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Xylan extraction strategies and the performance of the resulting high purity cellulose fiber to swelling and dissolution

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1 Xylan extraction strategies and the performance of the resulting high purity 2 cellulose fiber to swelling and dissolution

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10

11 Abstract

12

13 In this study, we investigated the influence of hemicelluloses removal treatment on the
14 reactivity of the resulting pulp. The idea was to develop treatment strategies consisting of
15 mechanical refining (different refining technologies), chemical treatment (CCE), and xylanase
16 treatment that enabled both quantitative xylan removal as well as good reactivity to
17 dissolution without the need for additional post-extraction treatments (cellulose activation)
18 to improve reactivity. Cellulose post-extraction treatments result in additional production
19 costs. The reactivity of the extracted pulps was evaluated based on the degree of swelling in
20 NaOH and dilute cupriethylene diamine solution (CUEN), the solubility in 8% NaOH at -10 °C,
21 and the Fock reactivity. The result obtained showed that hemicelluloses removal strategies
22 that included mechanical refining treatment led to better pulp reactivity than unrefined pulp.
23 The best result was obtained with refined pulp extracted with 6% soda (cellulose II not
24 detected). In addition, we obtained a Fock reactivity ranging from 60 to 70%. The good
25 correlations found between fiber swelling, solubility in caustic soda, and Fock reactivity
26 suggest that the tedious Fock test could be substituted by the much simpler swelling and
27 solubility measurements. The negative impact of cellulose II on pulp reactivity is due to the
28 higher number of hydrogen bonds formed under dewatering and drying. This problem would
29 most likely be averted in the ideal case where pulp dissolution is integrated into the pulp mill.

30

31 **Keywords:** Paper-grade pulp; mechanical refining; Cold caustic extraction; Xylanase treatment; Dissolving pulp;
32 cellulose fiber swelling; cellulose dissolution

33

34

35 Introduction

36

37 Due to the natural structure and the presence of a multitude of intermolecular hydrogen
38 bonds, the cellulosic fiber has very low reactivity. This explains why very few systems have
39 been shown to be able to solubilize cellulose molecules. In both viscose and Lyocell
40 processes, special attention is paid to the parameters which control the chemical reaction
41 with CS₂ or the solubilization in NMMO. For this, so-called fiber reactivity measurements have
42 been developed. The reactivity of dissolving pulp is the ease with which the hydroxyl groups
43 on cellulose chains react with the reagent in the derivatization process or the solvent during
44 the dissolution process. Factors such as the chemical composition of the dissolving pulp, the
45 structure, and the morphology of the fibers significantly impact the reactivity (Tian et al.,
46 2014). Generally, dissolving pulp properties are influenced by the source of the raw material
47 (cotton, wood, or bamboo), the pulping process (acid sulfite or pre-hydrolysis kraft), and
48 bleaching conditions. Compared to the sulfite process, the kraft pulping system has been

49 reported to yield cellulose with low reactivity (to xanthation). This has been attributed to the
50 hemicelluloses removal mechanism. Hemicelluloses extraction in alkaline medium proceeds
51 *via* a swelling mechanism where the cellulose fibrils expand, leaving room for the
52 solubilization of the hemicelluloses fraction entrapped within the cellulose matrix. After the
53 removal of the hemicelluloses, there is a kind of collapse of the fibrils closing up spaces freed
54 by the hemicelluloses leading to a reinforcing of the hydrogen bond network (aggregative
55 microfibril) (M. Y. Ioelovich, 2016).

56
57 Among the methods proposed in the literature to determine the reactivity of dissolving pulp
58 in the viscose process, the Fock test/reactivity is the most popular. The other methods are
59 the Chinese filterability test (Duan et al., 2015) and viscose dope Filter Value (Gehmayr et al.,
60 2011a). The Fock test determines the reactivity of dissolving pulp by quantifying the percent
61 regenerated/reacted cellulose in the viscose process. It follows a similar principle as the
62 viscose process, which involves (i) the swelling of pulp in strong NaOH solution
63 (mercerization), (ii) the derivatization to cellulose xanthate (xanthation: the reaction of the
64 hydroxyl groups on cellulose with carbon disulfide) (iii) the dissolution of cellulose xanthate
65 (iv) the regeneration of the dissolved cellulose (v) the oxidation and quantification of the
66 regenerated/reacted cellulose.

