CEBIPRO Business Finland Project: Key results

1.4.2025

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storaenso FIBERX WETEND Technologies Valmet AQUAFLOW UPM BIOFORE BEYOND FOSSILS

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Work packages

WP1: Structural Fingerprint: Fiber Morphology

- Pulp characterization.
- Identify key factors linking properties of particles and flocs to network properties.

WP2: MFC characterization, Flocs & Retention

- The potential of the Valmet Fractionator in MFC characterization and floc formation is evaluated.

WP3: Polymerization Index Development

- Development of new measurement methods based on NMR technology.

WP4: Modelling and Simulations

- Model creation – Variables connecting fiber properties to network properties.

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Work packages

WP5: Closed Process Water Loop Analytics

- Application of NMR technique in the analysis of organic compounds in wastewater.

WP6: Proof of Concepts & Piloting (PoC tests)

- To verify NMR analysis and fractionator at lab scale and industrial environment.

WP7: Business Case Evaluations

- Document the business potential and end-user benefits for NMR and fractionator.

WP8: Management, Collaboration, and Dissemination

- Project Management: Achieving stated objectives – Through Collaboration.

Work Package Overview
NMR Methods and PoC Testing (WP3, WP5, WP6)

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NMR methods used in the project

NMR = Nuclear Magnetic Resonance

- **NMR relaxometry** (WP3 and WP6) provides information on molecular mobility, dynamics, and interactions
- **Low-field NMR spectroscopy** (WP5) offers insight into the chemical composition and molecular mobility
- **High-field NMR spectroscopy** (WP5) provides more detailed information about the molecular structure and chemical composition (higher resolution and sensitivity).

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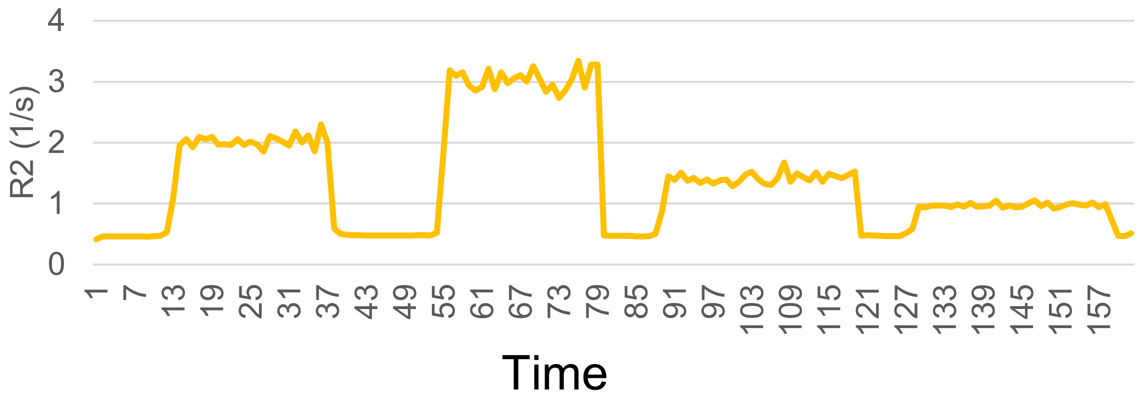
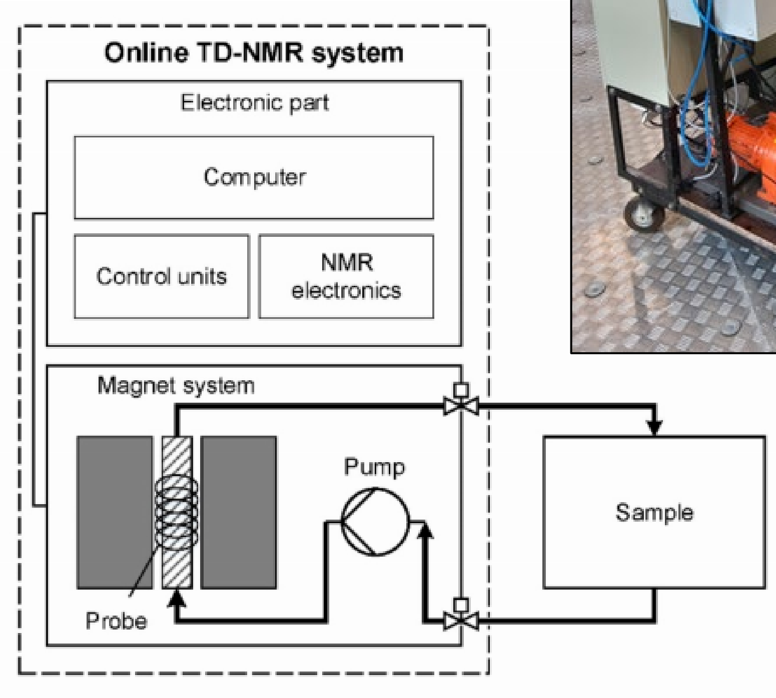
Online NMR relaxometry

- The instrument consists of a relaxometer, a flow tube, and a pump.
- The pump automatically changes the sample in the magnet, from which the T2 relaxation time or times are measured.
- In the PoC tests, the method's applicability for industrial measurements was evaluated.





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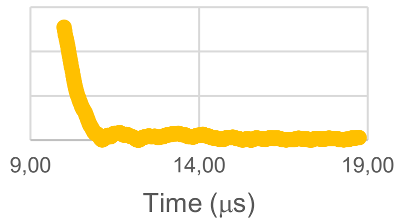
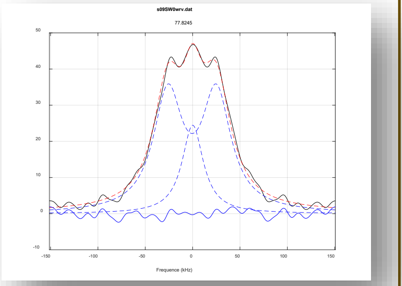
Analytical and measurement methods

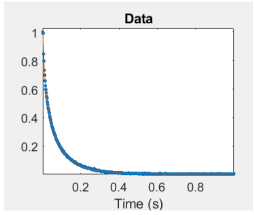
FID (Free Induction Decay) is a time-domain signal converted via Fourier transformation into a frequency-domain spectrum, revealing structural information (WP3 and WP5)

The CPMG pulse sequence is a technique used to measure T_2 relaxation times, providing valuable insights into molecular interactions and mobility (WP3 and WP6)

- A short T_2 indicates rigid, solid, or dense environments
- A longer T_2 corresponds to fluid, mobile, or less viscous conditions.





