# Alkaline pretreatment of wheat straw

"Analytical methods for non-wood raw materials and their products and processes"

COST FP0901 meeting, 19-21 August 2010, Hamburg

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# Outline presentation

- Wheat straw biorefinery
- Alkaline pretreatment
- Analytical tools
- Highlights results
- Available samples for Round Robin COST PF0901

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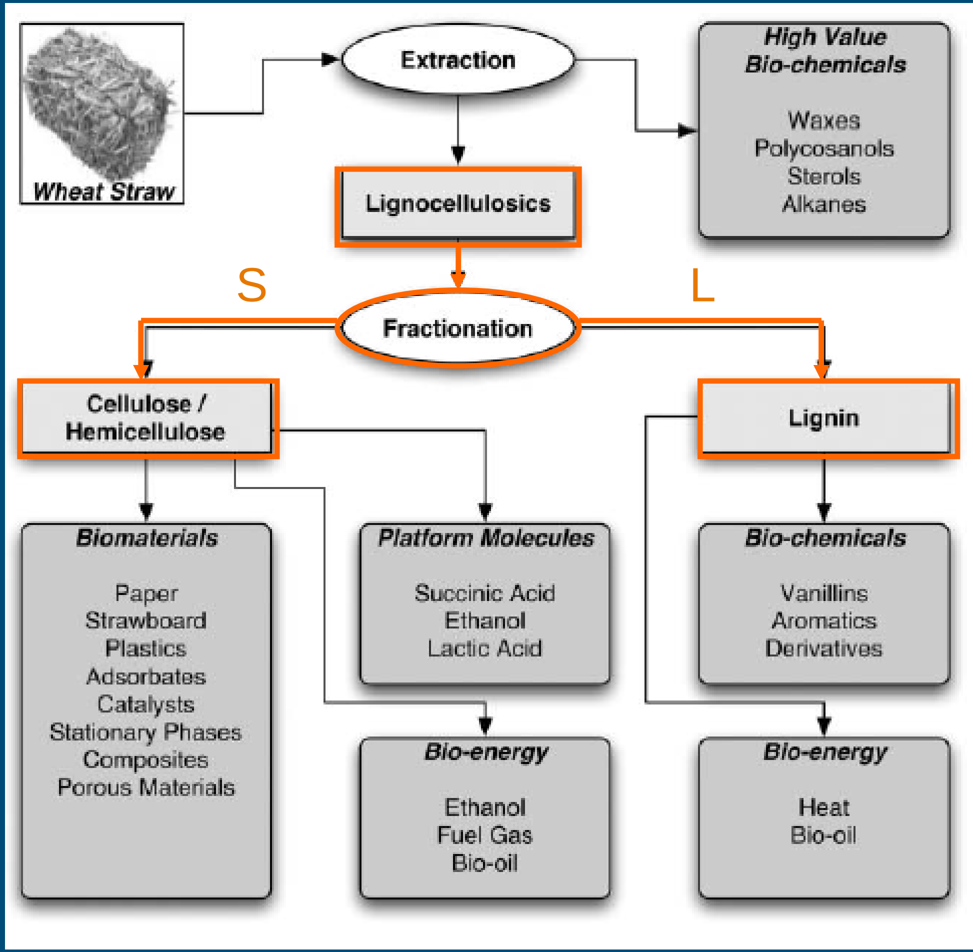
# Wheat straw biorefinery concept




*Clark et al. 2006*

# Pretreatment

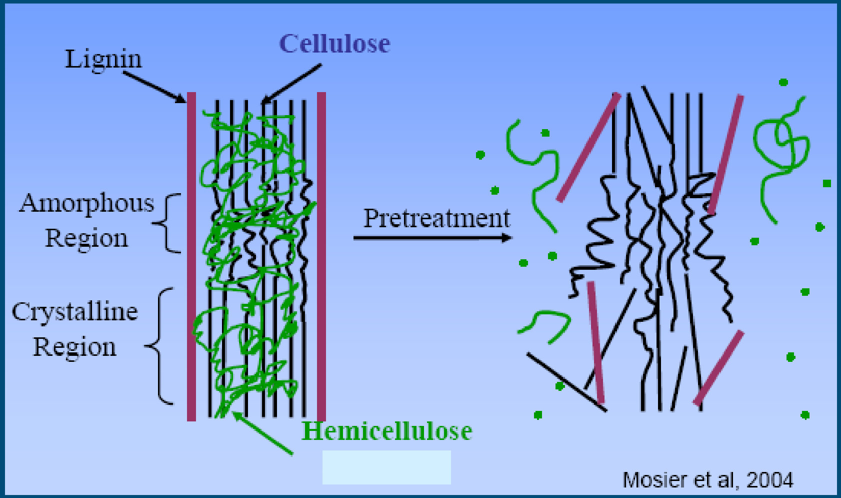
- Goal
  - Fractionation of lignocellulosic to cellulose, hemicellulose and lignin
  - Make cellulose and hemicellulose fractions more accessible for enzymatic hydrolysis
  - Make lignin available for higher-valued products

- Numerous processes
  - Mechanical, chemical, enzymatic
  - Acids, alkaline, organic solvents
  - Combinations thereof

# Alkaline pretreatment (high pH)

- Alkali induces swelling of biomass, leading to increase of internal surface area
- Disruption of lignin structure (lignin removal)
- Reduction of cellulose crystallinity

- Results in improved accessibility of cellulose and hemicellulose towards enzymatic hydrolysis

