



Bioalcohol production from lignocellulose

- a comparison of processing schemes for different lignocellulosic raw materials -

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Outline

- About the Paper and Fibre research Institute
- Liquid biofuels demo plants in the Nordic region
- Presentation of joint Nordic R&D project

PFI

Paper and Fibre Research Institute

- Independent research institute , est. 1923
- Area of operations: R&D on processes/products using lignocellulose as raw material
- Localized in Trondheim, Norway
- Focus areas:
 - Fibre and pulp
 - Printing paper
 - Packaging
 - New biobased materials (composites, MFC)
 - Biofuels/bioenergy/biorefinery
 - Characterisation of fibre structures and products
- Subsidiary of INNVENTIA AB since 2004



PFI

Biorefinery research activities

- ❑ Key competence
 - Pre-treatment processes for biochemical conversion (steam pretreatment, sulphite pretreatment, organosolv, strong acid)
 - Pre-treatment processes for thermochemical conversion (fast pyrolysis, torrefaction)
 - Biomass characterisation

- ❑ Typical project portefolio subjects
 - Production of biofuels and chemicals from lignocellulosic materials
 - Integrated bioenergy and paper production
 - Torrified wood pellets
 - Applications for fast pyrolysis bio-oils



Liquid biofuels in the Nordic region

- Lignocellulosic biomass from forestry and agriculture are important resources
- The region holds long traditions of pulp and paper production, especially Finland, Sweden and Norway
- Main softwood species are spruce and pine. Main hardwoods are birch and aspen. Main agricultural species are wheat, oats and barley
- Ongoing research activities are focusing both on biochemical and thermochemical conversion routes
- The region has significant water supply



Liquid biofuels in the Nordic region

- In Norway we also have a long history in fish farming and utilization of macroalgae
- There is ongoing research focusing on the breeding and utilization of seaweeds (macroalgae), which are rich in carbohydrates, for bioethanol production
- Research focus is on the cultivation systems, especially localization of breeding installations in the vicinity of fish farms to take advantage of excess nutrients



Liquid biofuels in the Nordic region

2G demo facilities (list may not be complete)

Biochemical technologies

- Denmark:
 - Inbicon (DONG Energy); Wheat straw to ethanol
 - Biogasol; Grasses & straw to ethanol
 - DTU; Wheat straw & corn fibre to ethanol

- Norway:
 - Borregaard Industries; Sulfite spent liquor (spruce, bagasse) to ethanol
 - Weyland AS; Coniferous wood & sawdust to ethanol

- Sweden:
 - SEKAB; Wood chips and bagasse to ethanol

Liquid biofuels in the Nordic region

2G demo facilities (list may not be complete)

Thermochemical technologies

- Finland:
 - NSE Biofuels Oy (Neste Oil/Stora Enso JV); Forest residues to FT-liquids
- Sweden:
 - Chemrec AB; Black liquor gasification to methanol, DME

Other technologies

- Denmark:
 - BFT Bionic Fuel Technologies AG; Straw pellets to diesel, hydrocarbons
- Finland:
 - Neste Oil; Hydrotreatment of oils and fats to diesel

Nordic bioethanol project: *New, innovative pretreatment of Nordic wood for cost-effective fuel-ethanol*

- Project duration: 2007 – 2010
- Budget: Approx. 1,5 M€
 - Funding from Nordic Energy Research and industry partners
- Participants from all five Nordic countries (Norway, Sweden, Finland, Denmark and Iceland)
- Project coordinator: Paper and Fibre Research Institute (PFI)

Nordic Bioethanol project

Background

- The Nordic region has a large surplus of wood which has a potential for providing a stable, long-term source of fuels
- The Nordic countries have complementary expertise used in the project:
 - Sweden, Finland and Norway: Wood chemistry and pulp and paper production
 - Norway: Use and production of fuels, including oil refining
 - Iceland: Isolation, modification and utilization of thermophilic microorganisms and enzymes
 - Denmark: Cellulose degrading enzymes