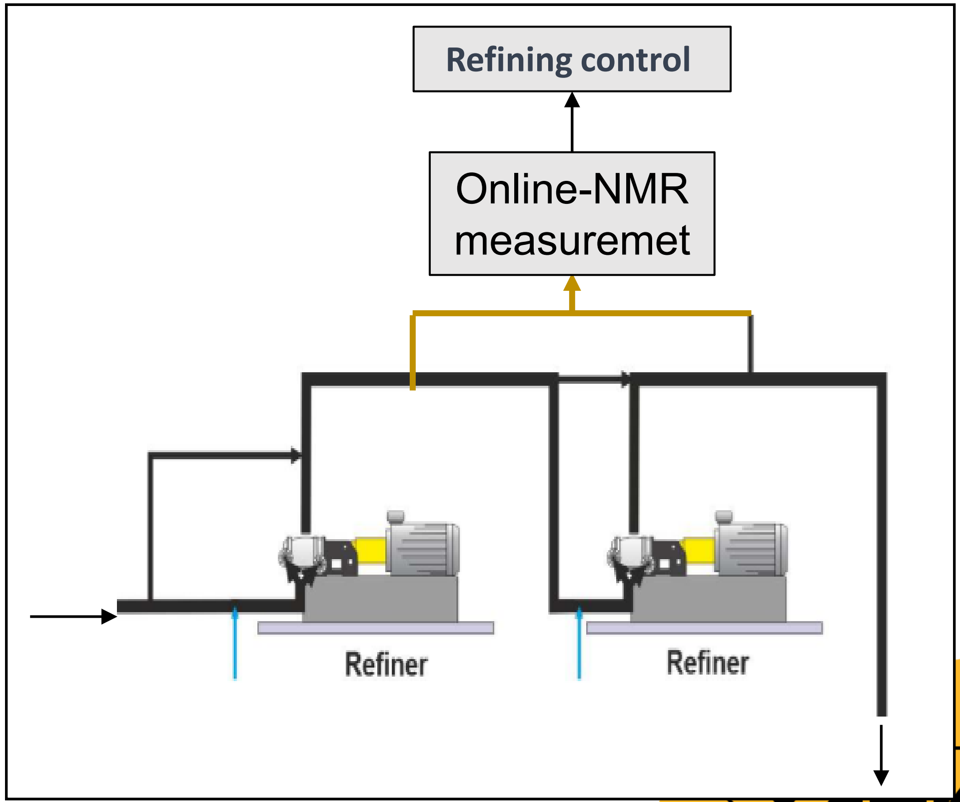


$$S = \sum_{i=1}^{n} A_i e^{t/T_{2i}}$$

where n = 1, 2, or 3
⇒ information about water states 1–3

MFC refining control by online-NMR (Patent application 20236370)

- Method for measuring micro- or nanofibrillated fiber suspensions
- An online NMR relaxometer can be used to determine the relative surface areas of different parts of the fibers (B_int, B_middle, and B_ext).
- Real-time decisions can be made to continue or stop processing, ensuring optimal energy efficiency and product quality.



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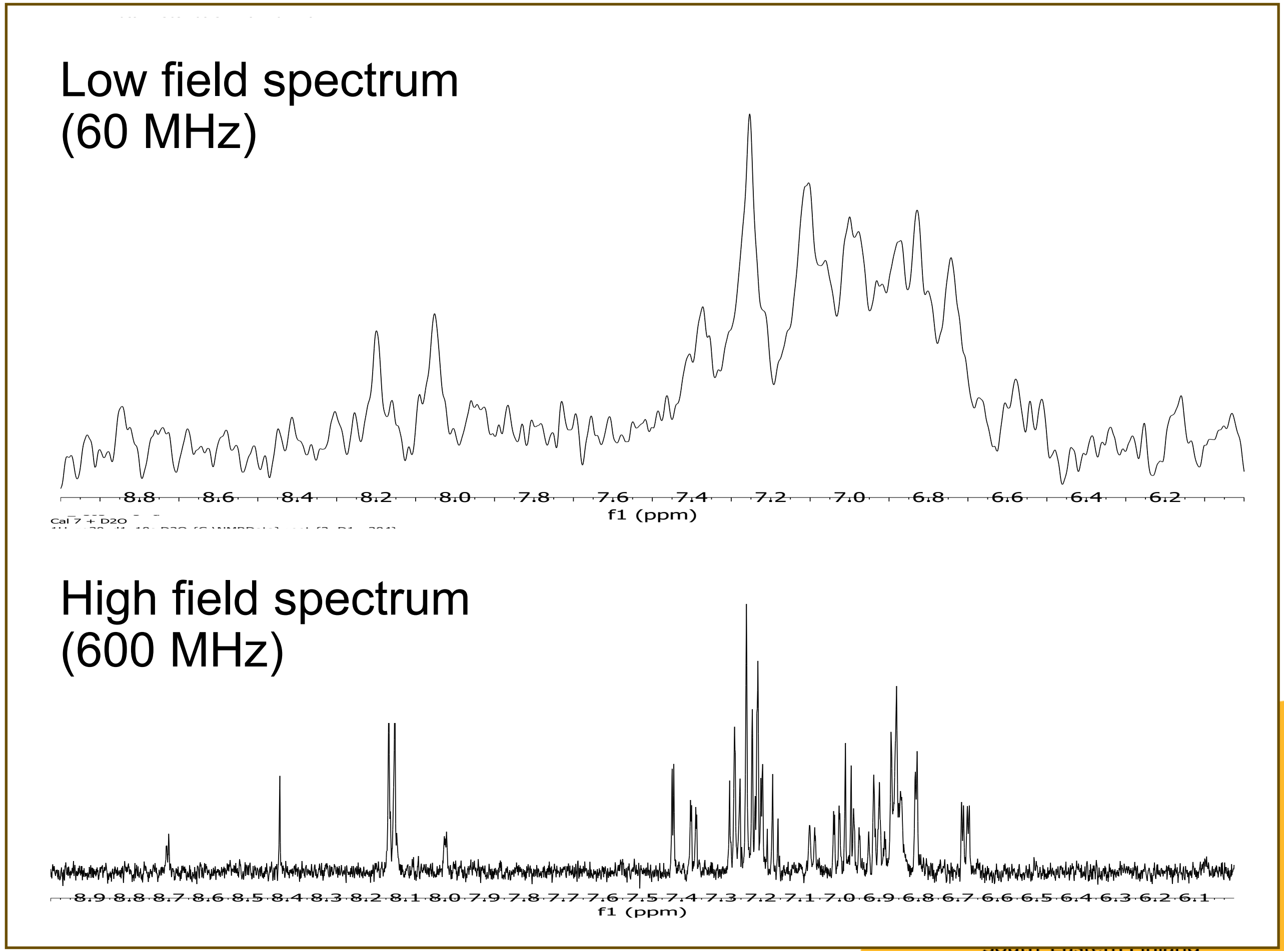
WP5: Process water

- Process and wastewater samples were analyzed using low- and high-field NMR spectroscopy.
- The research focused on the chemical composition, AOX compounds, and biodegradability of process waters.
- HF NMR spectroscopy provides significantly more detailed information, particularly at low chemical concentrations.



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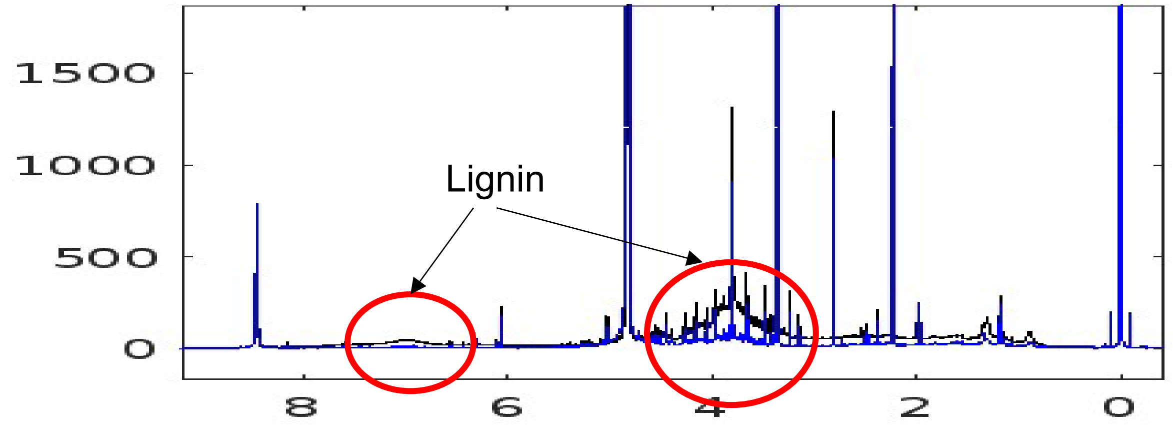
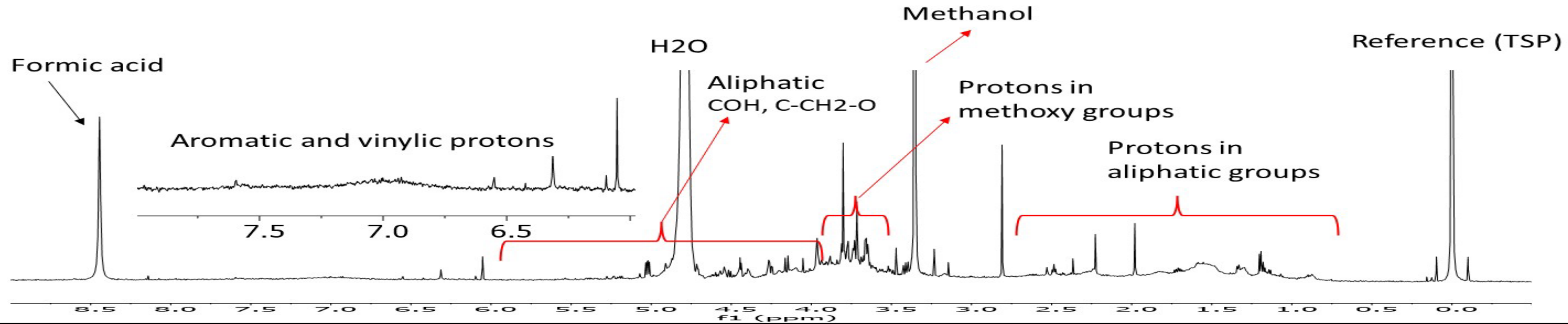
WP5: Process water - examples

