



Effect of *eucalyptus globulus* pulp properties on fock reactivity

André E. P. Cunha · Rogério M. S. Simões

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Abstract Dissolving-grade pulps serve as the primary material for producing regenerated cellulose fibers, and their utilization is steadily increasing. Despite extensive research efforts, it remains necessary to deepen our understanding of the inherent factors that impact pulp reactivity apart from the well-known degree of polymerization. The Fock reactivity test is commonly used to quantify the reactivity of cellulose pulp by measuring the percentage of cellulose that reacts with carbon disulfide. Dissolving pulps typically require a reactivity of over 90%. Hemicellulose content, intrinsic viscosity, cell wall porosity, crystallinity, and accessible area of four different pulps were characterized and distinct treatments were employed to try to separate the effect of different pulp properties and assess their effect on Fock reactivity. Hemicelluloses removal by xylanase and cold caustic treatments (86% removal) increased the Fock reactivity by 30%, from 55.7% to 71.3%. Assuming the hemicelluloses are fully accessible by the CS₂, cellulose reactivity increased from 35.6%

to 69.5%, but at the expense of an intrinsic viscosity decrease from 990 cm³/g to 689 cm³/g. This unexpected intrinsic viscosity decrease can be due to the cellulose de-shielding effect provoked by hemicellulose removal and some cellulose degradation during cold caustic extraction. Vibrational impact ball-milling applied on a pulp with 5% hemicellulose content notably boosted Fock reactivity by 56%, from 54% to 84.5%, but two pulp properties, intrinsic viscosity, and crystallinity, decreased concurrently due to the high-energy treatment. This phenomenon complicates identifying a direct correlation between heightened reactivity and a single parameter. To address this, endoglucanase treatment was used to separate intrinsic viscosity from crystallinity, clarifying their contributions to changes in Fock reactivity. Unfortunately, the effect of a given physical or bio/chemical pulp treatment affects more than one pulp property, always including the cellulose degree of polymerization, which has made it difficult to isolate the pulp properties that affect Fock reactivity. Several processes have been tested to obtain pulp with dissolving potential.

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A. E. P. Cunha (✉) · R. M. S. Simões
Fiber Materials and Environmental Technologies
(FibEnTech-UBI), Universidade da Beira Interior,
R. Marquês de Ávila e Bolama, 6201-001 Covilhã,
Portugal
e-mail: andre.palos.cunha@ubi.pt

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Introduction

The textile and fashion industry stands as one of the largest global sectors, yet controversies persist

regarding its environmental impact throughout the clothing life cycle. According to a wide variety of studies, the textile industry generates 8–10% of the total global greenhouse gas emissions and contributes to 20% of all wastewater pollution (de Oliveira et al. 2021; Sohn et al. 2021).

The sustainability of this industry has been a topic of widespread and ongoing discussion for several decades (Treiber et al. 1961), likely due to its inherent complexity, with economic, social, and environmental considerations.

Over recent years, there has been a significant global increase in demand for dissolving pulp for regenerated cellulose production, especially viscose fibers. The increased shifts of the textile industry's ideal raw materials from cotton to regenerated fibers are mainly due to concerns about the environmental impacts associated with cotton cultivation, including significant water usage, land usage, and the application of fertilizers (Kallio 2021). Consequently, there is a growing force to explore sustainable fiber alternatives, with dissolving pulps emerging as a promising solution.

The paper and pulp industry are experienced in producing pulps with specific properties and the understanding of the principal pulp properties that affect their reactivity and dope behavior is key for the smooth transition to the new increasing market that regenerated cellulose is becoming. Molecular weight distribution, pulp composition, crystallinity, surface area, porosity and even impurities such as metals all may contribute to good quality dissolving pulps (Köpcke et al. 2010; Li et al. 2018; Kallio 2021).

There is a global effort to optimize the wood-based pulps to suit the different grades of dissolving pulps (Balkissoon et al. 2023). Alongside optimizing cooking methods, various pre- and post-treatments are employed to boost pulp reactivity for different applications. These treatments include mechanical methods as explored in Li's study (Li et al. 2023), as well as chemical (Vera-loor et al. 2023), and enzymatic approaches (Rahikainen et al. 2020). The different post-treatments employed will enhance reactivity by changing some crucial properties mentioned above.

Using vertical vibrational impact ball-milling, Mattonai et al. (2018) reduced crystallinity and the degree of polymerization (DP) of four different cellulose samples. The two-hour treatment resulted in a substantial decrease (80%) in the crystallinity of

the samples while the degree of polymerization was reduced by 20%.

Within the chemical approaches, the caustic extraction under different conditions was extensively explored to optimize dissolving pulp production, including from paper-grade pulps (Fechter et al. 2020; Gong et al. 2022).

Enzymatic treatments can include xylanases to remove xylan in hardwood pulps and cellulases to control the cellulose molecular mass (Sharma PK and Chand D 2012; Bajpai 2014). Gehmayr and Sixta (2011) used endoglucanase at different doses to control the final cellulose molecular mass and, in this way, increase reactivity.

The diverse pre- and post-treatments aim to increase the pulp reactivity, but they usually affect more than one pulp property, so the assessment of how individual pulp traits affect the response is a difficult task.

On the other hand, the increasing need to reuse cellulosic textile waste poses additional challenges in terms of processes, including pre- and post-treatments. The aim is to produce dissolving grade pulps suitable for the different cellulose-derived products. Considering the specific requirements of the different products and the complexity of the processes, the suitability of the different pulps is only fully evaluated by simulating the conversion processes to the final products (Sixta 2006).

However, at the lab scale the Fock reactivity and the dope filterability (Treiber et al. 1961) are usually used to estimate the dissolving pulp suitability. But the facility to implement Fock reactivity at a lab scale, still makes it one of the most used methods for pulp characterization (Tian et al. 2013).

Fock reactivity defines the reactivity of dissolving pulp, primarily within the viscose process. It mirrors the pulp's tendency to undergo chemical transformations, including dissolution or derivatization, crucial in both fiber production and processing. In this way, Fock reactivity indicates how easily the pulp can be dissolved aiming for the regeneration process.

During this study, distinct treatments were applied to selectively modify various pulp properties and evaluate their impact on Fock Reactivity. To assess the effect of hemicellulose content, two different approaches were used: chemical treatment, with a concentrated alkaline solution, should allow

the removal of most of the hemicelluloses in the pulp (Ciftci et al. 2018), while for a more moderate removal, an enzymatic treatment (xylanase) was used.

In both approaches, the porosity, intrinsic viscosity and Fock reactivity changes were followed and correlated. One of the additional advantages of the enzymatic reaction may be the production of xylooligosaccharides, as a consequence of the hemicelluloses cleavage by the enzyme (Wang et al. 2011).

In summary, this study explored the application of mechanical, chemical, and enzymatic post-treatments to isolate specific pulps properties including hemicellulose content, intrinsic viscosity, crystallinity, and porosity aiming to investigate their correlation with Fock reactivity.

Material and methods

Materials

Eucalyptus globulus wood chips (8–12 years, 3–4 mm thick) supplied by Biotek S.A. (Vila Velha de Rodão, Portugal) were used in this study to produce the pulps. The chips were air-dried at room temperature and reached 8% moisture content before storage. The production of the different pulps comprises the following three steps: pre-hydrolysis, kraft cooking, and bleaching.

