatment of spruce

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



Separation and Washing

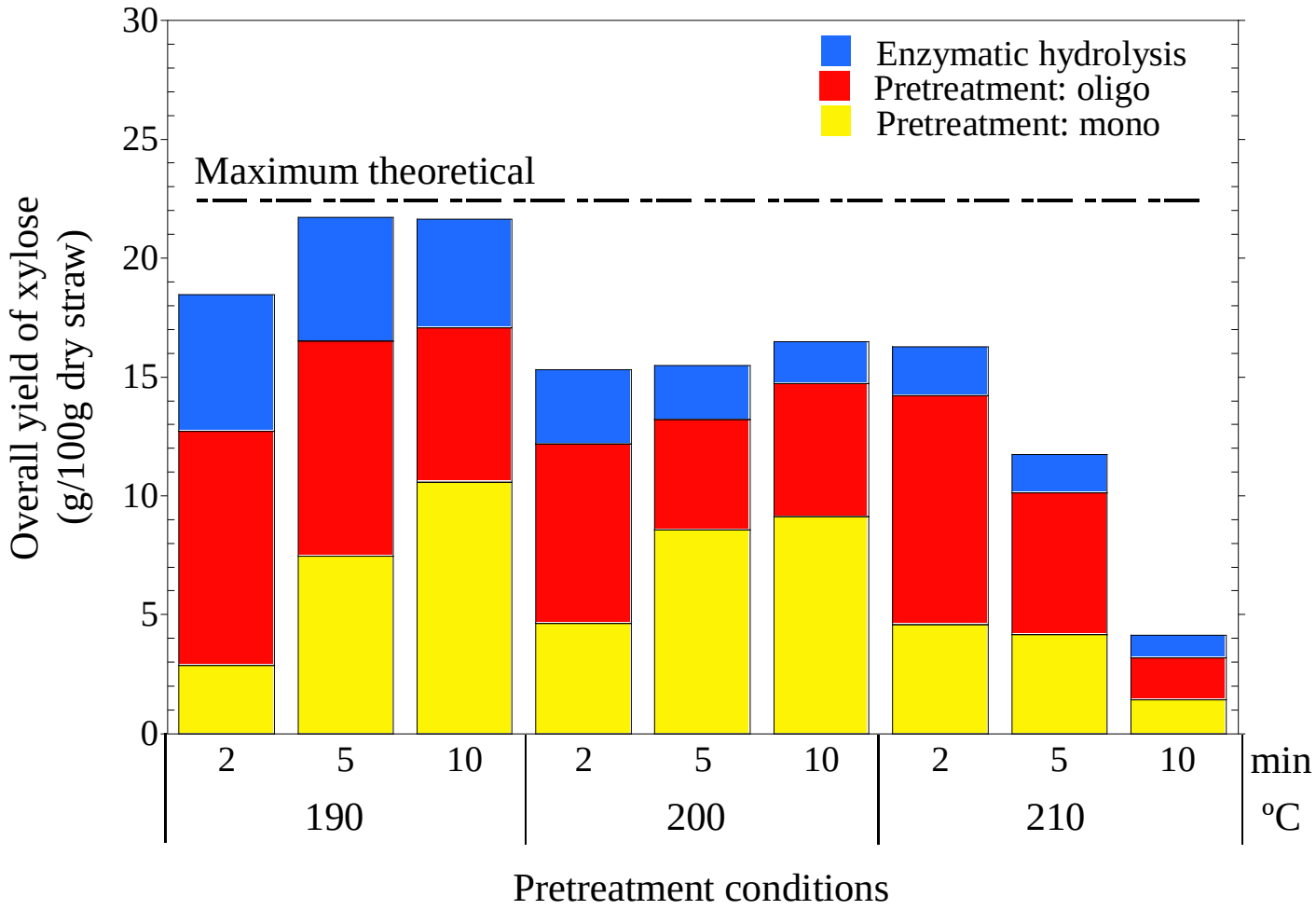
Temperature: 190 - 226 °C

Total residence time: 5 -12 min

2.5% (w/w) SO_2

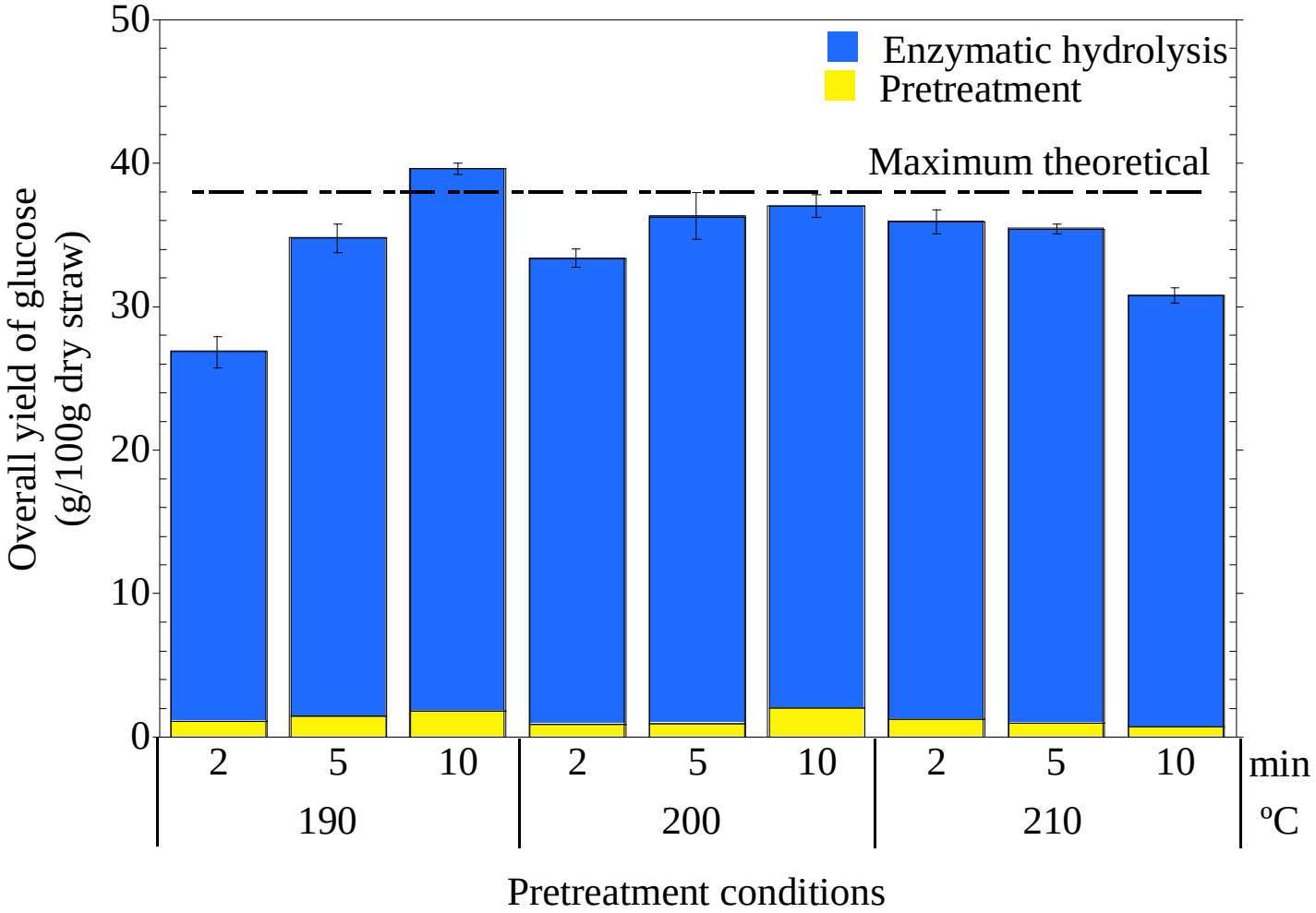
Monavari S. et al *Biotechnol. Progr*. 2010 26(4), 1054-1060

Pretreatment of wheat straw (Xylose yield)



Linde et al (2006)

Pretreatment of straw (Glucose yield)



Linde et al (2006)

Finally…

- **Several pretreament 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)

LUND UNIVERSITY

…

- **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 strea
- Investment 22 million Euro
- Inauguration: May 26 2004

Plan

Demo plant 2010/11

Industrial scale 2014

Etek
Etanolteknik AB

Problems in pilot plant (deposits)

Problems in pilot plant (leakage)