- Nanofiltration was tested, for example, for lignin removal.
- High-field NMR spectroscopy was used in the analysis (see image).
- Ozonation was also tested to improve process water biodegradability, with HF-NMR spectroscopy applied for its analysis.

Normal and nanofiltered samples

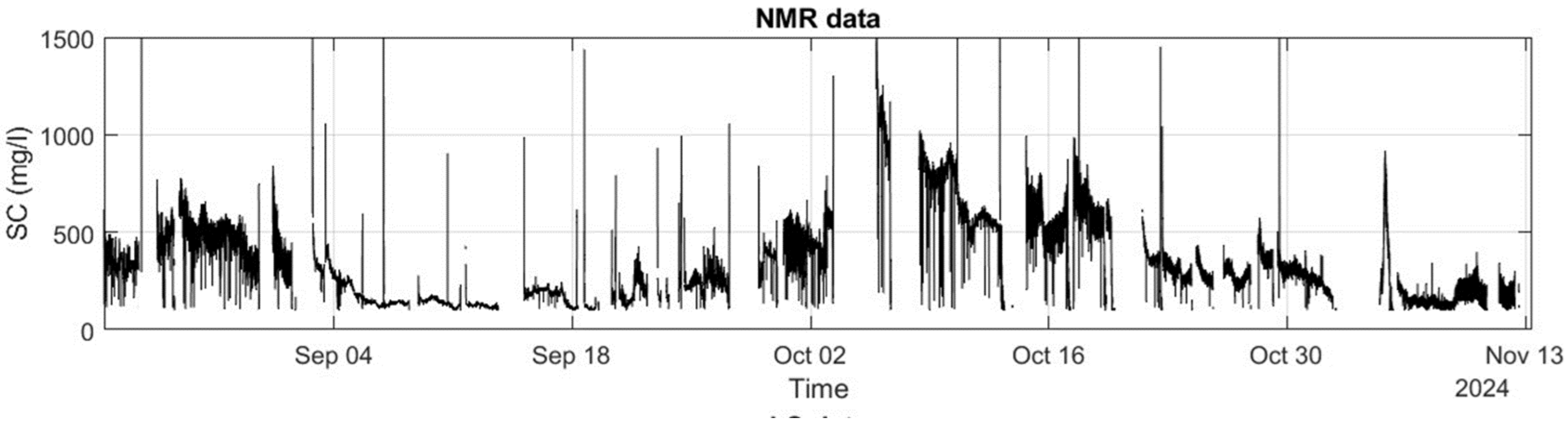




NMR PoC-tests

1. Online tests using Masuko refinder
2. Online NMR measurements at the Taskila water treatment plant

2. Online NMR measurements
- NMR device is located at the Taskila WWT plant in Oulu
- Over 100,000 measurements over a period of three months



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Conclusions

- NMR proved to be an effective method for measuring fibers and circulating water
- At low concentrations, HF-NMR is required to obtain reliable results
- Relaxation time measurements offer valuable insights into the state of water in various materials => enable the calculation of bound water in different states, which can be linked to relative surface areas => supporting a patent application
- The PoC test demonstrated the method’s functionality in a real process environment.

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Monitoring structural modifications of cellulose fibers using the ^{1}H Low-field Nuclear Magnetic Resonance (NMR) method

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^{1}H Low-field NMR method and online NMR system

Method

- Quantum-mechanical phenomenon
- Sensitive to variety of nucleus
- Magnetic field <2T (<85 MHz for ^{1}H)

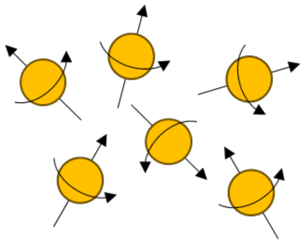
Devices are

- Transportable (weight less than 50kg)
- Non-fouling
- Suitable for industrial environment
- Robust (measurements every 1 minute 24/7)

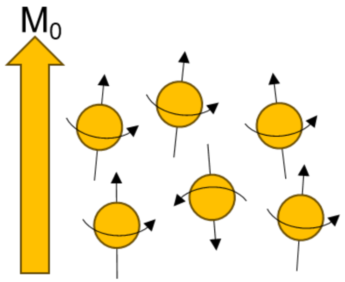
Online NMR system

- Electronics (Low-field NMR spectrometer/relaxometer, computer, and control units)
- Magnet system with a probe
- Pump

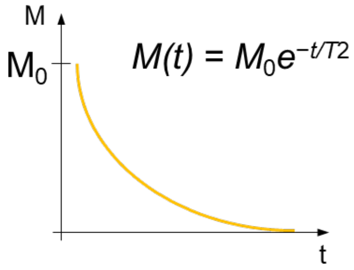
Nuclei



Nuclei in an external magnetic field (inside magnet system)



Signal after RF pulse sequence applied at resonance frequency



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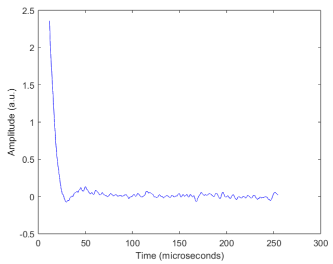
Structural parameters measured by ^{1}H Low-field NMR in cellulose fibers (WP3 and WP6)

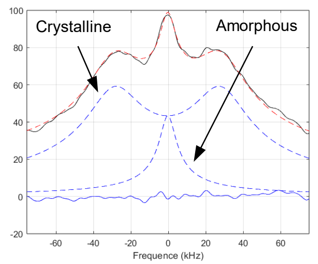
Parameter: **Crystallinity index (CI)**

- **Dry state**
- Signal from fiber
- Pulse sequence: FID
- Processing: FFT and fitting the spectra in the frequency-domain to model
- Method: ^{1}H Low-field NMR spectroscopy

FID



FFT + fitting

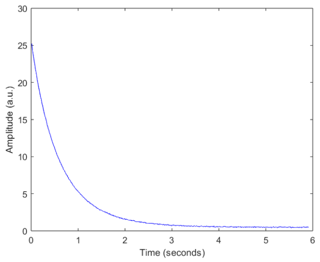


$CI = S_{Cr} / (S_{Am}+S_{Cr})$

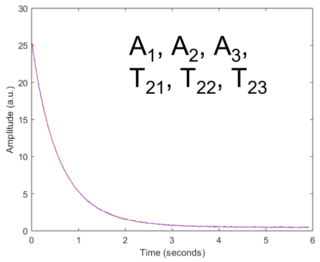
Parameters: **Relative surface areas (Bext, Bm, and Bint)**

- **Wet state**
- Signal from water
- Pulse sequence: CPMG
- Processing: fitting the T_2 NMR relaxation decays in the time-domain to mono-, bi-, or three- exponential model
- Method: ^{1}H Low-field NMR relaxometry

CPMG



Fitting



Bext, Bm, Bint

C, %	< 0.03	0.2-0.3	0.9-2.5	5-25
Mono	+	+	+	+
Bi	-	+	+	+
Three	-	-	+	+
Online	+	+	+	-