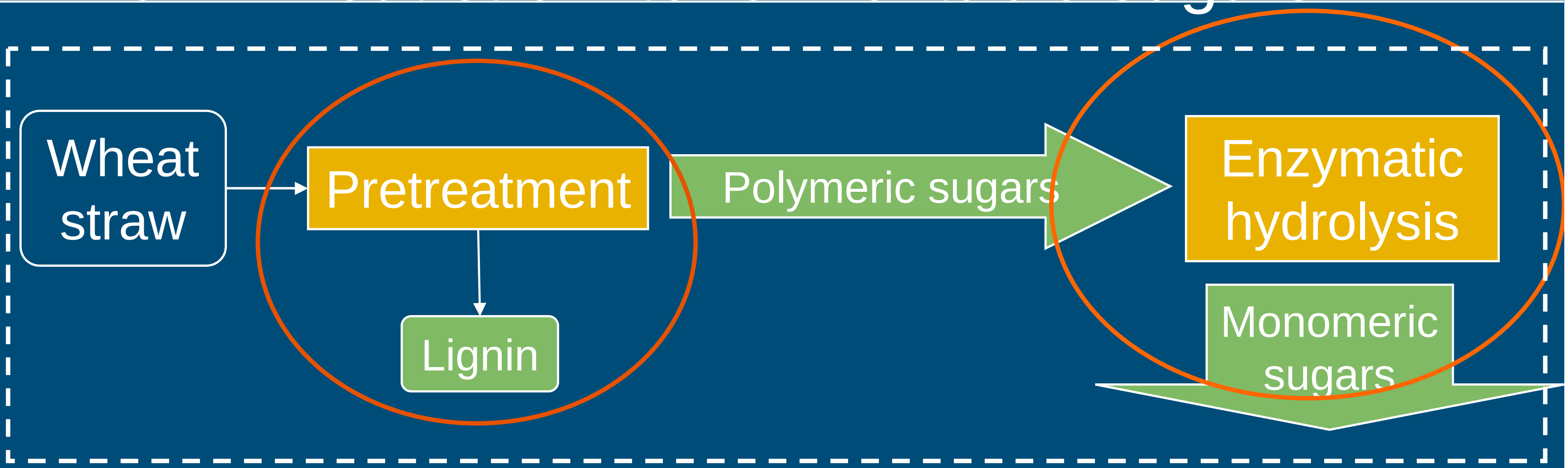


# Alkaline pretreatment

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

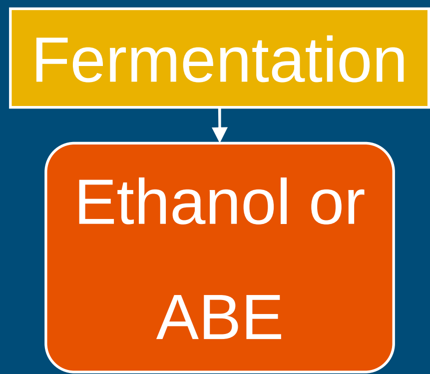
- Improve alkaline pretreatment
  - Apply milder process conditions
    - Less formation of degradation products (e.g. inhibitors)
    - Lower operational costs
  - Improve accessibility of sugars to enzymes
  - Obtain lignin of high purity

# From wheat straw to fermentable sugars




- Pretreatment efficiency
  - Properties of solid fraction (cellulose-rich)
    - Biochemical composition
  - Properties of liquid fraction
    - Sugars, organic acids and lignins in solution
    - Recovery of lignin

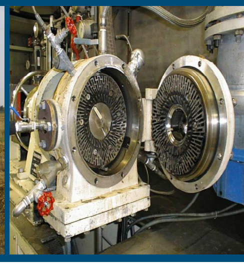
- **Enzymatic hydrolysis**
  - Conversion of solid fraction
    - Glucan to glucose
    - Xylan to xylose
  - Standard procedure
    - 50 ℃, 120h
    - Excess of enzyme (GC220)



# Experimental setup

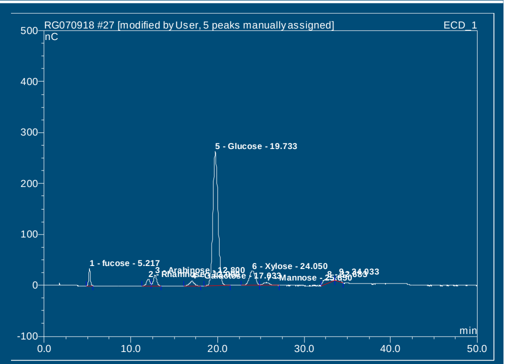
Base case: 4h alkaline pretreatment in stirred reactor

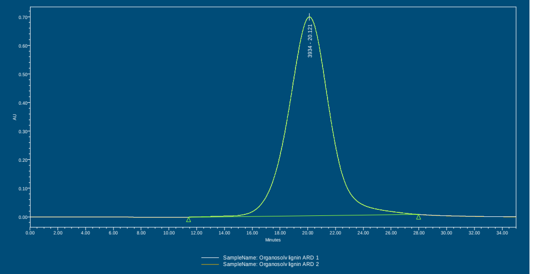
- Preliminary experiments (2 L, 70 ℃)
  - Base case
  - Effect NaOH-concentration
- Main experiments (200 L, 90 ℃)
  - Base case
  - Extrusion
  - Refining

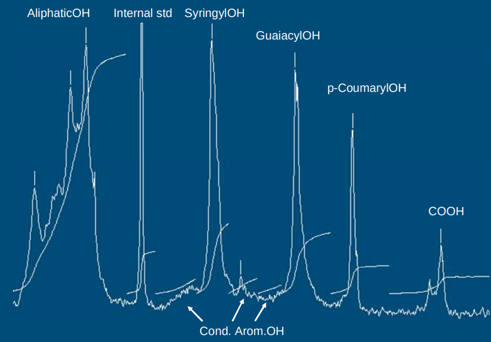




# Analytical tools (selection)

- Biochemical composition untreated & pretreated straw (solids)
  - Extraction (ASE)
  - Carbohydrates (HPAEC-PAD)
  - Lignin (AIL by weight, ASL by UV)
  - Ash (TGA, ignition)
  - Proteins (N by Kjehldahl or Dumas, AA by UPLC)
  - Morphology (SEM)
  - Cellulose cristallinity (WAXS)
- Liquids
  - Carbohydrates (monomers, oligomers)
  - Lignin
  - Fermentation inhibitors (phenolics, organic acids by LC)
- Isolated lignin
  - FT-IR
  - Impurities (carbohydrates, proteins, ash)
  - MWD (alkaline SEC)[1]
  - Functional groups ($^{31}P$ NMR)[1]