All the chemicals used in the experiments were of analytical grade and provided by Sigma-Aldrich (EUA). Commercial Birchwood xylan was also provided by Sigma-Aldrich.

Methods

Pulp production

PHK-Batch pulp

Pre-hydrolysis kraft (PHK) pulp was produced in 150 mL stainless steel reactors attached to a mechanical rotating shaft immersed in an oil bath with temperature control. This is a two-step process, where the treatment starts with a pre-hydrolysis followed by kraft cooking.

Before the chemical treatment, *Eucalyptus globulus* wood chips were impregnated with water overnight, using a Liquid/Solid ratio of 5:1. For the pre-hydrolysis, a heating ramp of 1.6°C per minute was used to reach 148 °C, the treatment continued for 210 min after which the reactor was cooled to stop the reaction. The resulting P-factor is about 360, based on Eq. 1, with an activation energy of 125.6 kJ/mol. (Sixta 2006).

$$P_{\text{factor}} = \int_0^t \exp\left(40.48 - \frac{15106}{T}\right) dt \quad (1)$$

where t is the reaction time in hours and T is the temperature in Kelvin.

The kraft cooking occurred in the same reactors after pre-hydrolysis liquor extraction. The reaction conditions were as follows: maximum temperature: 148 °C; time at maximum temperature: 180 min; alkali charge: 24% (as active alkali, expressed as NaOH and based on the wood); sulfidity: 30%; Liquid/Solid ratio: 5/1; H factor: 440. Afterwards, the pulp was washed with deionized water and stored for bleaching.

These pulps will be named PHK-Batch because both pre-hydrolysis and cooking were carried out in batch mode.

PHK-FTR pulp

The principal difference between this pulp (PHK-FTR) and PHK-batch pulp is the use of a flow-through mode (FTR) in the pre-hydrolysis process, which was proved to be more effective in hemicellulose removal than the auto-hydrolysis (Cunha and Simões 2023). In this case, dilute acid was used to remove the hemicelluloses from the wood. The aqueous solution was acidified to pH 3.5 with acetic acid (identical to the pH value and the acid resulted from the batch pre-hydrolysate) and pumped to a 300 mL fixed bed reactor (*Eucalyptus globulus* wood chips) after passing through a metal coil submerged in the oil bath for temperature control. A flow rate of 25 mL/min was employed, with the outflow managed by a needle valve to regulate and sustain the hydraulic pressure of the system. The temperature profile is the same as before.

The cooking process took place in the 150 mL stainless steel reactors as used for the PHK-Batch

pulps with the same conditions, with an H-factor of 440. More information about the methodology can be found in a previous work (Cunha and Simões 2023).

Commercial dissolving pulp (Commercial PHK)

A commercial pre-hydrolysis kraft dissolving pulp made from *Eucalyptus globulus* wood chips served as the reference material. The specific pre-hydrolysis and cooking conditions are not disclosed, but a Totally Chlorine-Free bleaching sequence was used.

Kraft pulp

A lab Kraft pulp was also produced in a 10 L reactor with liquor circulation. The reaction conditions were as follows: maximum temperature: 148 °C; time at maximum temperature: 180 min; alkali charge: 24% (as active alkali, expressed as NaOH and based on the wood); sulfidity: 30%; Liquid/Solid ratio: 7/1; H factor: 440.

Bleaching

An Elemental Chlorine-Free (ECF) bleaching sequence $D_0E_1D_1E_2D_2$ was used to bleach the lab-made pulps; the chlorine dioxide charges for each step were determined based on the pulp's initial kappa number. This process consisted of successive treatments of chlorine dioxide (D) followed by alkali extraction with sodium hydroxide (E). After each stage, the pulp was washed with demineralized water. The pulp was stored at medium consistency at 4°C until use. Every bleached pulp had less than 0.3% lignin in its composition. A TCF bleaching sequence would have been preferable, but there was no suitable equipment.

Pulp post-treatments

Hemicellulose extraction

Hemicelluloses were extracted from the lab Kraft pulp. A cold caustic extraction (10% NaOH m/m) was conducted at room temperature with mild agitation for 1 h at 2.5% consistency. To check the possible influence of oxygen in the process, the same assay

was carried out with oxygen-free water and under a nitrogen atmosphere.

Xylanase treatment

Xylanase X2573 from *Aspergillus oryzae* was supplied by Sigma-Aldrich (EUA). Activity measurement was conducted following the supplier's instructions. The enzymatic reaction with different substrates occurred at 50 °C in 0.1 M acetate buffer (pH=5), utilizing a charge of 5 units per gram of pulp at 1% consistency for two hours.

Endoglucanase treatment

Endo-1,4-β-D-glucanase produced from *Acidothermus cellulosilyticus* (E2164, Sigma-Aldrich) was used to evaluate cellulose depolymerization. Activity measurement was determined according to the supplier's protocol, defining one unit as the quantity of enzyme necessary to convert 1 μmole of 4-methylumbelliferyl-β-D-cellobioside per minute under a pH of 5.0 and 50 °C. For pulp treatments, a charge of 3 units/g of pulp was used, at 2.5% consistency, for three hours. To stop the reaction, the pulps were boiled and washed with demineralized water.

Ball-milling

PHK-Batch pulp was submitted to vibrational impact ball-milling in a Retsch CryoMill ball-mill between 2 and 30 min, operating at a frequency of 25 back and forth per second (1/s). The cryo system was not used. The pulps were air-dried before ball-milling, reaching around 9–10% moisture content.

Characterization methods

Pulp composition

A TAPPI standard method T222 om-02 (Acid-insoluble lignin in wood and pulp) was followed. This involved a two-step acid hydrolysis using 72% (m/m) and 4% (m/m) sulfuric acid concentrations. In the first step, the pulp was treated with 72% sulfuric acid at room temperature under occasional ultrasound effect. The final hydrolysis step was conducted

by autoclaving the sample at 121 °C for 60 min in a Tuttnauer TM autoclave.

The hydrolyzed samples were filtered (0.45 µm Nylon syringe filter by Kinesis®) and analyzed for monosaccharides and degradation by-products with High-Pressure Liquid Chromatography (HPLC). For this, two different detectors were used, a refractive index (RI) detector (RefractoMax 520) and a photodiode array (Accela PDA detector (80 Hz) from Thermo Scientific™, EUA).

The compounds were separated using a Rezex™ ROA-Organic Acid H+(8%) column eluted with 0.005 N H₂SO₄ at 300 µL/min and 70 °C. The compounds were quantified using calibration curves in the 0.1 to 3 g/L concentration range (glucose, xylose, arabinose, galactose, furfural and hydroxymethylfurfural).

Ash content

The ash content was determined according to the TAPPI standard method T 211 om-85: “Ash in wood and pulp”.

Kappa number

Kappa number was quantified by titration as described by the standard method ISO 302:2015: “Pulps — Determination of Kappa number”.

Pulp intrinsic viscosity

The measurements followed the ISO 5351:2004: “Pulps — Determination of limiting viscosity number in cupriethylenediamine (CED) solution”.

Water Retention Value (WRV)

The Water Retention Value (WRV) is a centrifuge test used to measure pulp swelling ability. It measures the water content remaining in the fiber cell wall after centrifugation. The water retention value (WRV) of selected samples was analysed according to the ISO 23714 method.