Nordic Bioethanol project

Objective

- Elucidate pretreatment and production schemes aiming to reduce the overall production costs for fuel-ethanol from Nordic wood
- Quantify the possibilities to reduce investment and operating costs by co-locating and integrating the ethanol plant with existing industry infrastructure (oil refinery)
- Join Nordic research resources in the liquid biofuels area

Nordic Bioethanol project

R&D partners

R&D PARTNER	SPECIAL COMPETENCE / WORKING AREA IN PROJECT
PFI (NO)	Raw materials, pretreatment, hydrolysis, separation, characterisation. Project owner
Matis-Prokaria (IS)	Thermophilic enzymes and microorganisms
SINTEF (NO)	Fermentation; fermentability screening / microorganisms
VTT Biorefinery Team (FI)	Fermentation; process configurations
INNVENTIA (S)	Pretreatment (soda cooking). Systems analysis. Process integration

Nordic Bioethanol project

Other partners

PARTNER	SPECIAL COMPETENCE
Norwegian Forest owners association (NO)	Raw materials
Norske Skog (NO)	Wood processing
Novozymes (DK)	Enzyme producer
SEKAB E-technology (S)	Wood-to-ethanol pilot facility
Borregaard (NO)	Biorefinery; wood based chemicals
Statoil (NO)	Oil and gas company. Fuel characteristics

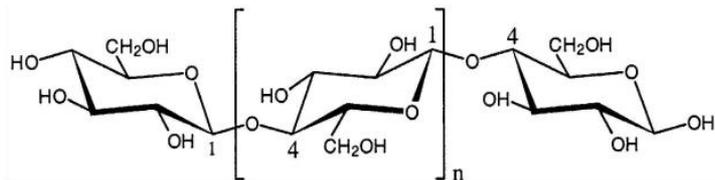
Nordic Bioethanol project

Project layout



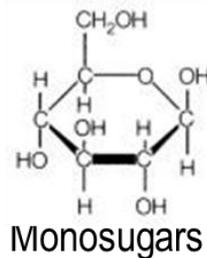
**Pretreatment
& separation**

Lignin,
extractives

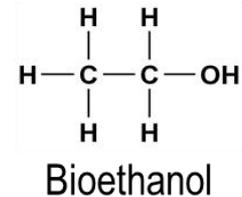


Cellulose / hemicellulose

Hydrolysis
(enzymes, acids)



Fermentation



Research focus: *Bioethanol from wood sugars*

- ❑ Raw materials, pretreatment and separation (PFI, INNVENTIA)
- ❑ Hydrolysis (Prokaria, Novozymes, PFI, SINTEF, VTT)
- ❑ Fermentation (SINTEF, VTT)
- ❑ Systems analysis & process integration with existing industry infrastructure (INNVENTIA)



Nordic Bioethanol project

Research tasks

Wood pretreatment and separation

- Chipping, drying and deconstruction of fibre structure / cellulose crystallinity
- Separation of wood polymers; lignin, cellulose, hemicellulose

Enzymatic hydrolysis

- Search for effective, thermo stable, cellulose degrading enzymes in Icelandic hot springs
- Examine hydrolysis yields following different pretreatments using commercial enzymes

Fermentation to bioethanol

- Isolation and modification of possible ethanol producing thermostable microorganisms
- Fermentability screening of differently pretreated wood hydrolysates
- Elucidate industrially-feasible process configurations (e.g. SSF/SHF, high dry-matter fermentation, feeding strategies of toxic hydrolysates)

Systems analysis

- Cost-benefit assessments of various process concepts
- Integration with existing industry infrastructure – oil refinery

Nordic Bioethanol project

The raw materials

Significant differences in composition and fibre structure of different raw material inputs complicates lignocellulose conversion