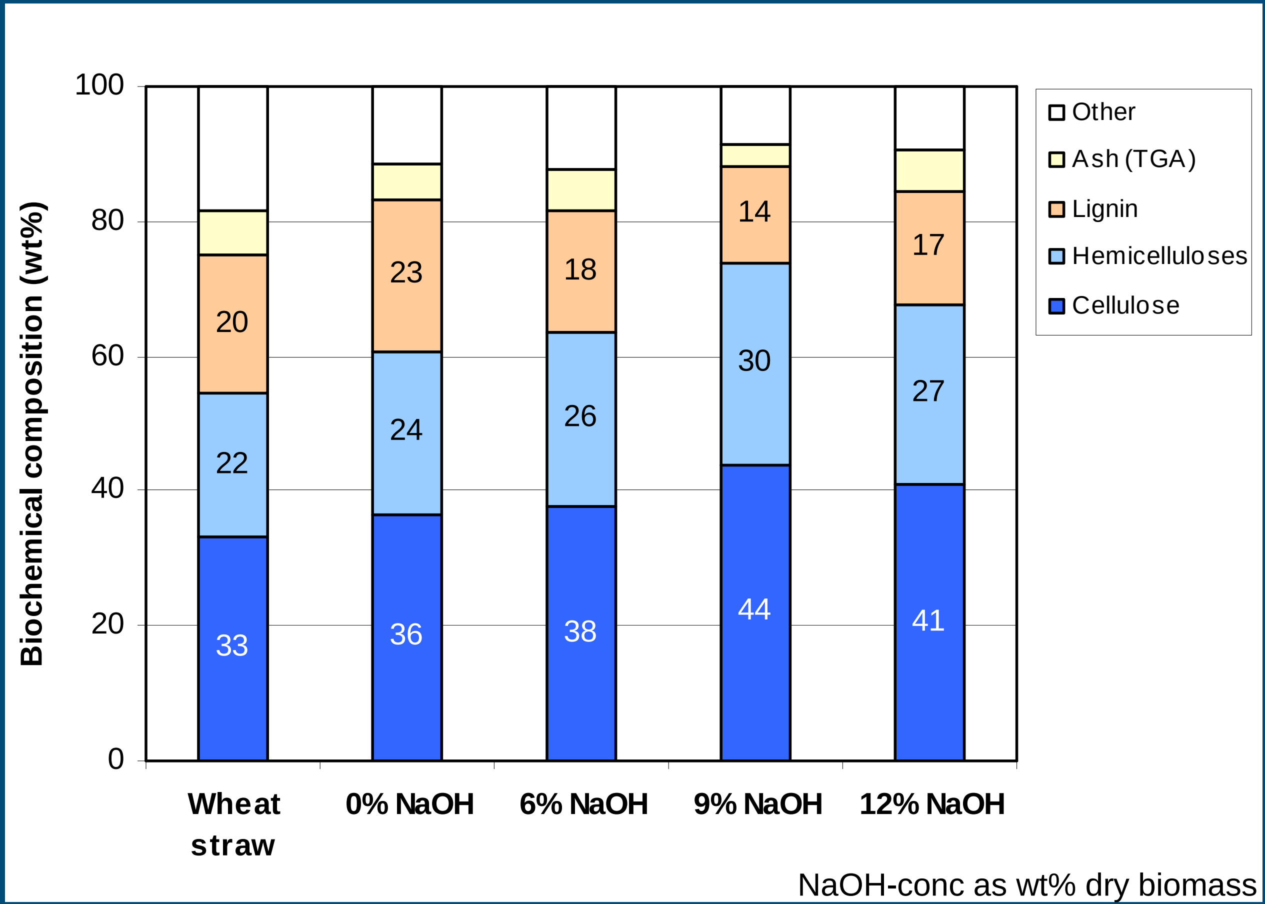


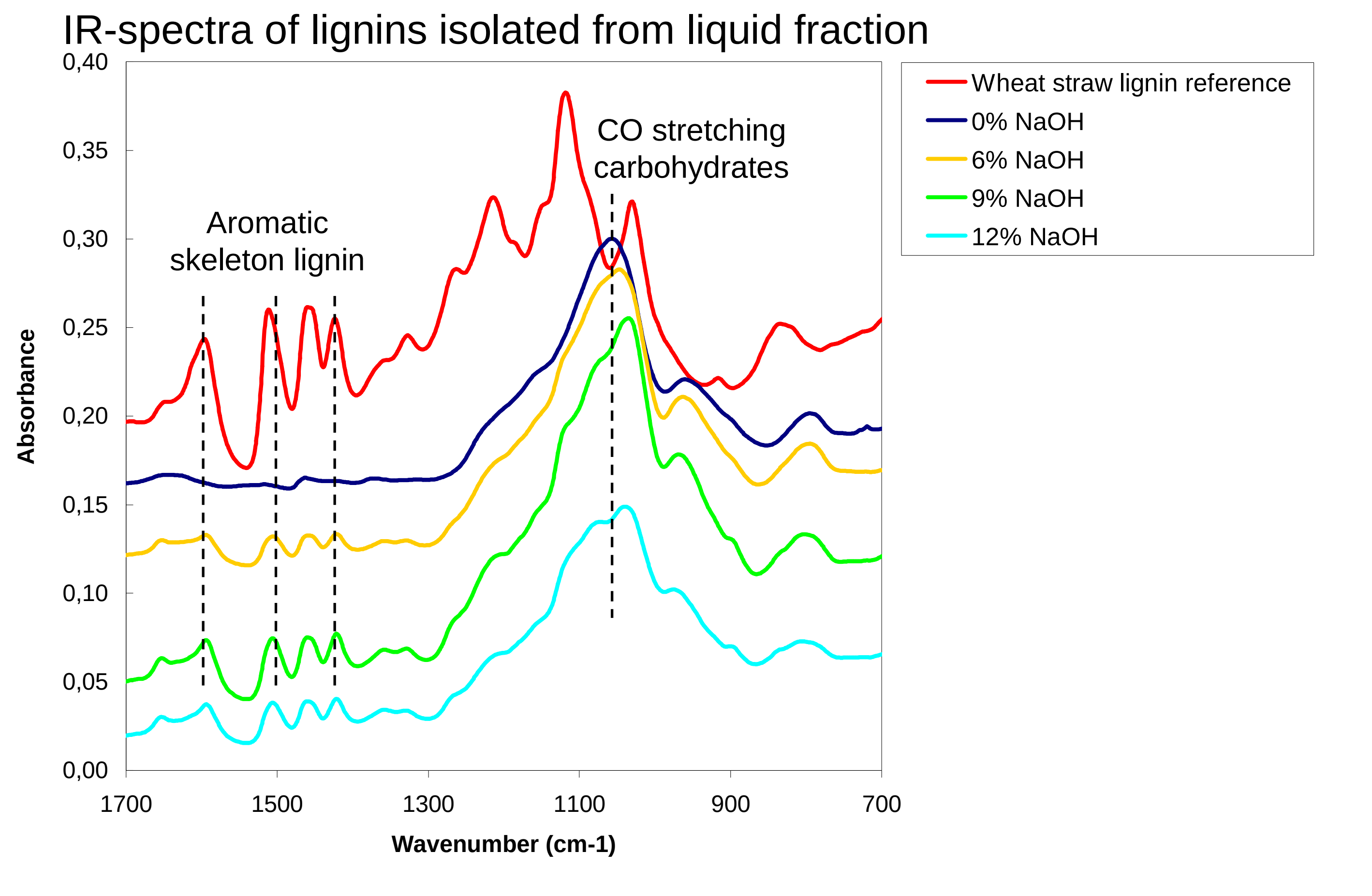



[1]Gosselink, R.J.A. *et al.* Holzforschung 2010

# Pretreatment efficiency *Solid fraction*



# Pretreatment efficiency *Liquid fraction*

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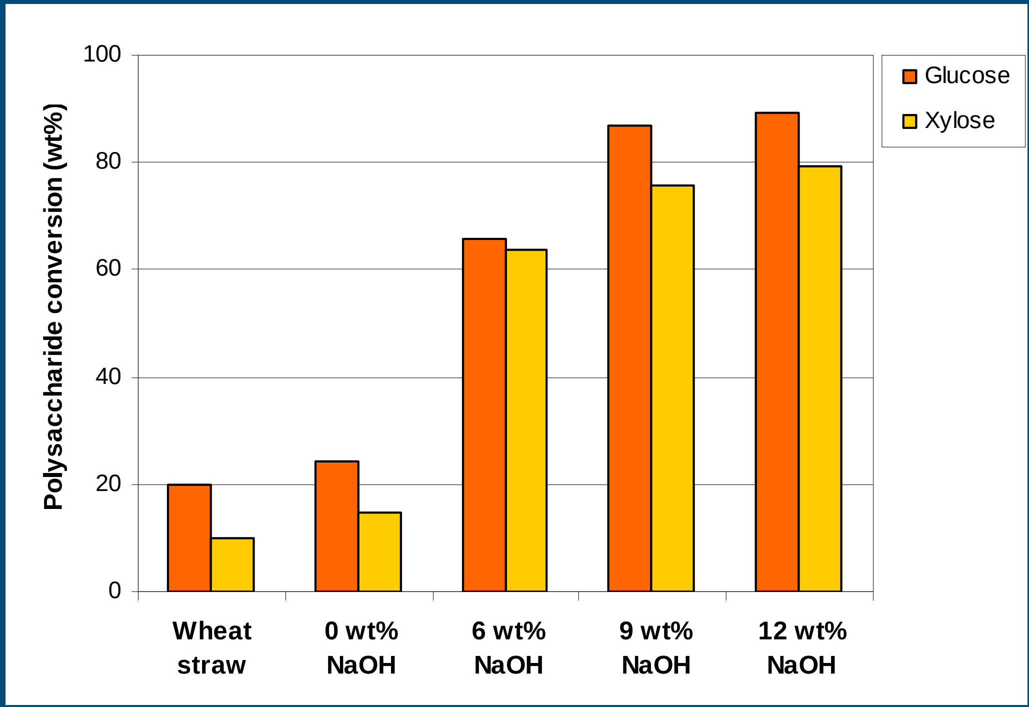
# Enzymatic hydrolysis *Solid fraction*




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

# Summary *Base case (2L)*

- Pretreatment
  - Main action is delignification (max 50%)
  - Minimum degree of hemicellulose and cellulose hydrolysis
  - Solid fraction enriched with sugars due to pretreatment (from 60% to 75%)