Fiber porosity (Solute exclusion method)

The pore volume and size were assessed using the solute exclusion test, considering the water within the pores cannot be accessed by molecules of varying larger sizes. The technique followed the method used by Grönqvist et al. (2014).

Micropore, mesopore, and macropore size classification goes along the conventional IUPAC definition, where micropores have a diameter < 3.2 nm, mesopores fall between 3.2 nm and 54 nm, and macropores exceed 54 nm. To assess this, dextran probes of 5 kDa (3.2 nm) and 2000 kDa (54 nm) were utilized. The fiber saturation point (FSP), representing the water inaccessible for a probe bigger than the largest pores in the cell wall, was quantified by using a dextran with a Stoke diameter of 54 nm (2 M kDa), as used by Grönqvist (Grönqvist et al. 2014).

The fiber porosity measurements were done at neutral pH.

The measurements were done by adding 0.8 g pulp (as dry weight) at 10% consistency to a disposable tube. Afterwards, 35 mL of 2% (m/m) dextran solution is added to the tube and the suspension is gently mixed with a thermostatic water bath oscillator for 1 h at 25 °C. The suspension is then centrifuged at 3 000 g for 15 min and the supernatant is filtered (0.45 µm Nylon syringe filter by Kinesis®) and injected into a 10 mL polarimeter tube for analysis.

The optical rotation was measured at 357 nm in an ADP 2000 polarimeter from Bellingham Stanley Ltd, UK. The pulp recovered after centrifugation was washed and the exact pulp used in the assay was measured by gravimetry after drying.

The pore volume (V) is measured by quantification of the water inaccessible to a dextran molecule by the following equation (Eq. 2), assuming that the dextran molecule does not interact with the fiber surface.

$$V = \frac{M_{\text{dex}} + M_{\text{water}}}{M_{\text{pulp}}} - \frac{M_{\text{dex}}}{M_{\text{pulp}}} * \frac{C_i}{C_f} \quad (2)$$

where, M_{dex} , M_{water} and M_{pulp} are the mass of dextran solution, water in the sample and dry pulp (after washing), respectively, and C_i and C_f are the initial and final concentration of the dextran solution (measured as optical rotation and quantified based on a calibration curve with dilution of the different dextran

solutions). Pore volume is given in mL/g, assuming 1 g/cm^3 as the water density.

Macropores are calculated roughly using the WRV and the pore volume value of $< 54 \text{ nm}$.

The accessible surface area (SA) was calculated by the subsequent equation (Eq. 3), following Grönqvist et al. (2014).

$$SA = \frac{V_{54 \text{ nm}} - V_{3.2 \text{ nm}}}{0.0116} \quad (3)$$

where $V_{54 \text{ nm}}$ represents the pore volume measured through FSP (54 nm dextran), while $V_{3.2 \text{ nm}}$ represents the pore volume assessed using dextran with a diameter of 3.2 nm. The value 0.0116 serves as a geometric constant derived under the assumption of cylindrical pores (Grönqvist et al. 2014).

Fock Reactivity

The methodology employed in this study was adapted from the optimization outlined by Tian et al. (2013). First, a 10% (m/m) NaOH solution (50 mL) at 15°C is prepared in a jacketed reactor. Then, 0.5 g of pulp (oven-dried basis) is added to the solution and left to react for one hour under mild agitation. Following this, 1.3 mL of carbon disulfide (CS_2), in stoichiometry excess, is introduced, and the reaction is allowed to proceed for 3 h.

After the 3-h reaction, the solution is diluted to reach 100 g and centrifuged at 3000 g for 15 min, allowing the separation of the cellulose xanthate from the undissolved cellulose. Subsequently, a 10 mL aliquot of the supernatant is pipetted into an Erlenmeyer and neutralized with 20% (m/m) sulfuric acid. This process is done overnight (15–20 h) and allows cellulose regeneration and degasification of the carbon disulfide.

The final step of the method is the oxidation of the regenerated cellulose; for this phase, 20 mL of 68% (m/m) sulfuric acid is added and the suspension is stirred for one hour. Afterwards, 10 mL of potassium dichromate (1/6 M) is added and the mixture is refluxed for another hour, to fully oxidize the regenerated cellulose.

After cooling, the solution is diluted to 100 mL and a 40 mL aliquot is used for titration. 5 mL potassium iodide (10% m/m) is added, and the solution is titrated with sodium thiosulfate (0.1 N). The

percentage of dissolved cellulose is given by Eq. 4 (Tian et al. 2013).

$$\begin{aligned} \text{Dissolved cellulose}(\%) \\ = \frac{\left(\left(v_1 c_1 - \left(v_2 c_2 * \frac{100}{40} \right) * \frac{1}{6} \right) * M * \frac{1}{4} * \frac{100}{10.4} \right)}{m} * 100 \end{aligned} \quad (4)$$

where v_1 is the volume of the added dichromate solution (0.01 L); c_1 is the concentration of $\text{K}_2\text{Cr}_2\text{O}_7$ solution (1/6 M); v_2 is the volume (L) of consumed $\text{Na}_2\text{S}_2\text{O}_3$; c_2 is the concentration of $\text{Na}_2\text{S}_2\text{O}_3$ solution (0.1 N); M is the molecular weight of glucose unit (162 g/mol); m is the oven-dry weight of pulp tested (g); (100/40) is the dilution of the 40 mL sample to 100 mL; (1/6) corresponds to each dichromate ion that consumes six thiosulfate ions, (1/4) means each glucose unit consumes four dichromate ions, and (100/10.4) is the 10 mL aliquot (equal to 10.4 g) taken out from the 100 g viscose liquid.

The Fock test is commonly employed to assess the reactivity of dissolving pulps. However, its correlation with the efficiency of actual viscose production processes is not guaranteed. More complex methods like the Treiber method offer a more thorough simulation of viscose production, enabling measurement of parameters such as filtration value and filter clogging. In summary, the Fock test offers a basic indication of pulp reactivity, and methods such as Treiber provide a more realistic simulation of the entire viscose production process.

Crystallinity and crystallite size—X-ray diffraction (XRD)

Crystallography analysis was conducted using a Rigaku DMAX III/C X-ray diffractometer. The intensity of Cu $\text{K}\alpha$ radiation, with a wavelength of 0.1542 nm, was measured within a 2θ range spanning from 5° to 40° at a velocity of $2^\circ/\text{min}$. The crystallinity index (CI) was determined by calculating the intensity minimum values (I_{am}) found between the 1–10/110 and the 200 peaks, and the value of I_{200} by the following equation (Eq. 5) as proposed by Segal et al. (1959). A background correction was applied by using an “environmental background” XRD pattern and subtracting the sample patterns. The Miller indices used are based on the Cellulose I β pattern depicted by French (2014).

$$CrI = \frac{I_{200} - I_{am}}{I_{200}} * 100 \quad (5)$$

The Scherrer equation (Eq. 6) was utilized to estimate the dimensions of the crystallites in the samples, where τ is the crystallite dimension, K is a shape factor which was set to 1.0 (as standard (Mattonai et al. 2018)), λ the wavelength of the incident light, θ the nominal diffraction angle for a given diffraction peak, and b the half-height width of the peak.

$$\tau = K\lambda/b \cos \theta \quad (6)$$

Results

In this study, pulps produced under different operating conditions and submitted to different post-treatments were used to explore the influence of hemicellulose content, intrinsic viscosity, porosity, and crystallinity on the Fock reactivity of the pulps.