- Mono → **Bext**
- Bi → **Bext, Bint**
- Three → **Bext, Bm, Bint**

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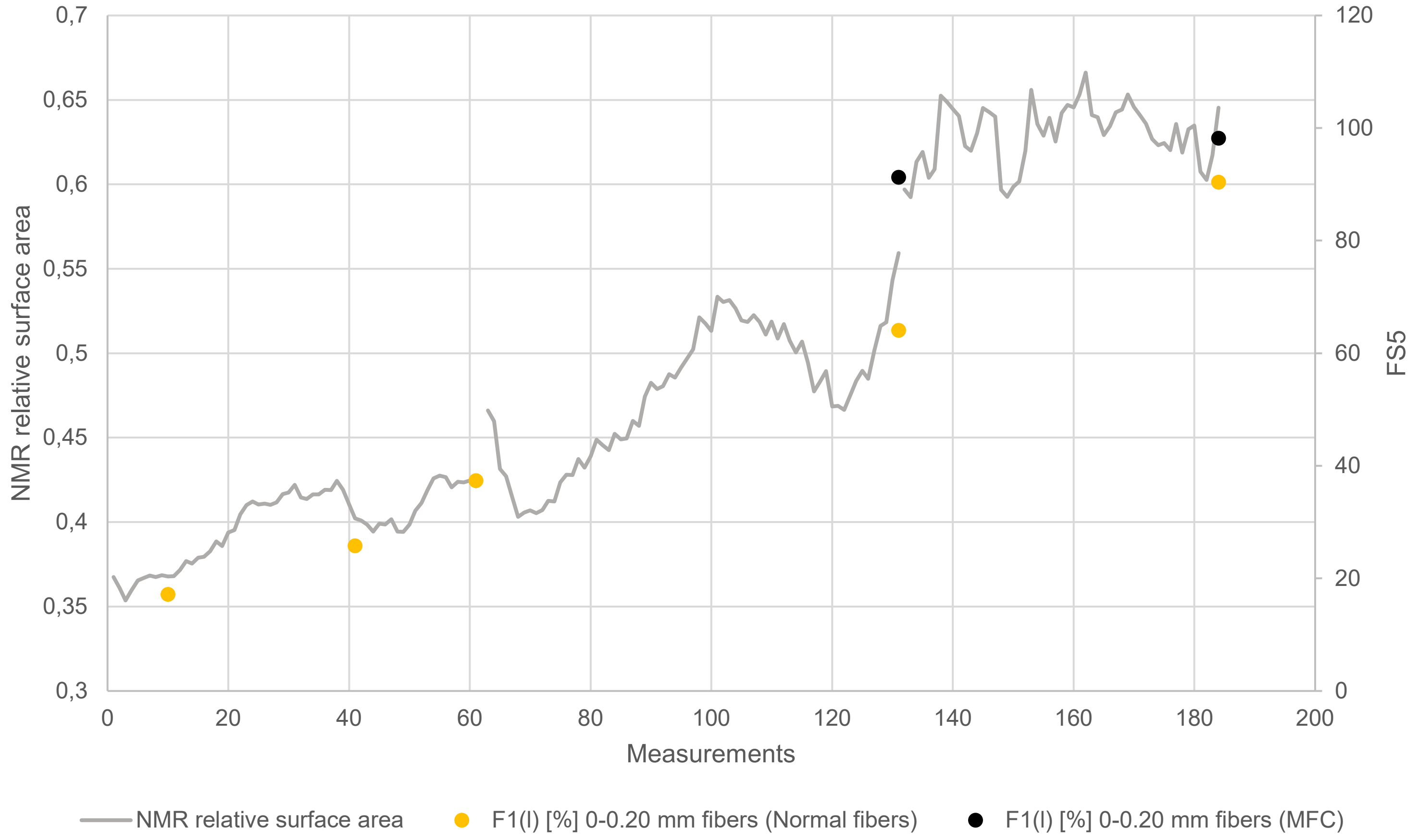
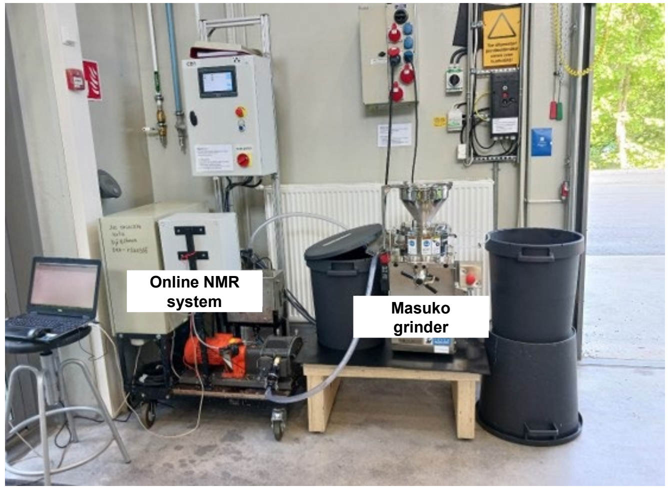
Example 1 Proof-of-Concept test: monitoring the process of the microfibrillated cellulose (MFC) manufacturing from birch pulp (WP6).





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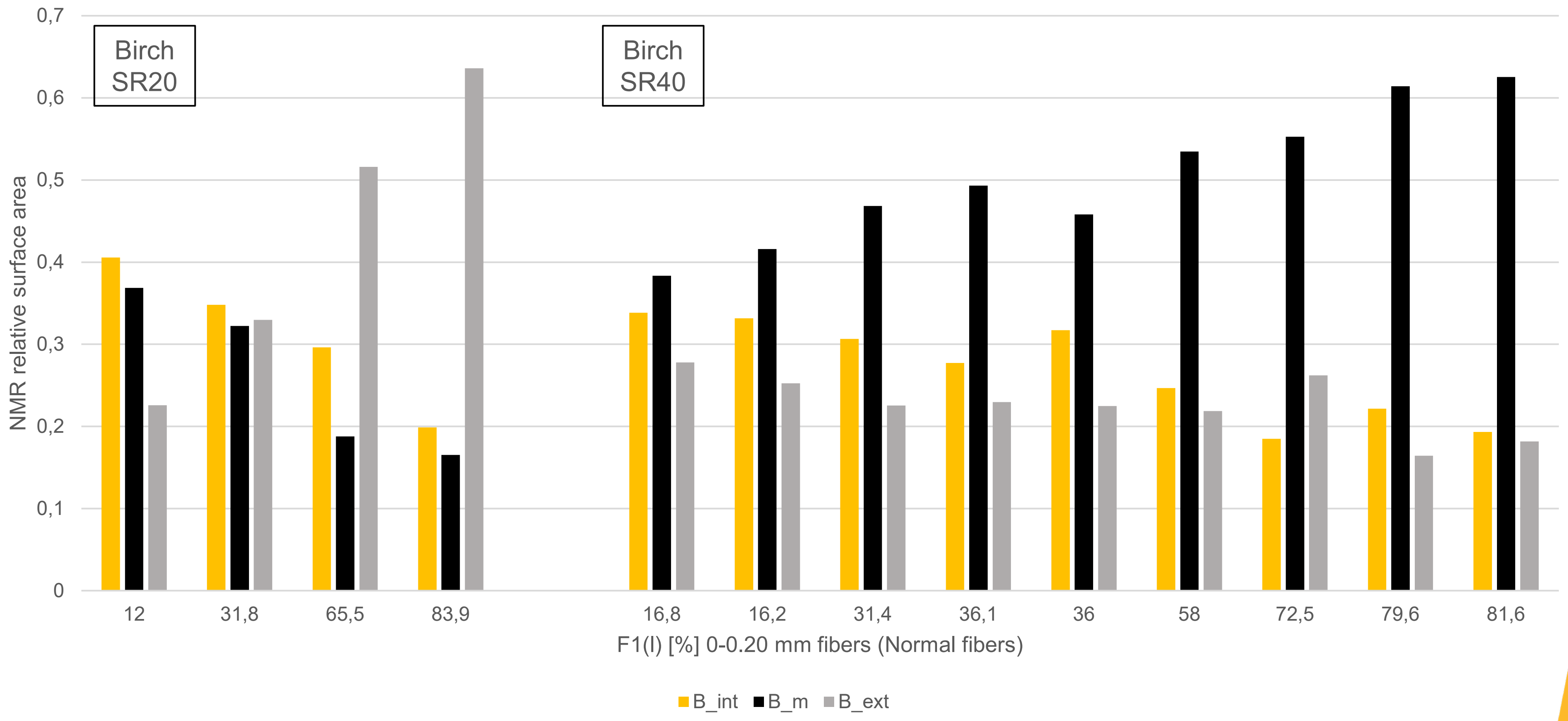
Example 2 Monitoring the distribution of relative surface areas during MFC manufacturing from birch pulps with different initial refining degrees (WP6).