  - Optimal NaOH concentration 9 wt%
- Lignin
  - Low purity

- Enzymatic hydrolysis
  - Conversion of glucan and xylan improved from < 20% to > 80%

- Input for further experiments
  - Increase T from 70 to 90 ℃
  - NaOH concentration 6-9 wt% NaOH

# Experimental setup

<u>Base case</u>: 4h alkaline pretreatment in stirred reactor

- ✓ Preliminary experiments (2 L, 70 ℃)
  - ✓ Base case
- Main experiments (200 L, 90 ℃)
  - Base case
  - Extrusion
  - Refining

# Base case

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

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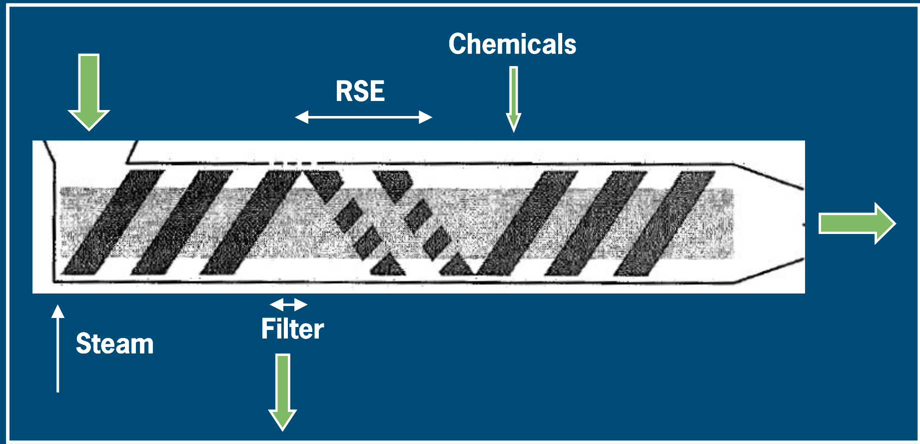
# Extrusion