Among the different properties influencing cellulose dissolution, the cellulose molecular degree of polymerization stands as one of the most widely recognized and studied factors but others can play a role (Balkissoon et al. 2023).

Fiber accessibility and pulp composition are likewise taken into consideration as important factors influencing dissolution, getting significant attention in research (Engström et al. 2006; Loureiro et al. 2010; Javed and Germgård 2011). However, this study also aimed to explore other influential properties such as porosity, crystallinity, and hemicellulose content, which could significantly affect cellulose reactivity.

Pulp fock reactivity

Table 1 summarizes the pulp composition, fiber porosity, and Fock reactivity for the following pulp types: Kraft pulp (produced by Kraft cooking), PHK-Batch pulp (produced by pre-hydrolysis and Kraft cooking, both under batch mode), PHK-FTR pulp (produced by pre-hydrolysis under flow-through mode and kraft cooking under batch mode), and Commercial pulp (representing standard dissolving pulp).

As expected, employing the kraft process without pre-hydrolysis led to a lower extraction of

Table 1 Pulps properties

	Cellulose, %	Hemi-cellulose, %	Kappa number	Intrinsic viscosity, cm ³ /g	WRV, g/g	FSP, mL/g	Micro Pore, mL/g	Meso Pore, mL/g	Macro Pore, mL/g	Fock Reactivity, %	Fock Reactivity, Modified*, %
Kraft	79.7 ± 0.7	20.1 ± 0.6	2.5 ± 0.1	990 ± 20	1.93 ± 0.1	1.68 ± 0.06	0.46 ± 0.04	1.22 ± 0.05	0.25 ± 0.03	55.7 ± 2.0	35.6
PHK-Batch	94.7 ± 1.0	5.2 ± 0.3	1.6 ± 0.1	873 ± 20	1.37 ± 0.1	1.25 ± 0.05	0.03 ± 0.02	1.24 ± 0.07	0.09 ± 0.02	52.2 ± 2.0	47.0
PHK-FTR	96.9 ± 1.1	3.0 ± 0.2	1.0 ± 0.1	633 ± 15	1.67 ± 0.1	1.41 ± 0.06	0.64 ± 0.02	0.77 ± 0.06	0.26 ± 0.04	71.2 ± 2.4	68.2
Commercial	92.6 ± 0.8	7.4 ± 0.2	1.0 ± 0.1	491 ± 10	1.27 ± 0.1	0.57 ± 0.05	0.24 ± 0.05	0.33 ± 0.05	0.70 ± 0.05	90.7 ± 2.0	83.3

*Fock reactivity modified, assuming complete reaction of hemicelluloses

hemicelluloses compared to pulps that underwent an additional pre-hydrolysis step before cooking.

The acidic pH conditions and high temperatures during pre-hydrolysis effectively remove a major fraction of hemicelluloses from the pulp. After pre-hydrolysis, the solid residues underwent kraft cooking under the same conditions as the Kraft pulp production. However, the prior removal of hemicelluloses facilitates better impregnation of white liquor and enhances fiber accessibility, leading to increased delignification and further hemicellulose removal.

In this way, the Kraft pulp exhibits the highest hemicellulose content and intrinsic viscosity, and the lowest Fock reactivity, pairing with the PHK-Batch pulp, but the last one with much lower hemicellulose content (20.1% vs 5.2%), which deserves further analysis later in the paper.

The Kraft pulp will be used in subsequent trials to evaluate the influence of hemicellulose content on Fock reactivity and fiber accessibility. Two different approaches will be employed to reduce the hemicellulose content in the pulp: chemical and enzymatic.

In contrast with the Kraft pulp, the pulps subjected to the pre-hydrolysis treatment (to produce dissolving pulp) displayed a notable lower hemicellulose content. Despite the low hemicellulose content (5.2%) of the PHK-Batch pulp, where auto-hydrolysis was employed, the Fock reactivity remains unacceptable as dissolving pulp. The low hemicellulose content and the relatively high pulp viscosity make this pulp a good candidate to study the viscosity's influence on Fock reactivity, particularly since viscosity is the parameter that falls outside the standard range of dissolving pulp (400–600 cm³/g (Duan et al. 2015)).

The PHK-FTR pulp produced under a flow-through mode in the pre-hydrolysis resulted in a pulp with behavior closer to the commercial dissolving pulp. In this case, the acid-dilute hydrolysis enhanced the hemicellulose removal (from 5.2% to 3.0%) and provoked additional cellulose depolymerization; the Fock reactivity increased by 36%, from 52.2% to 71.2%.

On the other hand, the comparison of the Kraft and PHK-Batch results suggest that hemicellulose content may not be a key parameter for the Fock reactivity, as the Fock reactivity of these two pulps is similar (55.7% vs 52.2%) despite the significant differences in hemicellulose content (20.1% vs 5.2%). However, this direct comparison can lead to misinterpretation,

because the Fock test represents the contribution of the two pulp components – cellulose and hemicelluloses – with completely different accessibility and reactivity (Götze 1967). In fact, when the Fock reactivity was applied to a commercial xylan its Fock reactivity was well above 90%, as expected considering its solubility in the alkali solution and the consequent high accessibility to the reagent, CS₂. Therefore, if we assume complete reaction of hemicelluloses, we can assess the Fock reactivity of cellulose. So, we can suggest that cellulose reactivity in the Kraft pulp is significantly lower (about 35.6%) than the cellulose reactivity in the PHK-Batch pulp (about 47.0%), which puts in evidence the positive effect of the auto-hydrolysis pretreatment on cellulose reactivity. The crystallite size of the two pulps was also significantly different (3.36 nm vs 2.56 nm), which can contribute to these modified Fock reactivity.

On the other hand, the substantial increase in Fock reactivity (about 20 points) from the PHK-Batch to PHK-FTR could be due to the decrease in the DP of the cellulose and cellulose supramolecular structure changes and not to the hemicellulose content, which only decreased from 5.2% to 3.0%.

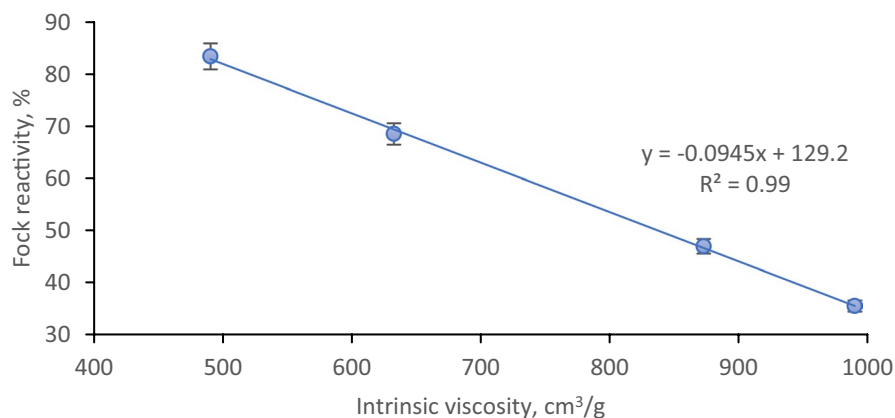
The commercial dissolving pulp had the expected reactivity (>90%) for good quality dissolving pulps, despite being a dried pulp, and was used as a standard for comparison with the lab-produced pulps (never dried).