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Conclusions

- Important structural characteristics of cellulose fibers such as crystallinity and relative surface areas can be measured by ^{1}H Low-field NMR in dry and in wet states
- Method can be used both in offline and online modes
- ^{1}H Low-field NMR method allows online monitoring the structural changes in cellulose during refining and controlling the process of microfibrillated cellulose manufacturing
- ^{1}H Low-field NMR provides unique information on the distribution of relative surface areas in cellulose fiber porous system

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Fractionator in Fiber Analysis (WP2)

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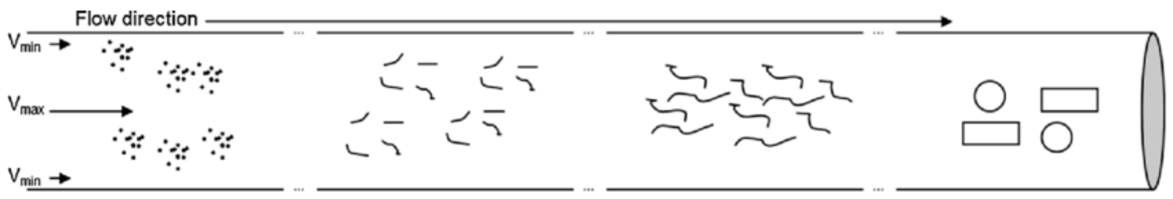
What is Fractionator?

Figure 1. Valmet Fractionator (Valmet)

Tube Flow Fractionation

- **A furnish sample is injected into the water flow through a tube**. According to their **true hydrodynamic resistance**, these elements will be **separated** within this flow.

- The **highest flow speed** is in the middle of the tube; **large elements**, such as **fiber flocs**, are driven by the flow faster than **smaller elements** such as **fillers or fines**.



Fractionator UHD-camera

- The UHD camera enables the analysis of **fiber dimensions** and **properties** and the **visualization** of fiber structure through stored images.

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MFC Retention and Formation of Agglomerates & Fiber Flocs in Wet-End Processes

🔍 **Research Objectives:**

- Analyze MFC retention and agglomerate/floc formation using advanced imaging.

🛠️ **Methods:**

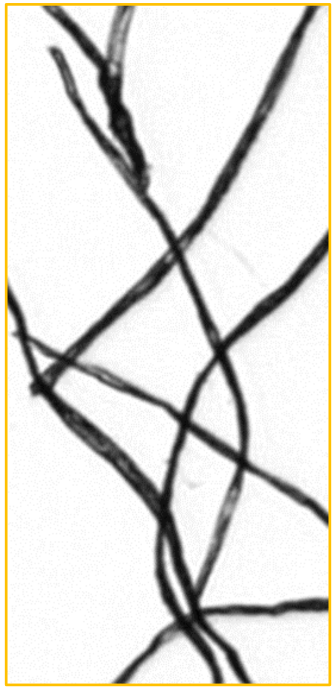
- **Valmet Fractionator:** Separates and characterizes different fiber fractions for detailed analysis.
- **UHD Camera Technology:** Captures high-resolution images of microfibril attachment and agglomeration.

💡 **Key Findings:**

- **MFC and fines** form **agglomerates** with retention chemicals.
- **MFC attaches** to fibers, affecting **measured fiber thickness**.
- **Significant fiber flocculation** occurs **only after increasing** the retention chemical dosage.

🚀 **Impacts for Production & Product Development:**

- Crucial for optimizing costly fibrils to enhance board strength and resource efficiency.



Reference pulp

Reference pulp with MFC and chemicals

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Index to Monitor Pulp Refining

🔍 **Research Objectives:**

- Fibrous index can be used to monitor pulp refining.

🛠️ **Methods:**

- **Valmet Fractionator:** Separates and characterizes different fiber fractions for detailed analysis.
- **Optical measurement:** Optical signals can distinguish fibers from fines.

📊 **What it indicates:**

- It shows whether the sample is made of fibers or fines.
- **Higher index** value indicates **fibers.**
- **Lower index** value indicates **fines.**

🖥️ **Application:**

- Helps assess whether the sample consists mainly of fibers or fines.
- Supports process optimization in refining.

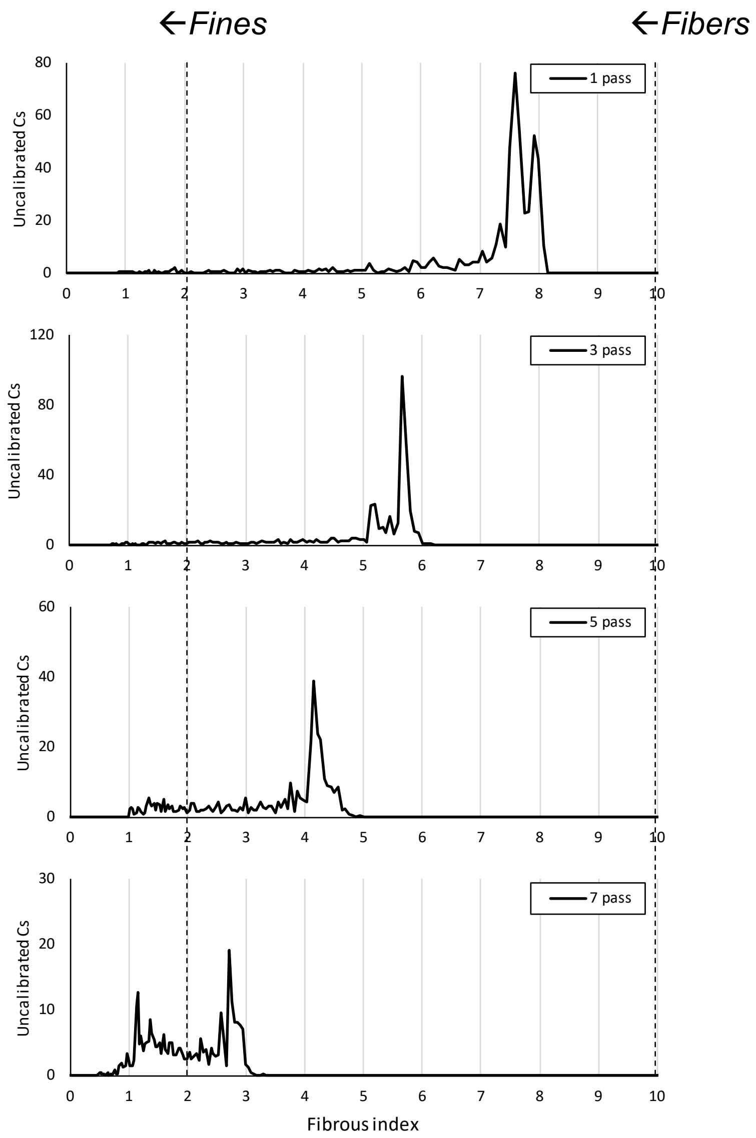

Figure 3. Fibrous index of the pulp sample series ground with a Masuko grinder. The fiber fibrillates during refining and generates more fines.

Figure 2. Masuko grinder (Masuko)

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Conclusion

Tube Flow Fractionation: Fractionates fiber samples using water flow and hydrodynamic resistance, improving analysis methods.

UHD Camera (commercialized method): Enables more accurate analysis and visualization of fiber dimensions and structure.