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



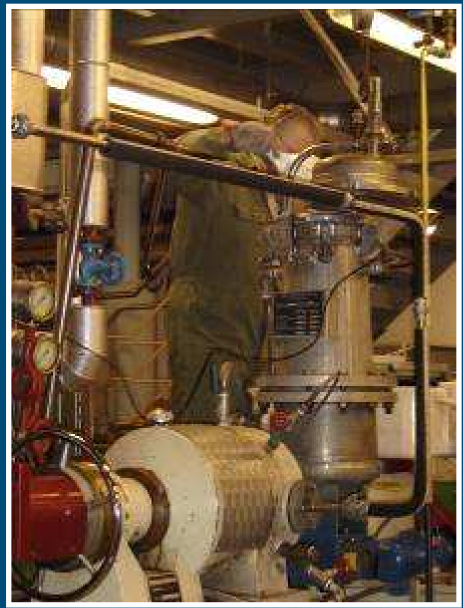

2nd Delignification
6 wt% NaOH, 2h, 90 ℃

- 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

# Refining

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

→



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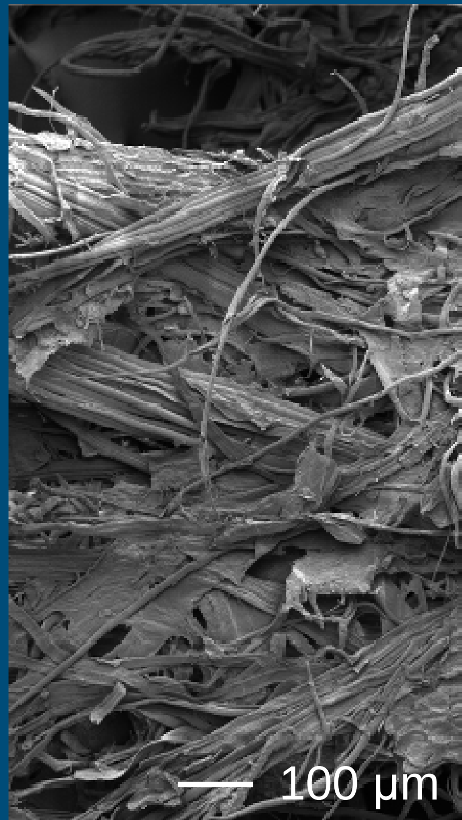
2nd Delignification
6 wt% NaOH, 2h, 90℃