While the pulps presented in Table 1 exhibit significant disparities, a very strong negative correlation ($R^2=0.99$) between the modified Fock reactivity (corrected by the hemicellulose content) and the intrinsic viscosity was observed (Fig. 1). If the standard Fock reactivity was used, the correlation would be much poor ($R^2=0.88$), further supporting the proposal of the modified Fock reactivity.

The correlation achieved in Fig. 1 is expected, considering that lower molecular weight cellulose suggests some type of deconstruction of the supramolecular structure of the original cellulose, which facilitates accessibility.

The relationship between the degree of polymerization and crystalline content/crystallite size may also give a deeper understanding of the increased reactivity. In Hamad and Hu (2010) study, the lower crystallite size has as a consequence the lower DP of cellulose. Engström et al. (2006) and Hernandez-Varela et al. (2020) showed that both properties, crystallinity

Fig. 1 Correlation between modified Fock reactivity and intrinsic viscosity for the pulps presented in Table 1



and DP, influence the reactivity by increasing solvent access.

Regarding the water retention value, it should be emphasized that the commercial dissolving pulp was dried and therefore its WRV is significantly lower than the PHK lab pulps. Within the lab PHK pulps, the PHK-FTR pulp presents a much higher WRV, despite the slightly lower hemicellulose content, suggesting higher fiber wall internal porous, as the porosity measurement using probes demonstrates; the Fock reactivity also increased. However, when the dry commercial dissolving pulp is introduced in the analysis, the positive correlation between fiber wall porosity and Fock reactivity does not occur, indicating that intrinsic viscosity and possible associated supramolecular properties prevails. It should be emphasized however that the WRV and the porosity are determined under neutral pH, whereas the reaction with the CS₂ occurs under strong alkaline conditions.

Regarding the porosity of the lab-made pulps, the values are, in general, similar to the ones found in literature. Grönqvist et al. (2014) assessed the porosity of dissolving pulps using the solute exclusion method and reported a micropore volume of 0.42 mL/g. Additionally, the total pore volume and fiber saturation point (FSP) also follow the work of Alince (2002) and Ceccherini and Maloney (2019). Although important information is provided by the solute exclusion method, when comparing pulps with very different hemicellulose content, the values should be analyzed with caution. The water strongly bonded in the hemicelluloses gel can be accounted as a pore volume lower than the probe size, even though it may not represent the actual pore volume. This can be the reason

for the high micropore and FSP values of the Kraft pulp (high hemicellulose content).

The commercial dissolving pulp used in this study was previously dried, and as expected, hornification was observed, leading to lower overall porosity, particularly in smaller-sized pores due to pore collapse. Similar observations were reported by Park et al. (2006). Although it is widely recognized that hornification is an irreversible process at moderate pH (Scallan and Laivins 2018; Ding et al. 2019), it is expected that in a strong alkaline environment some of the fibril collapse can be reversed. If so, the effective porosity of the cell wall would be greater, not constituting a restriction on the extent of the reaction.

Effect of hemicellulose content on fock reactivity

In dissolving pulp, the presence of hemicelluloses often poses challenges as it adversely impacts the quality of the resulting dope, namely its viscosity and filterability, and its content must be accounted for (Fischer and Schmidt 2008).

Cellulose and hemicelluloses are both polysaccharides found in the plant cell wall. The key distinction between them lies in their structural arrangement: cellulose forms a straight-chain polymer with high crystallinity, whereas hemicelluloses are amorphous. Due to these structural differences, hemicelluloses are much more reactive but can negatively impact the performance of the regenerated fibers. In theory, a higher content of hemicelluloses in the pulp results in higher reactivity, however, it will result in a poor dope quality (Spönlä et al. 2023).

To evaluate the possible effect of the hemicellulose content on the Fock reactivity, two distinct methodologies—enzymatic and chemical—were employed to remove the hemicelluloses. The results are presented in Table 2. The cold caustic extraction was significantly more effective in extracting hemicelluloses than the enzymatic treatment, aligning with the results reported by Ceccherini et al. (2021a) and Jiang et al. (2024).

The removal of hemicelluloses from pulps typically increases their intrinsic viscosity, primarily because hemicelluloses have a lower degree of polymerization (80–200 DP) (Sun et al. 2004) compared to cellulose. Additionally, during the alkali extraction, there is a tendency for low molecular weight cellulose to be dissolved and removed (Gehmayr and Sixta 2011), which further contributes to an increase in intrinsic viscosity. However, contrary to these expectations, this study found that the pulps after hemicellulose removal exhibited lower intrinsic viscosity. This suggests that the process of hemicellulose removal might trigger some degree of cellulose depolymerization. The same trend was reported by Ma et al. (2021), who also explored the relationship between intrinsic viscosity and hemicellulose content. In their research, Ma observed a decrease in viscosity from 910 to 740 cm³/g when hemicellulose content decreased from 4.9% to 0.9%. However, it's important to consider that the pulps were obtained using different bleaching techniques, which may also induce cellulose degradation. Cellulose depolymerization under strong alkaline conditions, moderate temperature and in the presence of oxygen can occur due to the hydrogen peroxide formation and their corresponding radicals (Sixta 2006; Fechter et al. 2020).

To further investigate this matter, the hemicellulose extraction process (NaOH, 10% (m/m)) was

applied to the PHK-FTR pulp (low hemicellulose content pulp), and the viscosity followed. The results show that the cold caustic procedure resulted in no decrease in viscosity (from 633 to 680 cm³/g); on the contrary, a minor increase occurred, probably due to the dissolution of smaller degrees of polymerization cellulose chains during the extraction.

In addition, to investigate the possible effect of radical generation by O₂ from the air, the cold extraction of the kraft pulp was repeated now under a nitrogen atmosphere and the decrease in intrinsic viscosity remained high (from 990 cm³/g to 710 cm³/g). One possible reason for this viscosity decrease can be the OH[−] accessibility to labile groups in cellulose, after hemicellulose removal. Sarosi et al. (2020) and Hellström (2012) suggests that hemicelluloses can act as a protective shield; so, after removal, all reactions will be increased, including the alkaline hydrolysis and the reaction with CS₂.

In this way, the removal of hemicelluloses and its collateral effects significantly improve the Fock reactivity by 22% (from 55.7% to 68.0%) despite the removal of xylan, which has shown above to have extremely high reactivity with CS₂ (reactivity > 90%). Therefore, the modified Fock reactivity, which excludes the hemicelluloses contribution, fully shows the effect of CCE on cellulose reactivity (from 35.6% to 63.5%). It should be emphasized that CS₂ was used in stoichiometric excess and therefore it is unlucky that the huge increase in modified Fock reactivity is due to reagent limitation.

The influence of hemicelluloses on the viscose process was first examined in Treiber (1983) research. This study evaluated how hemicellulose affects the processibility of chemical pulps, revealing that hemicelluloses interferes with the viscose process.