- Applications: For example, optimization of MFC fiber bonding in paper and cardboard production together with retention chemicals.

Fibrous Index (non-commercialized method): Distinguishes fibers and fines based on light scattering.

- Applications: Monitoring pulp refining through fibrous index, for example, optimizing nanocellulose production.

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Development and Creation of a Model – Relationships between fiber network characteristics to strength properties of paper pulp (WP1, WP4)

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Modeling and validation of fiber length distribution from pulp mixtures

The simulation of model is based on the relative summation of mass quantities and fiber length distributions, and it illustrates how the fiber length distribution changes with different MFC mixture ratios. Figure 1 shows the simulated fiber length distribution (weighted by fiber length) when MFC fines (microfibrillated cellulose) are added to reference birch pulp. Figure 2 presents the length distribution of fibers measured with the Valmet FS5 Analyzer with the same mixture quantity as in the simulation.

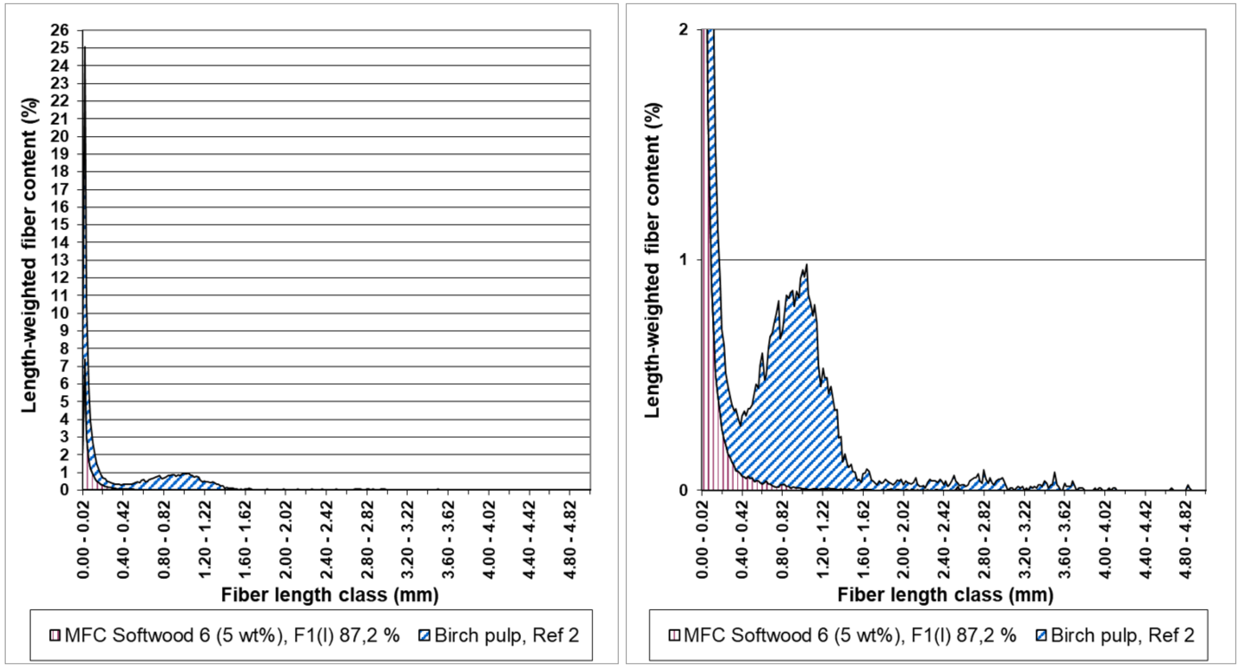

Figure 1. Simulation of fiber length distribution with MFC fines addition at 5 m% MFC mixture ratios.

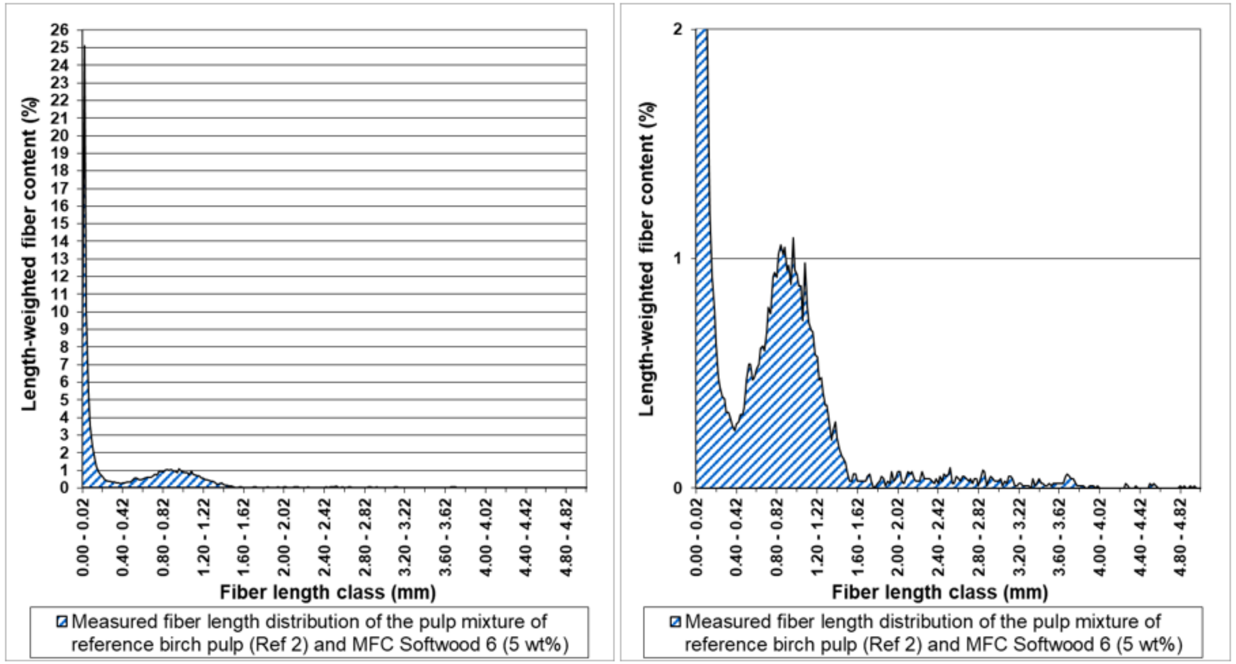

Figure 2. FS5 analysis results of fiber length distribution at 5 m% MFC mixture ratios.

The successful validation of the fiber length distribution model demonstrates its potential as a tool for predicting the relative distribution of pulp mixtures. The method could also be used for various pulp mixtures, which may contain several fiber fractions.

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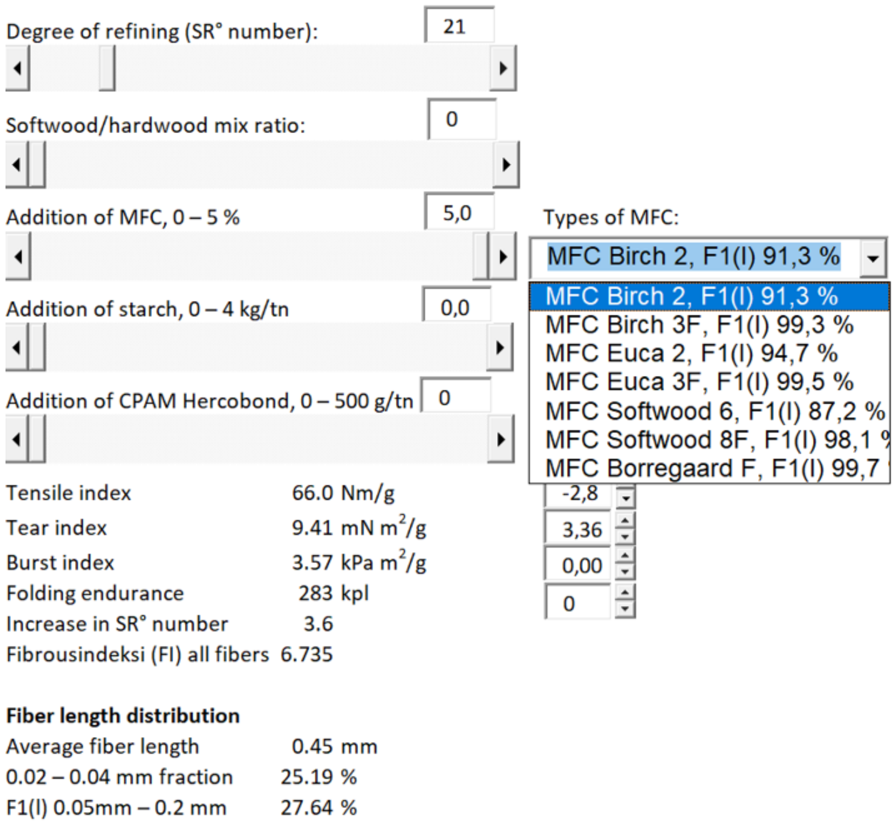
Scroll bar controls in the modeling application