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

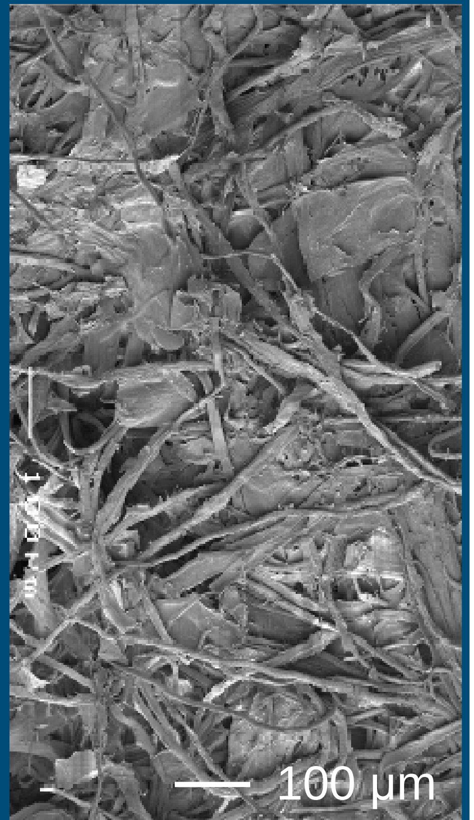
# Scanning Electron Microscopy


Wheat straw


Base case

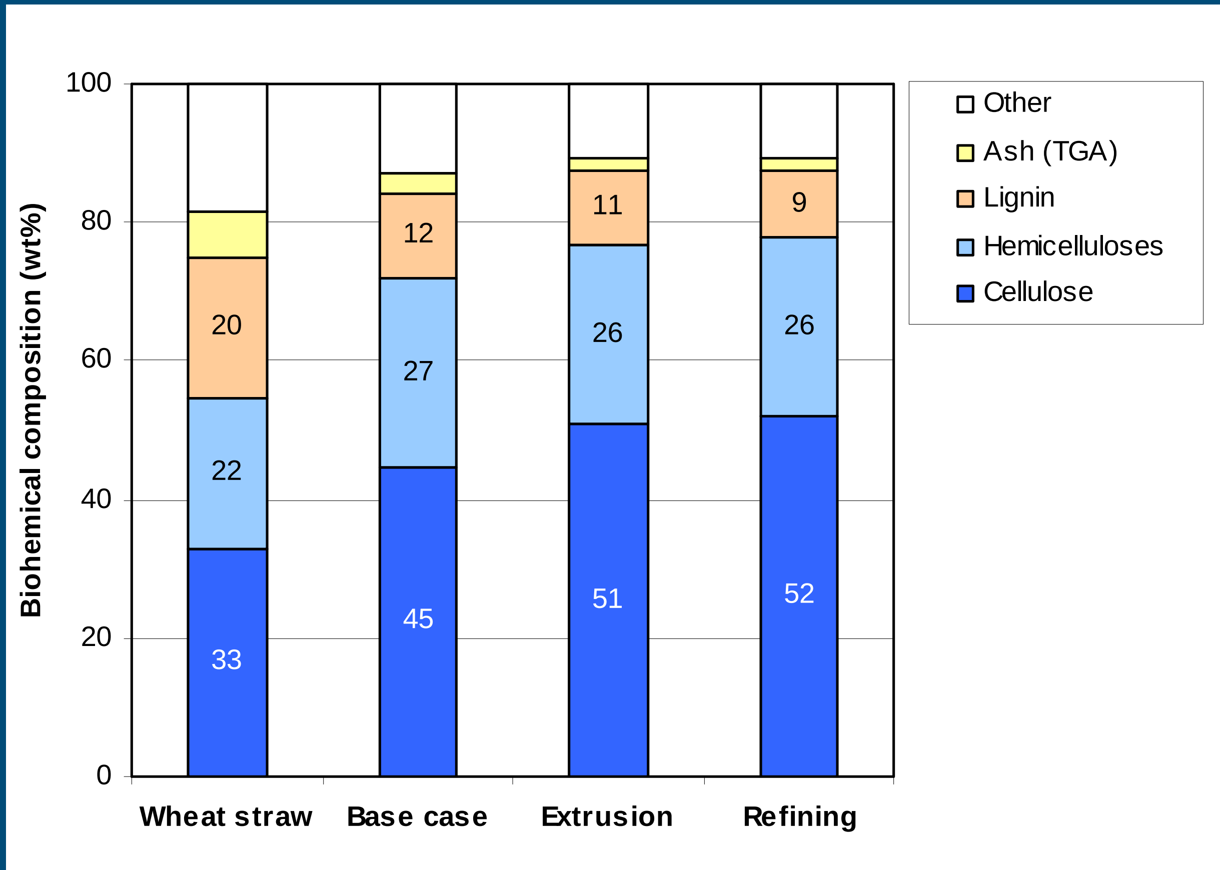



Extrusion




Refining

# Pretreatment efficiency *Solid fraction*

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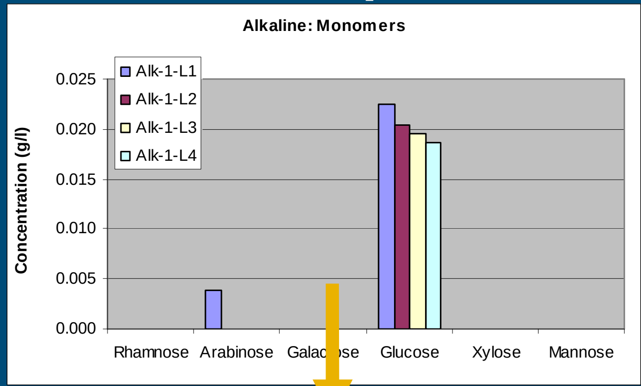
# Pretreatment efficiency *Liquid fraction*

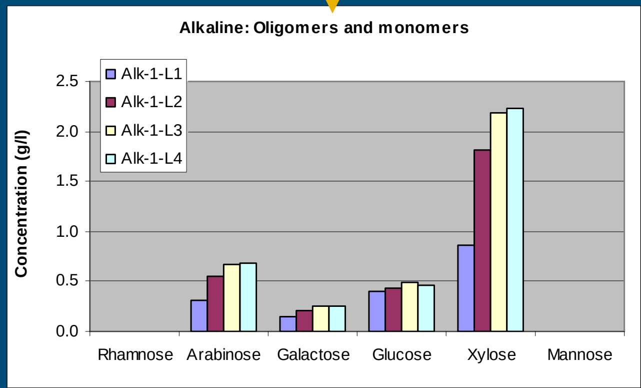
- Direct analysis of sugar monomers

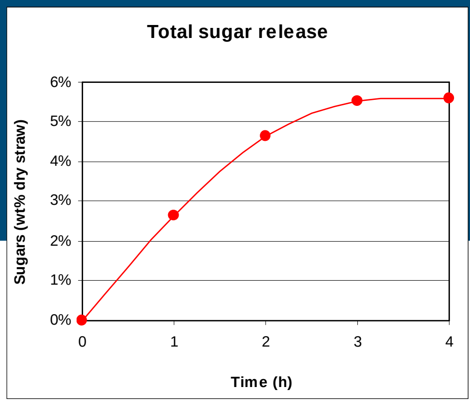
- After acid hydrolysis, 3h, 100℃

  - Substantial increase of sugars

- Liquid fraction
  - Sugars mainly present as oligomers (total 6%)