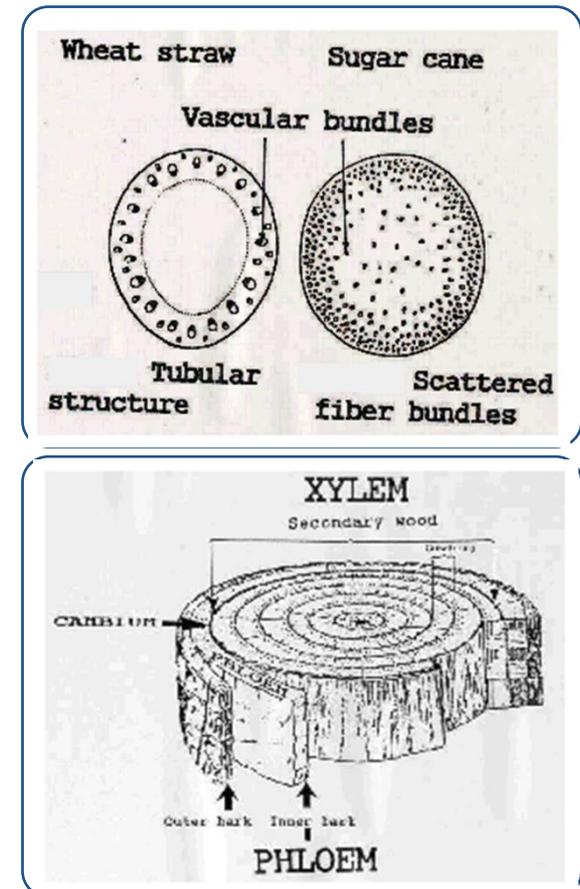
Component	Pine <i>Pinus Sylvestris</i>	Aspen <i>Populus Tremula</i>	Bagasse*	Wheat straw*
Cellulose [%]	44.2	46.7	44	39
(Gal) Glucomannan [%]	18.2	5.2	2.0	1.8
(Ara) Xylan [%]	7.8	23.1	27	23
Lignin (Klason and acid soluble) [%]	28.5	22.5	19	20
Extractives (cyclohex/acetone) [%]	1.3	2.5	1.0	3.5

*: Outside the Nordic project

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Pretreatment and separation

- Wood fibres are more recalcitrant to deconstruction than annual plant fibres due to a more complex structure
 - Challenge in the pretreatment step
- “By-products” may be very important for profitability in these processes

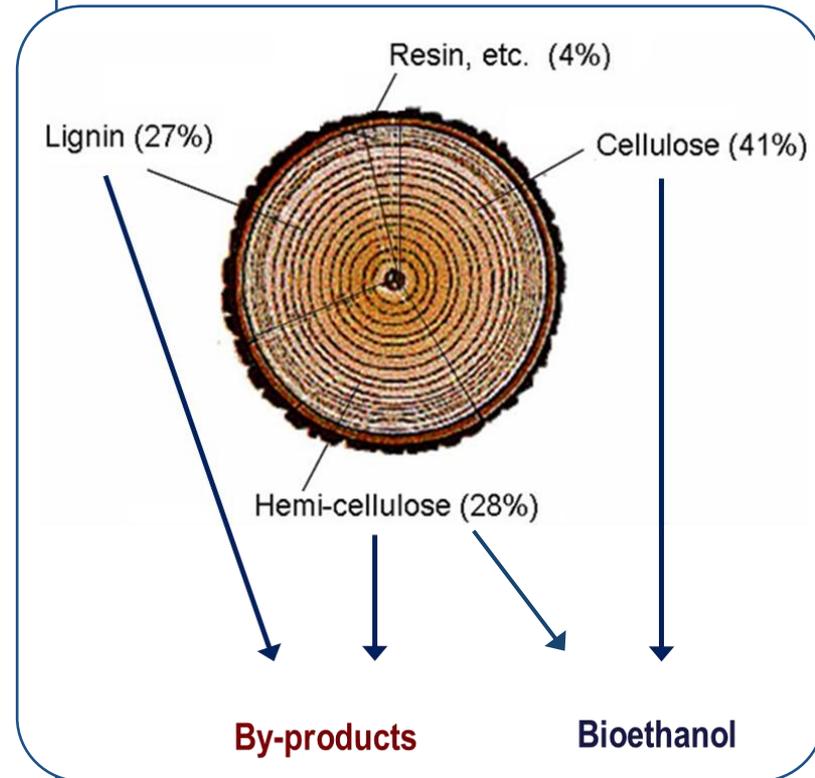


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Pretreatment and separation

■ Aims:

- Make cellulose more accessible to hydrolyzing enzymes, by breaking the 3-D lignin network, disrupting the crystalline structure and increase surface area
- Efficient lignin separation
- Limit formation of degradation products that inhibit growth of fermentative microorganisms



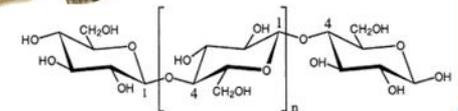
Nordic Bioethanol project

Pretreatment and separation

Processes studied:

- Alkaline cooking (cf. kraft pulping)
- Steam pretreatment
- Strong acid pretreatment and hydrolysis
- Sulphite based pretreatment

An overall aim: To enlighten the strengths and weaknesses of each process



Nordic Bioethanol project

Steam pretreatment

The process

- Biomass is subjected to high pressure steam (180-225°C, 15-30 bar, 2-5 min). Acid catalyst was added to obtain harsh treatment conditions.

Strengths and weaknesses

- + Low-cost, rapid process with no/minor use of chemicals
- + High wood to liquid ratio
- ± Harsh process conditions gave good biomass fragmentation/enzyme accessibility (+), but caused hemicellulose degradation/formation of inhibitors (-). This limits possible production of value-added products from hemicellulose (-)
- ± Mild conditions limit hemicellulose degradation (+), but reduce biomass fragmentation (-)
- Harsh conditions caused moderate enzymatic saccharification for softwood due to formation of lignin-carbohydrate complexes during pretreatment (Li et al 2009)

Nordic Bioethanol project

Steam pretreatment - improvements

Hemicellulose pre-extraction during harsh conditions:

- + Efficient separation of hemicelluloses as monomers and oligomers – inhibitor formation reduced
- + Good biomass fragmentation for both pine and aspen – giving high sugar yields
- + Hemicellulose may be used for production of value-added products



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Sulphite based pretreatment

The process:

- Sulfite treatment under acidic conditions.

Strengths and weaknesses:

- + Lignin sulphonation facilitated lignin removal
 - High degree of sulphonation needed in order to obtain good lignin solubilisation/separation
 - Lignosulphonates are high-value products which may contribute significantly to the overall profitability of the process.
- + Fairly high sugar yields obtained, but could be improved
- + Low inhibitor formation
- Chemical recovery system needed

Nordic Bioethanol project

Strong acid based pretreatment

The process:

- Concentrated acid used to decrystallize cellulose followed by dilute acid hydrolysis to monosugars (no enzymes needed). Acid recovery is critical
- In this work different decrystallization conditions were studied:
 - Acid concentration (65-80 wt%)
 - Temperature (35-70°C)
 - Reaction time (60-180 min)

Findings:

- + High sugar yields obtained
- + Low inhibitor formation
- ± There is variation of conditions required for optimal production of individual sugars, i.e. the conditions that maximizes the total sugars are not necessarily the same as those maximizing the individual monosugar yields.
 - Need to predefine the goals on the desired sugars to be optimized.
- Acid recovery system needed

Nordic Bioethanol project

Pretreatment by alkaline cooking

The process:

Modifications in the kraft cooking process to separate wood to a carbohydrate fraction for ethanol production and to a lignin fraction.

- An "optimum" lignin content was defined as lignin content before the yield of carbohydrate fraction/pulp starts to decline substantially with decreasing lignin content; a lignin content of approx. 2.5% on pulp seemed optimum for aspen and approx. 5% on pulp for pine with respect to yield of carbohydrate fraction and fermentable sugars.