The modeling application uses scroll bar controls to adjust the refining degree, mass fractions, starch adhesive, and pulp additives. These controls simplify the adjustment of process parameter changes while allowing the user to monitor their effect on paper strength estimated by the model.



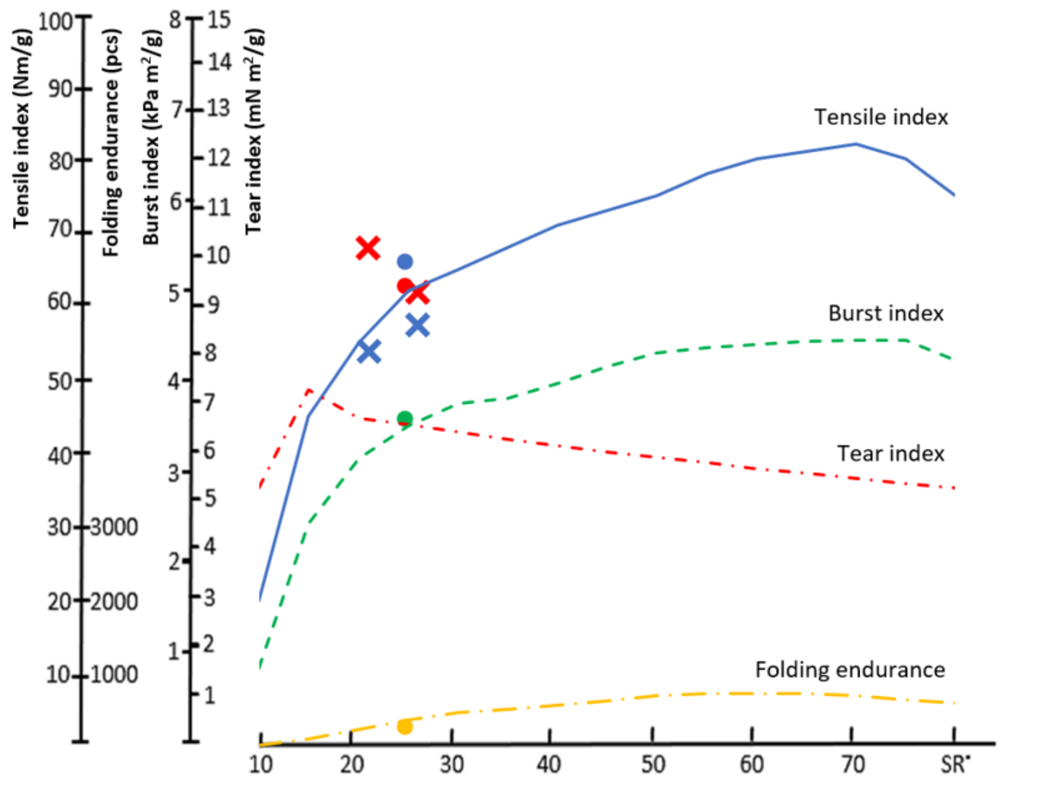


Figure 1. Changes in the strength properties of bleached aspen pulp during refining.

Figure 3. The scroll bar controls of the modeling application simplify the adjustment of refining degree, mass fractions, and pulp additives.

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Mathematical basis for summing changes of paper strength properties

In the modeling, the summing of paper strength changes is based on correlation functions determined from the measurement results of paper strength tests. These correlation functions describe the effects of different factors (n), such as mass fractions, refining degree, and pulp additives on paper strength.

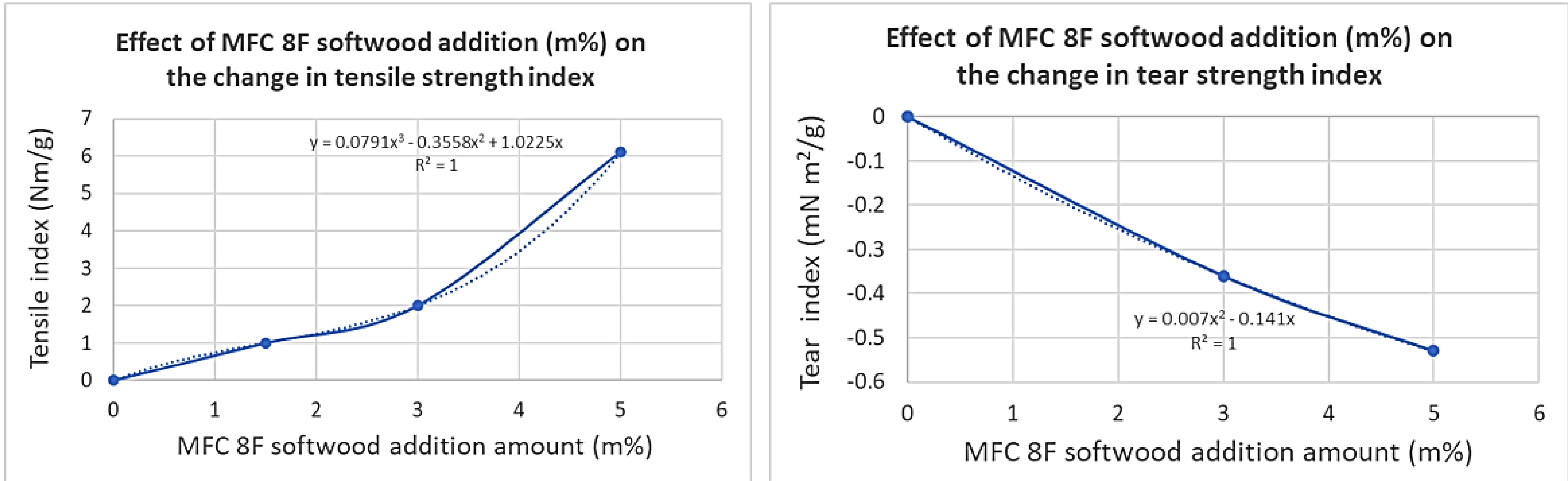

Figure 4. Correlation functions describing the change in paper strength from the initial level.

These functions allow individual effects to be calculated and summed to estimate the overall strength. Mathematically, this can be expressed as follows

$$PS_{total} = \sum_{i=1}^{n} f_i(x_i)$$

Equation for estimating total paper strength based on various factors, where (PS_{total}) is the change in total strength, (f_i) is the correlation function, and (x_i) is the value of the change factor. By summing the different factors in this way, the modeling evaluates how changes in the different factors affect the overall strength of the paper.