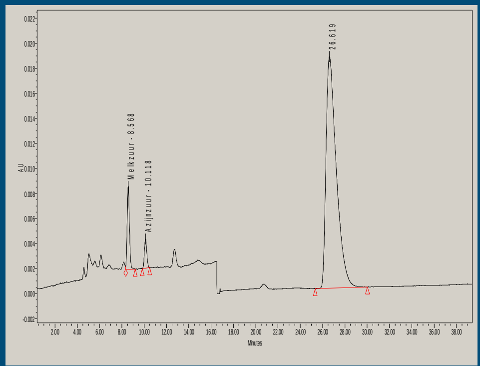



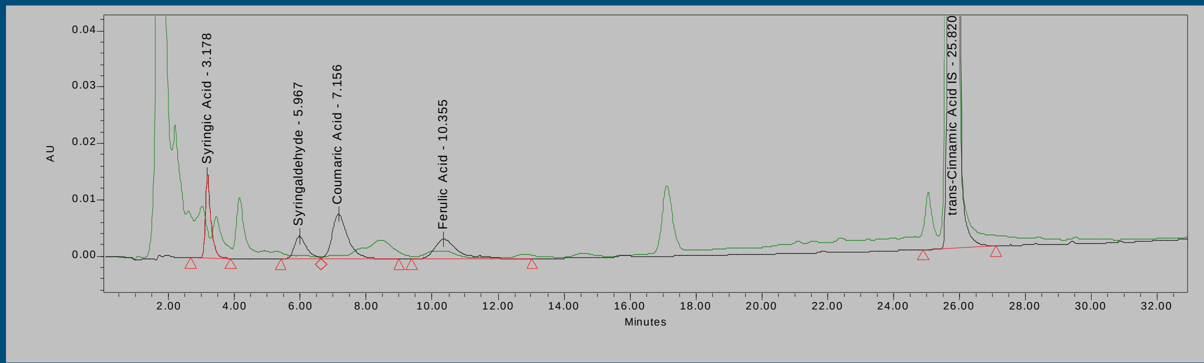




Amounts 100x lower

# Pretreatment efficiency *Liquid fraction*

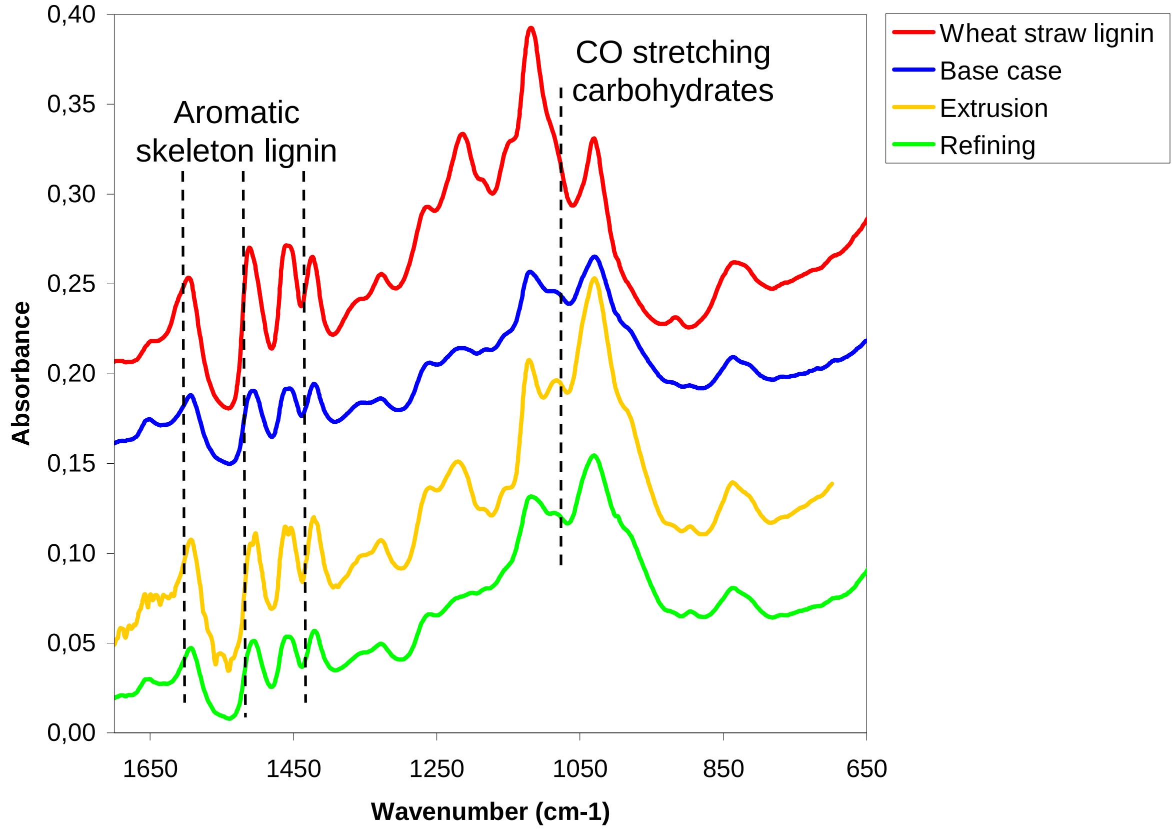
- Liquid fraction
  - Acetic acid primary fermentation inhibitor
  - Lactic acid present
  - Phenolic compounds present at very low levels



# Pretreatment efficiency *Liquid fraction*

IR-spectra of lignins isolated from liquid fraction

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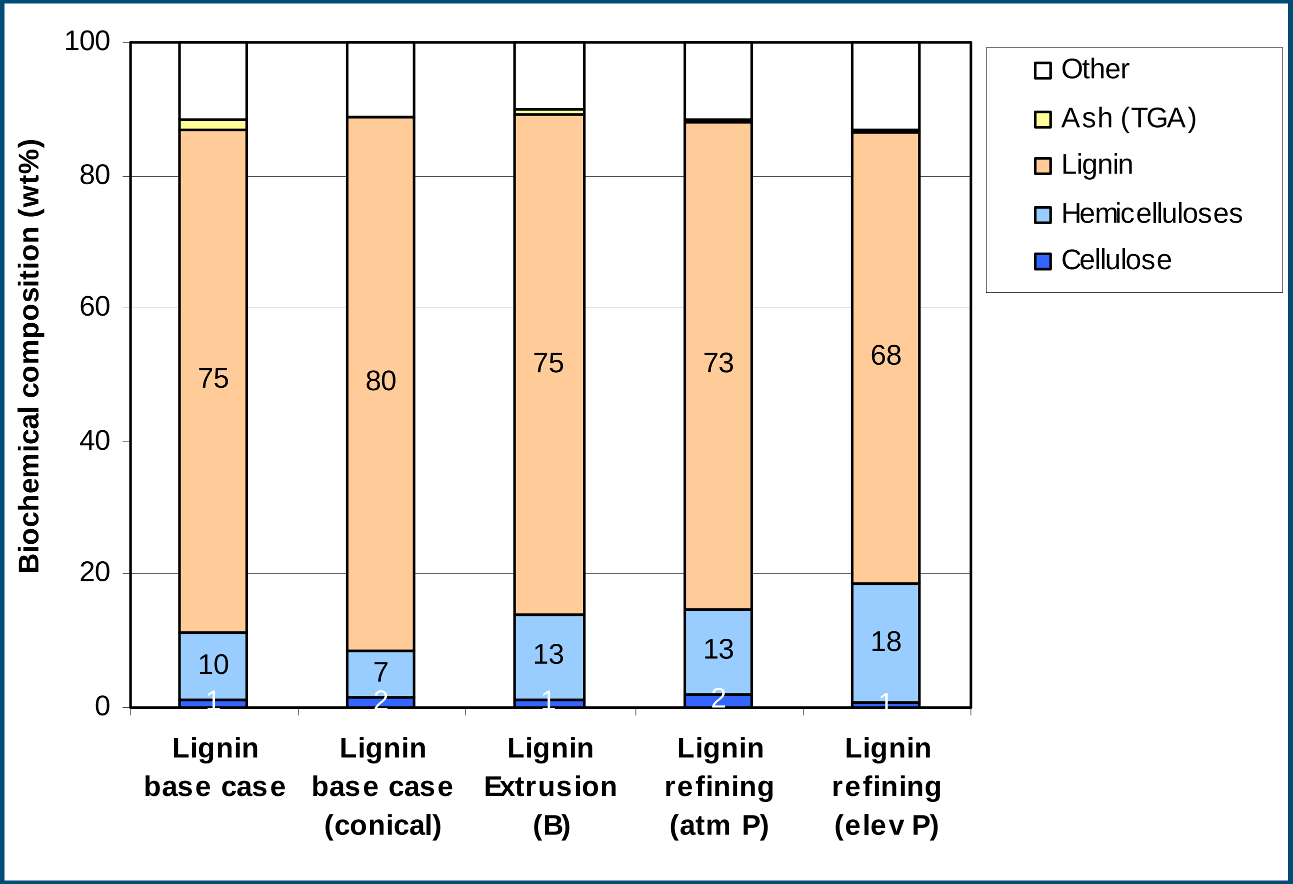
# Lignin: Chemical composition

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# Lignin: MWD by alkaline SEC

| Parameter | Reference lignin[1] | Base case | Extrusion | Refining (atmP) | Refining (elevP) |
|---|---|---|---|---|---|
| Mn (Da) | 700 | 690 | 1000 | 900 | 890 |
| Mw (Da) | 8100 | 5300 | 18000 | 17000 | 28000 |
| PD | 10 | 8 | 18 | 19 | 32 |

- Depending on pretreatment method different lignins obtained
- Biomass more accessible due to mechanical pretreatment: less degradation of lignins?