Findings:

- + High sugar yields obtained
- + Low inhibitor formation
- Chemical recovery needed
 - Aspen wood required lower alkali charge and lower temperature than pine wood (as expected).

Nordic Bioethanol project

Pretreatment studies

All these pretreatment processes show promising results when necessary process adjustments are made.

However, as Nordic wood is a rather expensive feedstock and biofuels are low-value products, biorefinery concepts are needed.

	Alkaline cooking	Steam explosion		Strong acid	Sulphite based
		<i>Extensive, acid catalysed</i>	<i>Hemicellulose pre-extraction</i>		
Chemical costs	High	Low	Low	High (recovery)	High (Recovery)
Sugar yield	High	Low (hemicellulose degradation)	High	High	High
Inhibitor formation	Low	High	Moderate	Low	Low

Nordic Bioethanol project

Summary of findings in the overall project

Pretreatment:

- Comparison of different pretreatments on the exact same raw materials, using the same characterisation methods
- All pretreatment processes studied shown promising results when necessary process adjustments are made (e.g. pre-extraction of hemicelluloses).
- Strengths/weaknesses of the processes illustrated
- Potential process improvement clarified

Thermophiles:

- Thermophilic species isolated from hot springs, however the cellulolytic capabilities of these species need further improvement
- Thermophilic ethanol producers were also found – current ethanol production is low, but these will be further improved by genetic tools

Nordic Bioethanol project

Summary - continued

Fermentation:

- Different industrially-feasible fermentation process configurations investigated focusing on
 - High density fermentation (up to 15% dry matter)
 - Washing and feeding strategies to minimize inhibition gave good results

Techno/economic evaluations

- Preliminary evaluations performed, pointing to improvement potentials in the different processing schemes

Process integration:

- Co-localization with an oil refinery has advantages that would lead to reduced ethanol production cost compared to a stand-alone plant.

Nordic Bioethanol project

- In this project we reached no final solution to the processing of Nordic wood to bioethanol – however the work gave a good foundation for further cooperation through a new Nordic project that started late 2010.

Many thanks to all my Nordic R&D colleagues who participated in the project

**Gudmundur Oli Hreggvidsson, Matis, Jaana Uusitalo, VTT, Nils Dyrset and Mimmi
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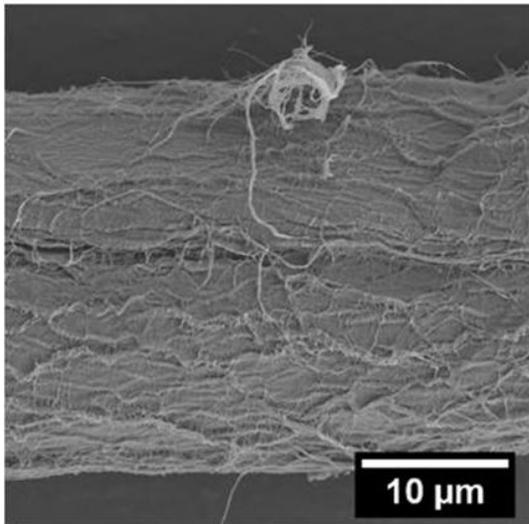


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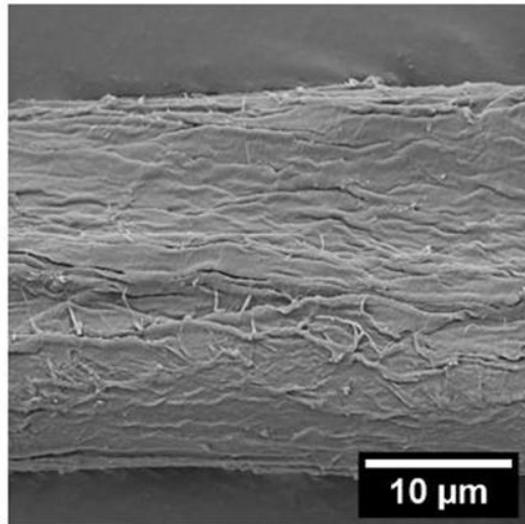
Morphological characterisation tools