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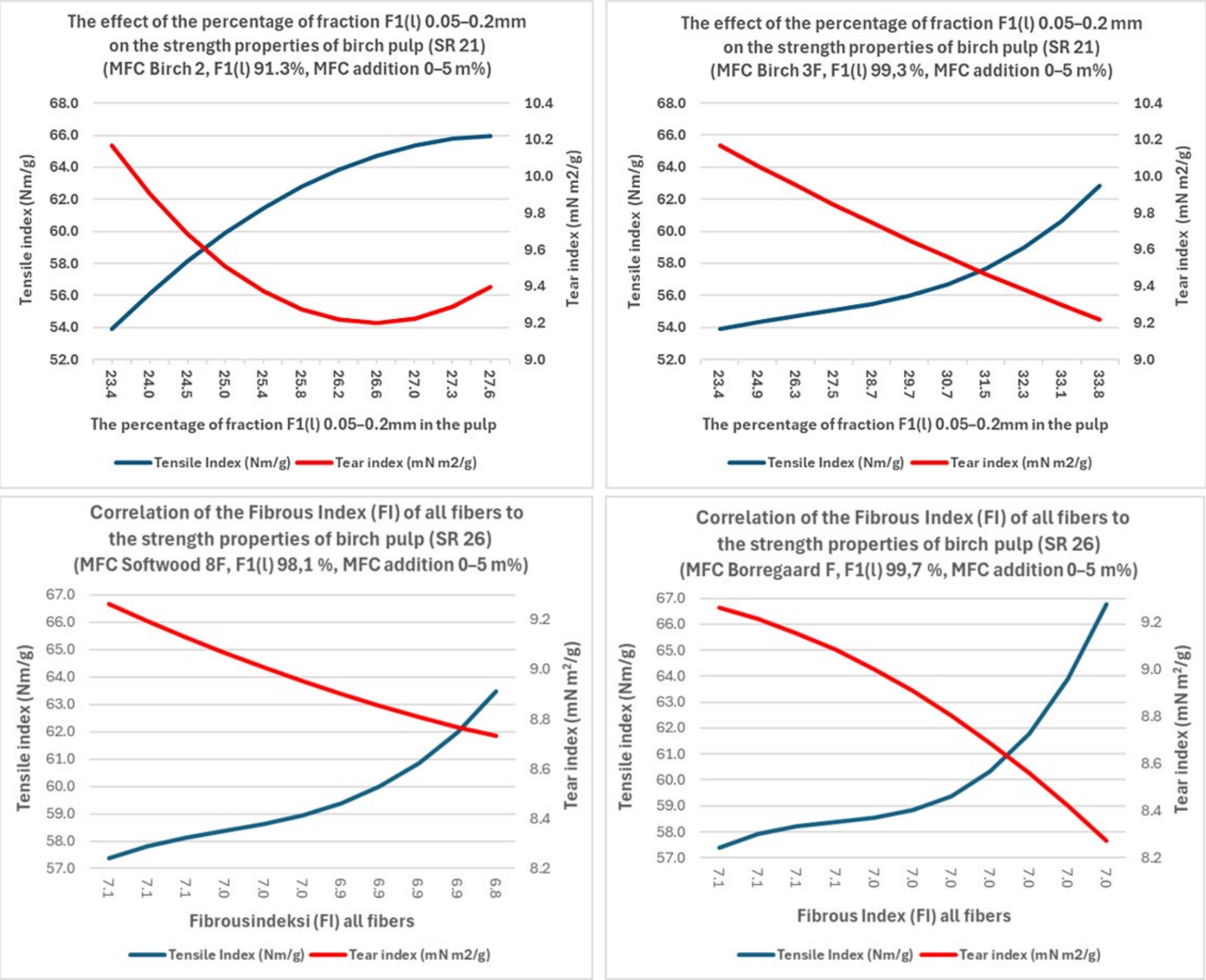
Predicting changes in pulp strength properties using fiber distribution and fibrous index

Simulated results can be used to make correlations, for example, on the effects of fiber fractions of the fiber distribution and fibrous index on changes in the strength properties of paper pulp.



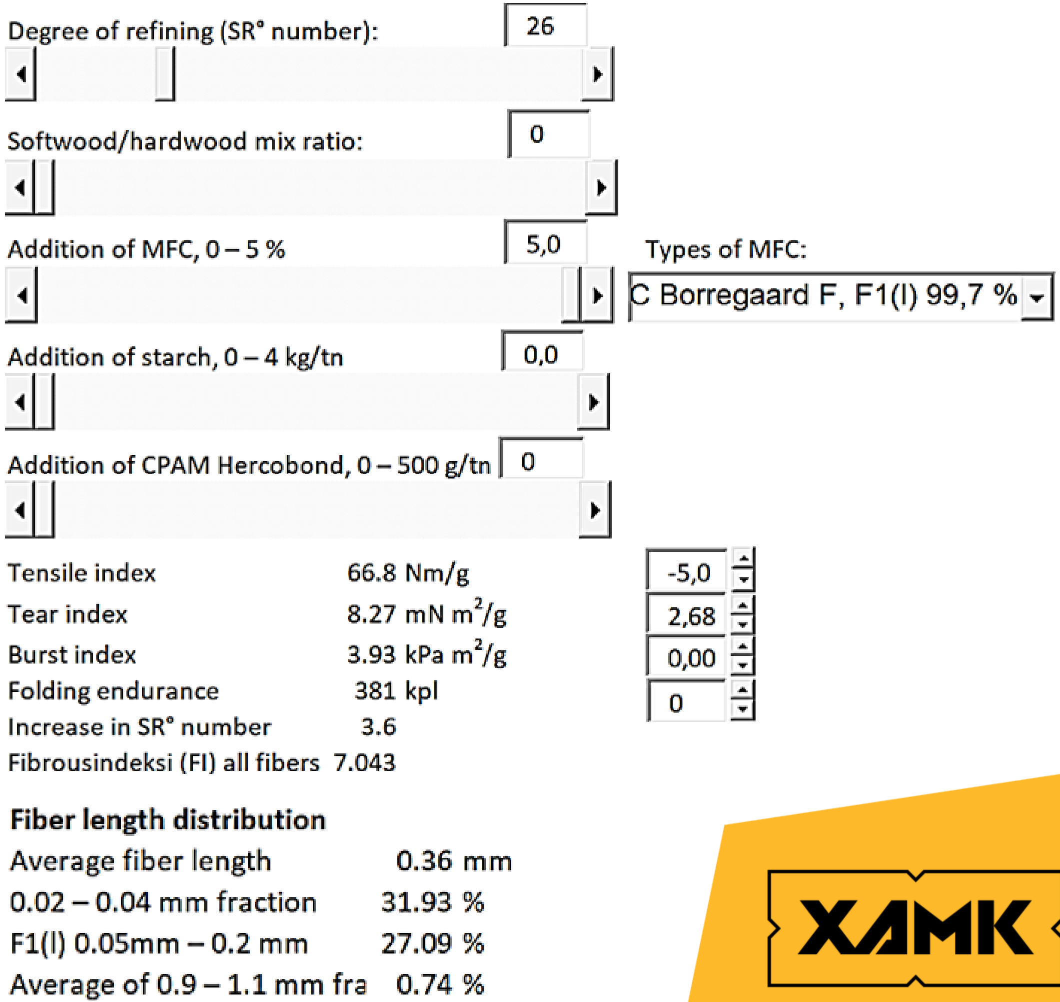


Figure 5. The modeled changes in tensile and tear indices in relation to the F1(l) fraction and fibrous index.

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Conclusions

- **The aim of the modeling work** has been to model the properties of changes in the fiber network and their effect on the strength of the paper pulp.
- **Correlation values of the simulation model are based on** tensile and tear strength values measured in the project (data matrix) and fiber length distributions measured with the Valmet FS5 analyzer.
- **Modeling and validation of fiber length distribution:** Successful validation of the simulation model shows its potential to predict the relative distribution of pulp mixtures.
- **Scroll bar controls in the modeling application:** These controls simplify the adjustment of process parameters and allow monitoring their effect on paper strength.
- **Mathematical basis for summing changes in paper strength properties:**
    - Summing changes in paper strength is based on correlation functions determined from paper strength test results.
    - Correlation functions describe the effects of changes in various factors on the strength of paper.
    - The individual correlation functions results are summed in the modeling to estimate the overall paper pulp strength.
- **Predicting changes in pulp strength properties by the modeling:** Simulated results can be used to make correlations e.g., on the effects of fiber fractions and fiber index on paper pulp strength properties.

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Thank you!

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