67
68 Several approaches have been proposed to improve the reactivity of dissolving pulp,
69 enzymatic and mechanical treatments being the most common. The activation of cellulose
70 fibers prior to dissolution has been reported in the literature. This process involves the
71 chemical, enzymatic and mechanical treatment applied to improve cellulose solubility.
72 Mechanical treatments like ball milling, steam explosion, Valley beater refining, and PFI
73 milling of dissolving pulp have been reported to enhance dissolving pulp reactivity to
74 xanthation (Budtova & Navard, 2017; Gehmayr et al., 2011b; Köpeke et al., 2008; H. Li et al.,
75 2018; Miao et al., 2014; Tian et al., 2014; Zhou et al., 2018). In these reports, the already
76 produced dissolving pulp is subjected to additional treatments (activation) to facilitate
77 dissolution, which means additional production costs. (Tian et al., 2014) explored the effect
78 of mechanical treatment by PFI (refining) and coffee grinder on the reactivity of PHK
79 dissolving pulp. They found an increase in Fock reactivity from 49% to 72% after grinding for
80 6 minutes. Refining the pulp with the PFI at 25000 revolutions increased the Fock reactivity
81 from 49% to 58%. The less impressive result obtained with the PFI was attributed to the inter-
82 intra fibril/fiber hydrogen bonding enhanced by fibrillation during the PFI refining, which
83 limits chemical accessibility. Also, the application of endoglucanase to 9% CCE extracted pulp
84 increased the Fock reactivity from 23 to 62% (Duan et al., 2016a). Likewise, a study by (Miao
85 et al., 2014) showed that PFI refining treatment alone at 5000 revolutions had no significant
86 effect on Fock reactivity (and DP of cellulose), but the enzymatic treatment (cellulase)
87 increased the Fock reactivity from 50 to 76%.

88 Actually, mechanical and enzymatic treatment (cellulases) of dissolving pulp may modify the
89 morphology of the fibers as well as the DP of cellulose. Several reports on enzymatic
90 modification of cellulose reactivity have attributed the increase in Fock reactivity to the DP
91 adjustment brought about by the enzymatic degradation of cellulose chains. However,
92 according to (Ferreira et al., 2020), the influence of the supramolecular structure of cellulose
93 on reactivity (fibril aggregates dimension) outweighs the effect of the degree of
94 polymerization. The authors reported that even with low DP (intrinsic viscosity < 500 cm³/g)

95 and low crystallinity index (< 50%), the Fock reactivity was influenced more by the lateral fibril
96 aggregation.

97

98 In the present study, the idea was to produce dissolving pulp with high reactivity from the
99 paper-grade pulp by ensuring that the hemicelluloses removal processes employed also
100 improved the dissolution potential of the resulting dissolving pulp. In order to obtain these
101 conditions, the fibers were subjected to mechanical refining with different technologies, and
102 the xylan extraction was performed at 60 and 100 g/L NaOH. In some cases, an additional
103 xylanase treatment was included in the treatment sequence. In a previous study (Ngene et
104 al., 2022), several strategies were explored to improve the purity of paper-grade cellulose by
105 removing the residual hemicelluloses content. Mechanical refining pretreatment showed
106 promise with a xylan removal degree of over 80%. Therefore, in this study, the effect of the
107 xylan removal treatment on the reactivity of the extracted cellulose was assessed by the
108 degree of swelling in NaOH solution, Cupriethylene diamine solution, and the solubility in
109 NaOH. These results were then compared with the reactivity to xanthation (Fock reactivity).
110 Since cellulose swelling precedes dissolution, the hypothesis of the study was that the
111 swelling degree could predict the reactivity of the cellulose fibers. The influence of the
112 crystallinity index and degree of polymerization on reactivity was also discussed.

113

114 **Materials and methods**

115

116 **Materials**

117 Bleached mixed hardwood kraft dry sheets were supplied by Fibre Excellence St-Gaudens, a
118 paper mill in France. The xylan content and degree of polymerization of the pulp before
119 treatment were 20% and 1294, respectively. No other hemicelluloses were present in a
120 significant amount. (Details of the pulp properties are shown in Appendix (Table A1)). The
121 xylan-degrading enzyme β -xylanase was purchased from Megazyme (Bray, Ireland). Other
122 chemicals used were NaOH (≥ 99 % for analysis, Roth, Karlsruhe, Germany), sulfuric acid (95-
123 97% for analysis, Roth), dimethylacetamide (≥ 99 % for analysis, Roth), lithium chloride (≥ 99
124 %, Sigma Aldrich, St. Louis, MO, USA), and cupriethylene diamine solution (1.0 M, Sigma
125 Aldrich).