Table 2 Chemical composition and Fock reactivity of the extracted pulps

	Cellulose, %	Hemicellulose, %	Kappa number	Intrinsic viscosity, cm ³ /g	Fock Reactiv- ity, %	Fock Reactivity, modified*
Kraft	79.7 ± 0.7	20.1 ± 0.6	2.5 ± 0.1	990 ± 20	55.7 ± 2	35.6
Kraft—10% NaOH	95.5 ± 1.0	4.5 ± 0.2	1.5 ± 0.1	698 ± 10	68.0 ± 2	63.5
Kraft—Xylanase	84.9 ± 0.5	15.1 ± 0.3	2.3 ± 0.1	879 ± 15	60.7 ± 2	45.6
Kraft- Xylanase + 10% NaOH	97.2 ± 0.6	2.8 ± 0.2	1.5 ± 0.1	689 ± 10	72.3 ± 2	69.5

*Fock reactivity modified, assuming complete hemicellulose reaction

An additional ash analysis was conducted on these pulps. The Kraft pulps had an ash content of $0.44\% \pm 0.01$, whereas the Kraft pulps after CCE exhibited a lower ash content of $0.21\% \pm 0.02$. Alongside the decrease in viscosity and the removal of hemicellulose, the reduced ash content may also contribute to the higher Fock reactivity.

The effect of hemicelluloses extraction on pore size, WRV, FSP and accessible surface area can be observed in Table 3. Regarding the pore size, there is a drastic decrease of the micro (by 80%) and mesopores (by 49%) with the severe hemicellulose removal by the cold caustic extraction, while the xylanase treatment provoked a much less impact on both the porosity and on the hemicellulose content (Table 2).

The impact of hemicelluloses removal on fiber wall porosity was reported by several authors (Christov and Prior 1993; Ambjörnsson et al. 2014; Kaur et al. 2016; Ferreira et al. 2020) and may result from microfibril aggregation as a consequence of the hemicellulose extraction, resulting in an internal collapse of the fiber wall (Wan et al. 2010; Ceccherini et al. 2021b).

In our results, the internal collapse of the fiber wall resulted in a maximum decrease in fiber saturation point of 74%. The FSP represent the water accumulated in the micro and mesopores and can be seen as the amount of water in the cell wall; it is considered the most direct measurement of fiber swelling, but it's needed to consider that fiber damage and fibrillation may impact the fidelity of the result (Berry and Rodrick 2005).

The pulp after cold caustic extraction (CCE) presents a huge decrease in the FSP (from 1.68 mL/g to 0.44 mL/g). On the contrary, the WRV only decreased about 30% suggesting a substantial increase of macropores in the external fibrils. Lovikka et al.

(2016) have reported a similar reduction in WRV (from 1.67 g/g to 1.50 g/g), when comparing Kraft pulps before and after extraction.

The xylanase treatment was used as a different extraction process and compared to the chemical method. This process removed approximately 25% of the initial hemicellulose content from the pulp, whereas the CCE removed roughly 90%.

With xylanase, there was an overall decrease in water retention value of 9.8% (from 1.93 to 1.74 g/g), while the FSP decreased by about 4.3%. This behaviour is different from the one found in cold caustic extraction. Following the moderate hemicellulose removal, the micropores and mesopores had a slight decrease.

In conclusion, the cold caustic extraction was very effective in removing the hemicelluloses from the kraft pulp while the xylanase treatment was much less effective. In both cases, the removal of hemicelluloses resulted in higher reactivity.

The hemicelluloses extraction provoked a marked decrease in the micro and mesopores in the fiber wall. However, the Fock reactivity (including the modified) increased significantly, suggesting that the fiber wall porosity in the range reported in Table 3 and measured at neutral pH, apparently plays no significant role on CS₂ reactivity, which can be explained by the low molecular size of CS₂ and/or the much higher fiber wall porosity under strong alkaline conditions. The very high Fock reactivity obtained for the dry commercial dissolving pulp goes in accordance.

Ball-milling effect on viscosity and fock reactivity

Ball-milling is a widely recognized physical treatment method capable of increasing reactivity by reducing particle size and amplifying the surface area of the material. When applied to cellulose fibers, it

Table 3 Porosity, WRV, and FSP of the extracted pulps

	Micropore (<3.2 nm)	Mesopore (3.2–54 nm)	Macropore (> 54 nm)	WRV g/g	FSP (= 54 nm)	Accessible Surface area, m ² /g	Micro / macro
Kraft	0.46 ± 0.04	1.22 ± 0.05	0.25 ± 0.03	1.93	1.68 ± 0.05	104.9	185.3
Kraft—10% NaOH	0.10 ± 0.01	0.63 ± 0.02	0.73 ± 0.02	1.46	0.73 ± 0.01	54.8	7.6
Kraft—Xylanase	0.28 ± 0.01	1.16 ± 0.01	0.30 ± 0.01	1.74	1.44 ± 0.01	72.3	94.6
Kraft- Xylanase + 10% NaOH	0.12 ± 0.02	0.32 ± 0.05	0.90 ± 0.05	1.34	0.44 ± 0.05	19.8	13.7

is acknowledged for its ability to decrease particle size, crystallinity index, and cellulose polymerization degree (Acharya et al. 2021; Lan et al. 2022). These are critical properties that can influence its reactivity and interaction with solvents.

The effect of the vibrational impact ball-milling treatment length on the crystallinity index and Fock reactivity of the PHK-Batch (hemicellulose content = 5.2%, intrinsic viscosity = 873 cm³/g) pulp is presented in Fig. 2.

The decrease in the crystallinity index with the treatment time can easily be followed in Fig. 2. After 30 min, a reduction of around 50% was achieved (from 60.5% to 29.6%) with the reactivity increasing by 55.5%, reaching 84.6%.

Both crystallinity index and Fock reactivity exhibit a strongly non-linear behaviour; there is a sharper decrease in crystallinity in the first minutes (2–5 min) accompanied by a corresponding increase in reactivity. In fact, 61% of the Fock reactivity increase occurs in 5 min, which suggests that there is no justification for extending the treatment beyond 5 min. Additionally, the size of the crystallites was also followed (Fig. 3), and the treatment resulted in a significant decrease, from 2.55 nm to 1.64 nm after 5 min, decreasing moderately thereafter.

The findings about the ball-milling treatment follow similar tendencies to those found in the work of Avolio et al. (2012) and Phanthong et al. (2016) on different cellulosic materials; in the first work a 30 min planetary ball-milling treatment resulted in around a 50% decrease in crystallinity, while in the

second work, a 34% decrease was achieved after a 1 h treatment. The differences compared to our results are probably due to the grinding conditions and materials used.

Regarding the crystallite size, a decrease could also be followed in Hernandez-Varela et al. (2020) study. However, higher treatment times were used, and a 71% decrease was achieved after 240 min of planetary rotational ball-milling treatment of cotton fibers. In our case, the decrease was about 60% for 30 min.

The hypothesis that crystallite size and crystallinity index can significantly influence the behaviour of cellulose fibers across various processing techniques, such as hydrolysis and chemical treatments, and therefore the Fock reactivity, is strongly supported by the literature (Hamad and Hu 2010; Hindi Sherif S. Z. 2017; Bhisikar et al. 2022). Figure 4 confirms this correlation.