- Fibre surface:
 - Example: Enzyme treatment – effect on fibre surface characteristics

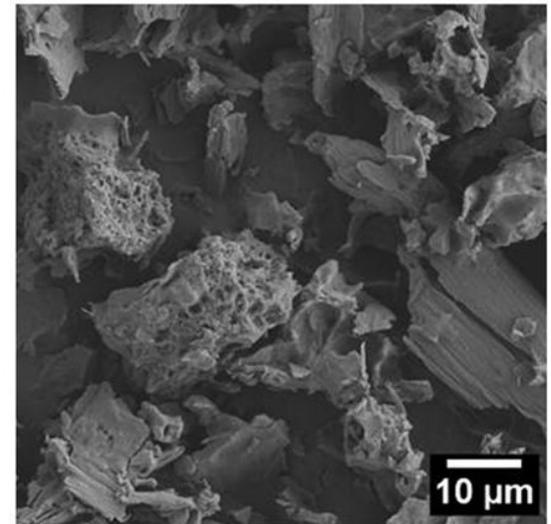
Untreated



Enzyme A



Enzyme B



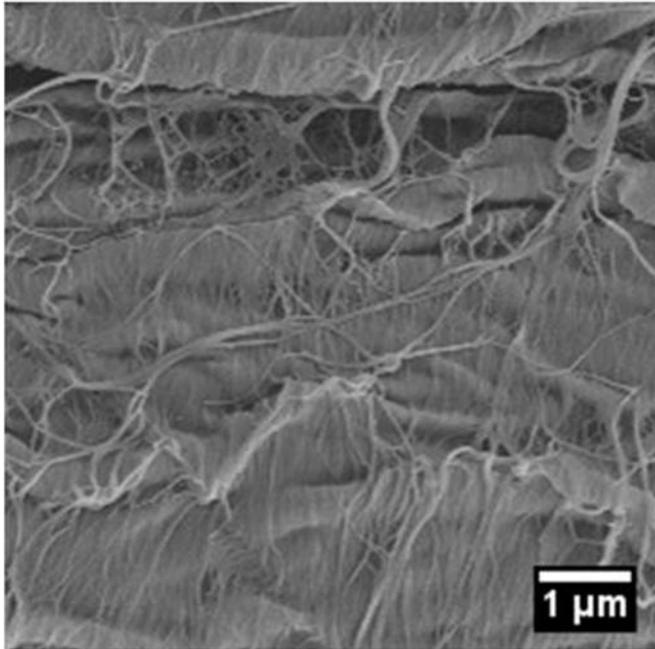
SEM Pictures by Per Olav Johnsen, PFI, 2008