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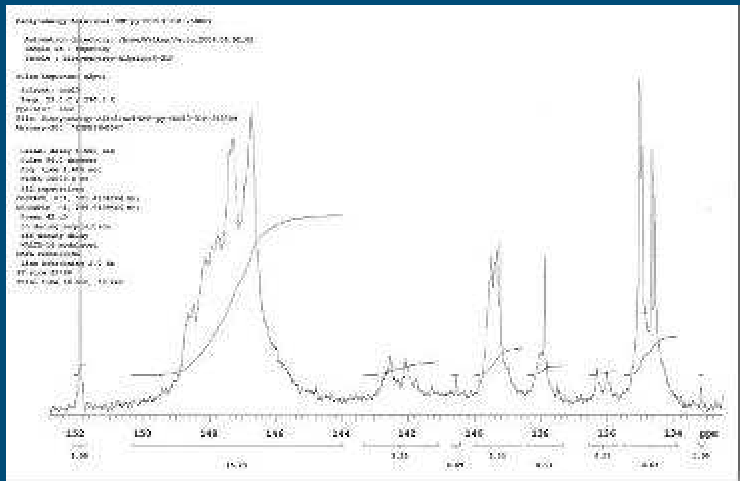
[1]Soda wheat straw lignin supplied by Granit SA

# Lignin: Functional groups by $^{31}P$ NMR

Amounts of different hydroxyl group species (mmol/g) in lignin

| Sample ID | Aliphatic OH | Aromatic OH | S+C | G | H | Carboxylic acid | Total OH |
|---|---|---|---|---|---|---|---|
| **Base case** | 3,72 | 1,14 | 0,30 | 0,62 | 0,22 | 0,89 | 5,75 |
| **Refining (atmP)** | 4,00 | 0,49 | 0,03 | 0,37 | 0,09 | 0,57 | 5,05 |
| **Refining (elevP)** | 3,97 | 0,85 | 0,24 | 0,48 | 0,14 | 0,68 | 5,50 |

S + C = Syringyl + Condensed phenolic units, G = Guaiacyl phenolic units and H = *p*-Hydroxyphenyl phenolic units



$^{31}P$ NMR analysis performed by VTT

IS = Endo-N-Hydroxy-5-norbornene-2,3-dicarboximide

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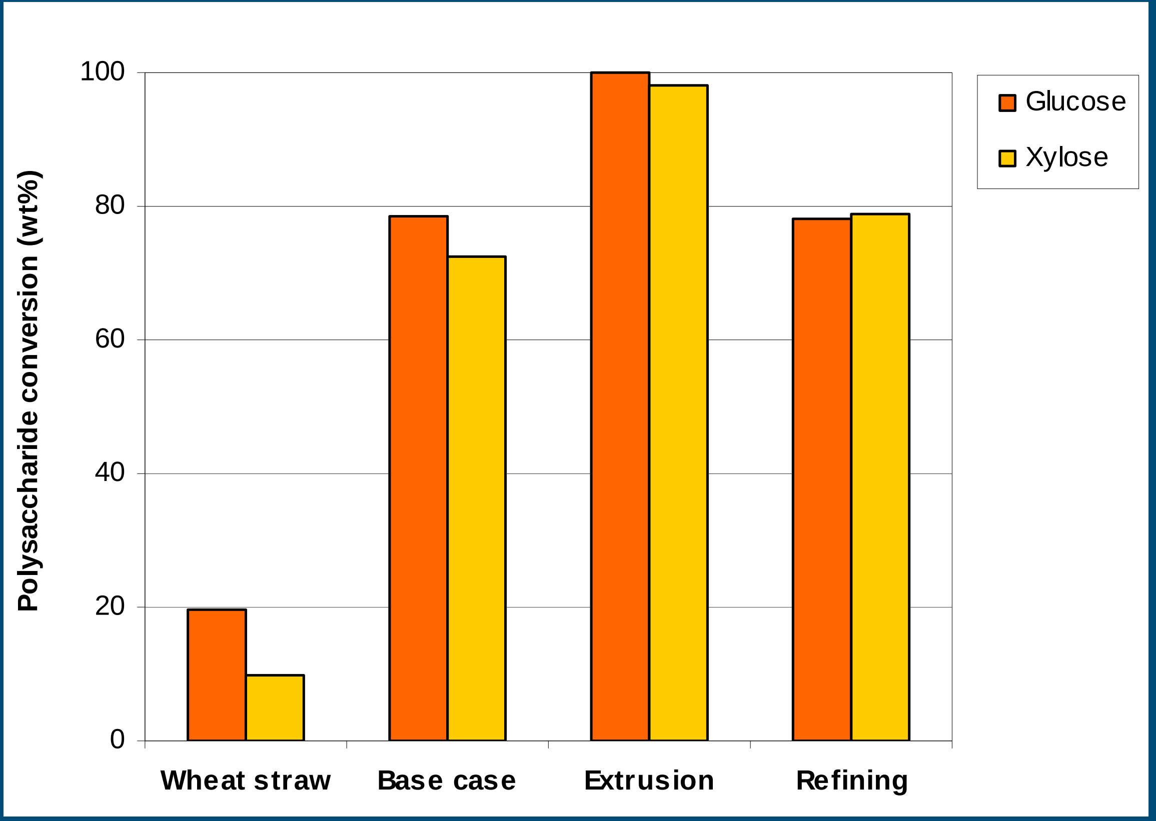
# Pretreatment efficiency

| | 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

# Enzymatic hydrolysis *Solid fraction*

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# Conclusions

- Alkaline pretreatment excellent for
  - Delignification (40-50%)
  - Improvement of enzymatic degradability (from 20 to 70-80%)
- Added value extrusion or refining
  - More delignification (70-80%)
  - Further improvement of enzymatic degradability (from 20 to 100%)
- Different lignins produced
  - Moderate purity (80%)
  - Molar mass relatively high
- Economic feasibility of combined mechanical/alkaline pretreatment depends on value of lignin produced
- Analytical tools suitable for process development

# Available samples for Round Robin

- Wheat straw (kg)
- Base case: Alkaline pretreated wheat straw (kg)
  - Neutralised + washed + stored @ -20℃
- Black liquor stored @ -20℃ (kg)
- Isolated soda wheat straw lignin (100-200g, expected early September)

# Acknowledgements

- Biosynergy www.biosynergy.eu
- Biobutanol www.biobutanol.nl

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www.biosynergy.eu

SIXTH FRAMEWORK PROGRAMME

# Thank you for your attention

## Any Questions?



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