Furthermore, the non-linear relationship between crystallite size and crystallinity can be followed in French and Santiago Cintrón (2013) research, with a special focus on Cellulose II and Cellulose I β . However, vibrational impact ball milling's high structural disruption capability also decreased intrinsic viscosity and a good correlation can be established between this parameter and the Fock reactivity (Fig. 5). This simultaneous decrease in intrinsic viscosity, crystallinity index and crystallite size are in good agreement with the literature results (Mattenai et al. 2018; Liu et al. 2019), but does not enable separating the effect of the pulp properties on Fock

Fig. 2 Effect of vibrational impact ball-milling treatment length on crystallinity index and Fock reactivity for the PHK-Batch pulp

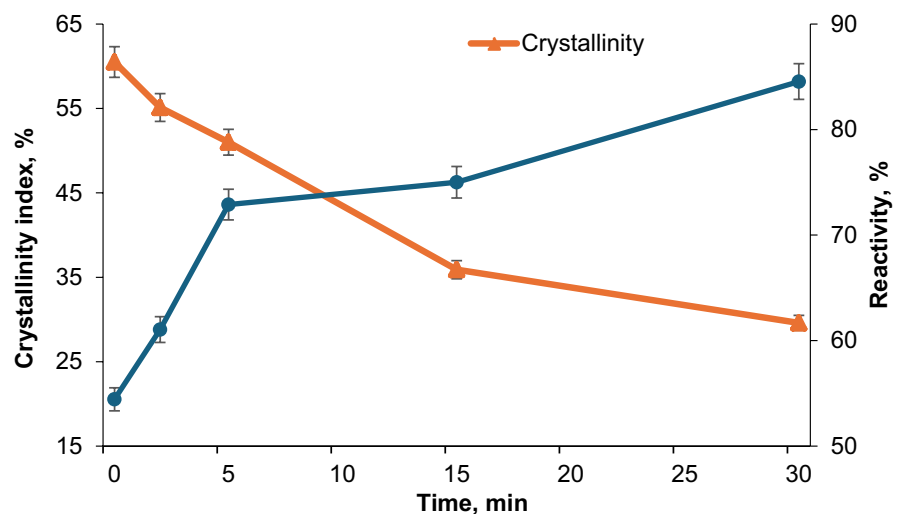
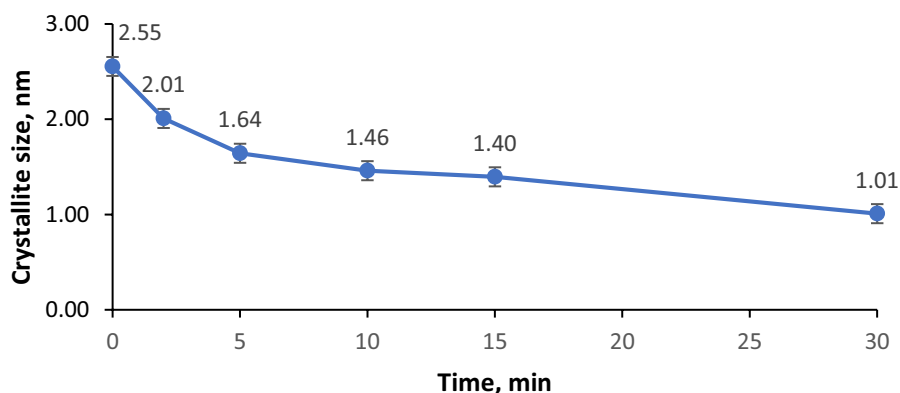


Fig. 3 Effect of the vibrational impact ball-milling treatment on the crystallite size



reactivity. In fact, there is a very good correlation between the intrinsic viscosity and the crystallinity index ($R^2=0.99$, data not shown), for the vibrational impact ball-milling conditions used.

Overall, the vibrational impact ball-milling process enhanced the Fock reactivity significantly by 55.5% (54.4% to 84.6%), however, the high energy treatment affects several pulp properties such as crystallinity (60.5% to 29.5%), the crystallite size (2.53 nm to 1.01 nm) and viscosity (873 cm³/g to 305 cm³/g), making difficult to separate the effect of the variables on Fock reactivity.

Interestingly the commercial dissolving pulp, with relatively high crystallinity (48%) and crystallite size (2.5 nm), exhibits excellent reactivity (90.7%), which demonstrated that low crystallinity and low crystallite size are not pre-requisites for

high Fock reactivity. Therefore, pulp viscosity is the only pulp property that rationalizes the results from the lab and industrial pulps.

Endoglucanase effect on pulp properties

Aiming to separate the effect of cellulose degree of polymerization and crystallinity, an enzymatic approach was used. The high specificity of enzymes and the less energetic treatment may reduce the structural changes observed in the vibrational impact ball-milling process.

Endoglucanases are enzymes that can hydrolyze the β -1,4-glycosidic bonds within cellulose chains, leading to the cleavage of cellulose molecules into smaller fragments (Ambjörnsson et al. 2014). This enzymatic depolymerization process results

Fig. 4 Correlation between crystallite size and Fock reactivity

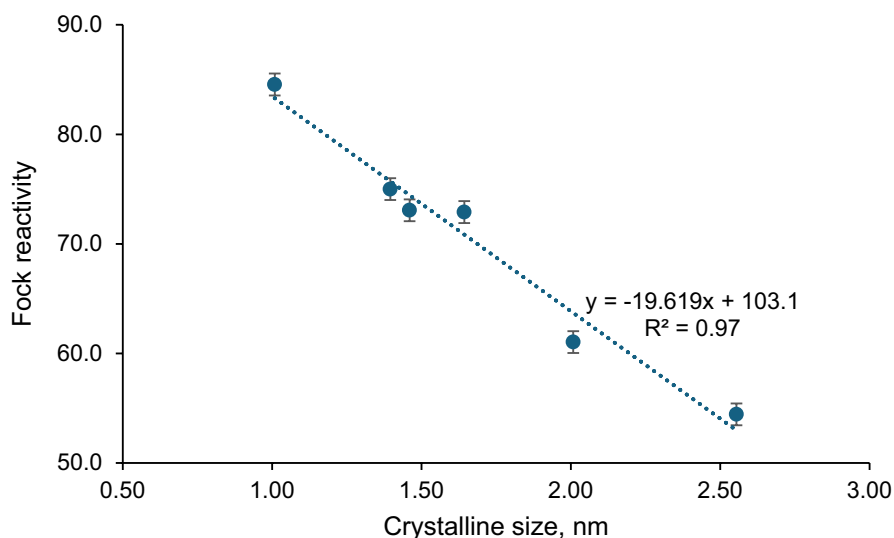
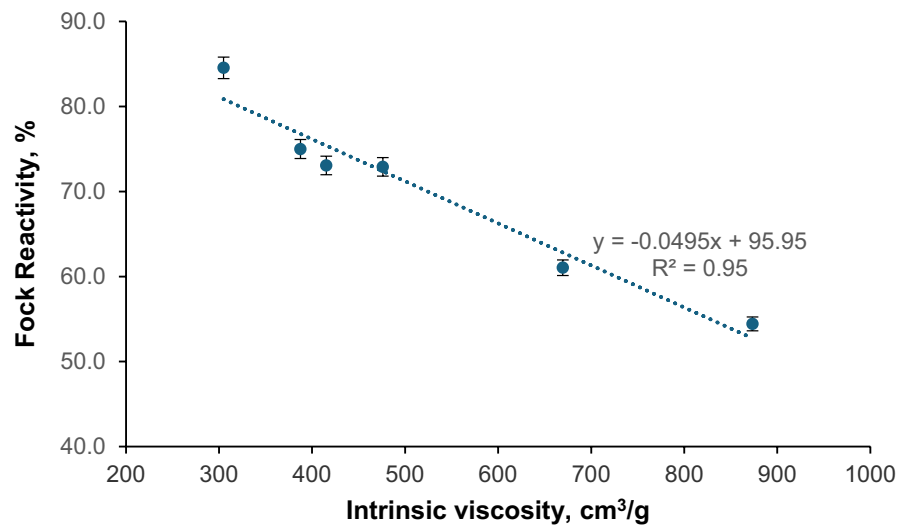