Nordic Bioethanol project

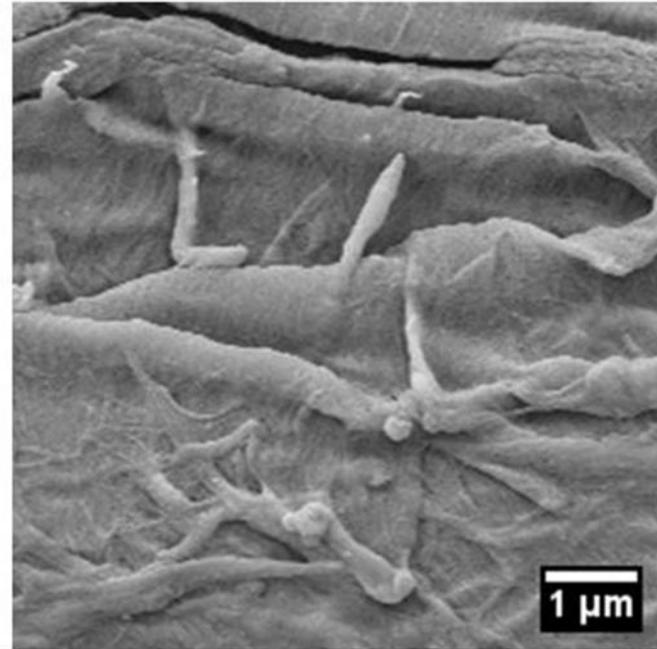
Morphological characterisation tools

- Fibre surface: Enzyme treatment

Untreated



Enzyme A

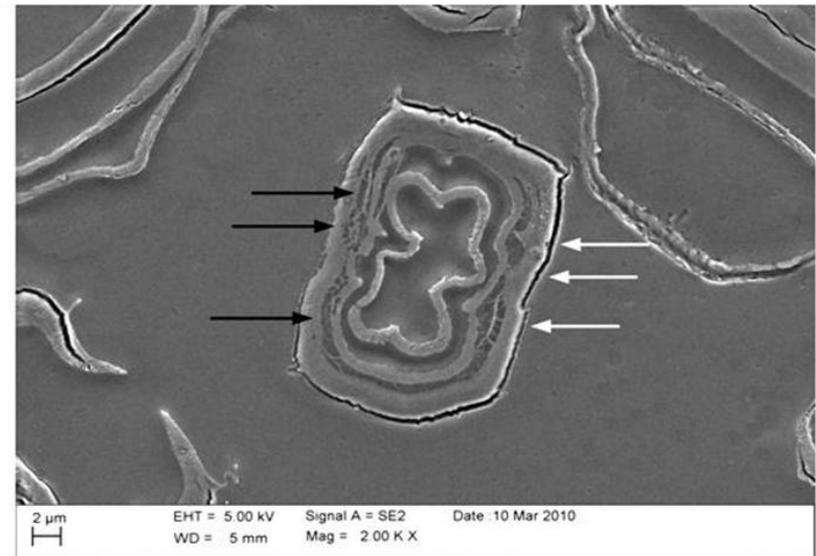


FESEM Pictures by Gary Chinga Carrasco, PFI, 2008

Nordic Bioethanol project

Morphological characterisation tools

- Fibre cross-section:
 - Example: Effect of sulphite pre-treatment
 - Black arrows indicate delamination of the fibre wall caused by pretreatment.
 - White arrows indicate artifacts caused by sample preparation.

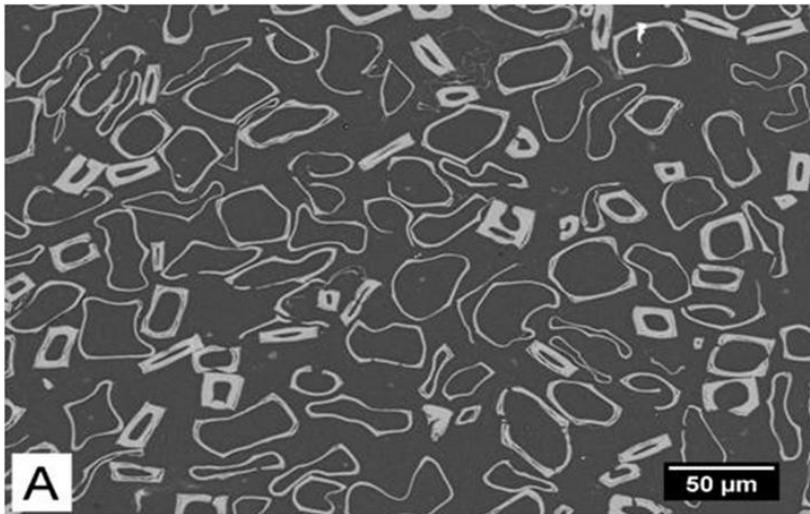


FESEM Pictures by Gary Chinga Carrasco, PFI, 2010

Nordic Bioethanol project

Morphological characterisation tools

- Fibre cross-section analyses by SEM:
 - Arrows indicate fibres with delaminated fibre walls



Reference sample; spruce fibres



Pretreated sample

SEM Pictures by Per Olav Johnsen, PFI, 2010