Fig. 5 Correlations between reactivity and viscosity of vibrational impact ball-milled samples



in a reduction in the average molecular weight of cellulose.

This post-treatment was applied to the PHK-Batch and PHK-FTR pulps, which exhibit similar compositions but divergent porosities and viscosities. Table 4 illustrates the impact of the enzymatic treatment on porosity, viscosity, crystallinity, and crystallite size, along with its influence on the reactivity of the pulps.

Following enzymatic treatment, despite the initial differences in porosity, both pulps exhibited similar behaviour in terms of porosity. There was a notable increase in macropores, with the PHK-Batch showing a 55% increase and the PHK-FTR a 35% increase. Conversely, mesopore volume decreased, with the PHK-Batch experiencing a 20% reduction and the

PHK-FTR a 31% reduction. These findings mirrored those observed with xylanase enzymatic treatment and may be associated with fibril collapse.

The PHK-Batch pulp demonstrated an exceptionally low micropore volume, nearly falling within the precision range of the analytical method, resulting in insignificant differences before and after enzymatic treatment. Conversely, the PHK-FTR pulp experienced a small but significant decrease in micropore volume.

In the paper and pulp industry, endoglucanases are often used in conjunction with other enzymes as a pre-treatment process to enhance fibrillation before some kind of mechanical treatment (Han et al. 2021). In this study, the enzyme was employed with the

Table 4 Porosity, WRV and FSP values of PHK-FTR and PHK-Batch pulps after and before enzymatic treatment (endoglucanase)

	PHK-FTR	PHK-FTR endo 3h	PHK-Batch	PHK-Batch endo 3h
Micropore (<3.2 nm)	0.64 ± 0.02	0.55 ± 0.05	0.03 ± 0.02*	0.09 ± 0.06*
Mesopore (3.2–54nm)	0.77 ± 0.06	0.53 ± 0.03	1.24 ± 0.07	1.0 ± 0.02
Macropore(> 54 nm)	0.26 ± 0.04	0.35 ± 0.02	0.09 ± 0.02	0.14 ± 0.03
WRV	1.67 ± 0.3	1.43 ± 0.2	1.37 ± 0.2	1.23 ± 0.2
FSP(= 54 nm)	1.41 ± 0.04	1.08 ± 0.01	1.28 ± 0.08	1.09 ± 0.02
Accessible Surface area, m²/g	66.6 ± 5.2	45.8 ± 6.0	107.2 ± 8.6	85.9 ± 6.9
Viscosity, cm³/g	633 ± 15	447 ± 12	873 ± 20	558 ± 10
Reactivity, %	71.2 ± 0.04	83.5 ± 0.04	52.2 ± 0.04	65.1 ± 0.04
Crystallinity, %	54.5 ± 0.3	51.1 ± 0.2	60.5 ± 0.5	53.8 ± 0.2

*Values that do not show statistical significance

specific objective of cleavage of the β -1,4-glycosidic bonds within cellulose chains, without significantly affecting other pulp properties. In fact, the crystallinity index and the crystallite size remain practically unaffected, and the intrinsic viscosity decreases significantly.

For the PHK-Batch, the viscosity decreased by 36%, from 873 cm³/g to 558 cm³/g, whereas the PHK-FTR decreased by about 29% from 633 cm³/g to 447 cm³/g.

The accessible surface area in Table 4 is quantified based on the enzyme's size and its ability to enter certain pores (it cannot enter micropores (Nagl et al. 2022)). Therefore, the higher volume of mesopores in the PHK-Batch and its higher enzyme accessibility may be linked to a greater decrease in viscosity.

Regarding the treatment impact on pulp reactivity, enzymatic treatment resulted in increased reactivity for both pulps. The PHK-Batch pulp reactivity rose by 25%, from 52 to 65%, while the PHK-FTR pulp saw a 17% increase, from 71 to 83%. Despite differing in other properties, a correlation of 90% was observed between viscosity and reactivity in both pulps. This correlation is lower compared to the correlation between the decrease in viscosity and reactivity within the same pulp, indicating that while other properties also influence pulp reactivity, viscosity has a more significant effect.

Interestingly, despite the low viscosity of both pulps, a difference of about 20 points in modified Fock reactivity remains, highlighting the importance of the pulp history on reactivity.

Conclusions

The utilization of various treatments across four initial pulps, including a commercial dissolving pulp, with diverse properties such as hemicellulose content, intrinsic viscosity, and Fock Reactivity, facilitated a more comprehensive understanding of how specific pulp properties impact Fock reactivity.

Applying a cold caustic extraction stage (CCE) (under a nitrogen atmosphere), in a high hemicellulose content pulp (kraft pulp) resulted in an increase in Fock reactivity by 22% (55.7% to 68.0%). To better represent the cellulose reactivity in pulps with different hemicellulose content, a modified Fock

reactivity was proposed, where the contribution of hemicelluloses was excluded. In this way, in the CCE, the cellulose reactivity increased from about 35.6% to 63.5%, representing an increase of about 78%. These results highlight the role of the CCE stage on both hemicellulose content, which impairs the dope properties, and cellulose reactivity. Further assessment of the results showed that the removal of hemicelluloses significantly decreases the intrinsic viscosity of the pulp, despite the removal of about 78% of the hemicelluloses, suggesting cellulose depolymerization in the CCE conditions, after cellulose de-shielding.

The comparison of the never-dried pulps (with higher porosity) with the dried commercial pulp (with lower porosity) suggests the reduced influence of porosity measured at neutral pH on the pulp reactivity with CS₂.

The vibrational impact ball-milling treatment increased by 64% the PHK-Batch reactivity, reaching 84.6%, while the crystallinity index and crystallite size decreased from 53.8% to 22.0% and from 2.53 nm to 1.01 nm, respectively. These results support the hypothesis that higher crystallite surface area increases the extent of the heterogeneous reaction of CS₂ with the hydroxyl groups of cellulose. However, the comparison with the commercial pulp apparently makes this hypothesis unfeasible, with intrinsic viscosity prevailing as the unifying parameter. The milder endoglucanase treatment did not significantly affect crystallinity and crystallite size, allowing for the separation of the effects of intrinsic viscosity.

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Data availability No datasets were generated or analysed during the current study.

Declarations

Conflict of interest The authors declare no competing interests.

Ethical approval Not applicable.

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