126

127

128 **Methods**

129

130 *Mechanical refining*

131 Mechanical treatment was performed on the PFI mill, Valley beater (Voith, Heidenheim,
132 Germany), and the Disc refiner pilot. When the refining was performed on the PFI mill, 30 g
133 of the dry pulp was soaked overnight and disintegrated with the Lhomargy blender for 5 min.
134 After that, the pulp suspension was concentrated by filtration until a pulp consistency of 10%.
135 The suspension was then evenly distributed on the wall of the refining chamber and refined
136 to the desired SR° by controlling the revolutions. On the other hand, for refining on the Valley
137 beater, an equivalent of 440 g (oven-dried weight) of pulp was soaked in 2 L tap water
138 overnight and then drained and disintegrated with a pulper for 10 min. The disintegrated
139 pulp was correctly diluted to 22 L (making a pulp consistency of 2%) and then transferred into
140 the beater and refined to the desired Schopper-Riegler value (°SR). The disc refining was
141 performed on a disc refiner pilot at a consistency of 3% for 24 mins to reach a similar SR as

142 obtained with the PFI and Valley beater. After characterization, the refined pulp was then
143 centrifuged to remove excess water and transferred into a polyethylene bag for storage in
144 the refrigerator.

145

146 *Fiber characterization*

147 The fiber quality (length, width, fibrillation index, and fines content) was determined by the
148 Morfi fiber analyzer (Techpap, Grenoble, France). The water retention value was determined
149 by centrifugation of test pads at an acceleration of 3000 g for 15 min. Pulp's specific surface
150 area and total pore volume were determined by the Brunauer-Emmett-Teller (BET) analysis
151 of nitrogen adsorption. The measurements were carried out using the Nova 2200e device
152 from Quantachrome (Grenoble, France). Samples were degassed under vacuum at 105 °C for
153 16 hours to remove water molecules adsorbed on the porous surface of the sample prior to
154 determination. Fiber images were acquired by environmental scanning electron microscopy
155 ESEM (FEI, Tokyo, Japan).

156

157 *Cold caustic extraction*

158 The cold caustic extraction of the residual hemicelluloses was carried out at NaOH
159 concentrations of 60 g/L and 100 g/L. Other conditions chosen for the extraction were pulp
160 consistency of 5%, residence time of 30 minutes, and temperature of 25 °C. At the end of the
161 reaction, the pulp was washed with deionized water to a pH of 8. The resulting pulp was dried
162 by lyophilization.

163

164 *Xylanase treatment*

165 For the enzymatic extraction of hemicelluloses, pulp samples were treated with xylanase (500
166 U/g) at 3% consistency in a 0.1M sodium phosphate buffer solution. The pH of the buffer was
167 6, and the reaction was carried out in a plastic bag. The enzyme was first introduced into the
168 buffer solution and thoroughly mixed before pulp addition to ensure uniform distribution.
169 After homogenizing the pulp/xylanase suspension, it was incubated in a controlled water bath
170 at 50 °C for 2 h. The pulp/xylanase suspension was filtered and mixed with deionized water
171 at 90 °C. It was then placed in a water bath maintained at 90 °C for 30 min to deactivate the
172 enzyme. The pulp was washed with deionized water and stored at 4 °C.

173

174 *Analytical techniques*

175 The degree of polymerization was determined before and after treatment by dispersing the
176 pulp in deionized water and subsequent dissolution in cupriethylenediamine solution (CED)
177 according to the TAPPI T230 om-13 (2013). The degree of polymerization was then calculated
178 based on the formula proposed by (Sihtola et al., 1963)

179

$$180 \quad \eta = 954 \log V - 325 \quad (1)$$

$$181 \quad DP^{0.905} = 0.75 \times \eta \quad (2)$$

182 Where V is the viscosity from the capillary method (T230 om-13 (2013)), η is the intrinsic
183 viscosity, and DP is the degree of polymerization.

184 The molecular weight distribution of pulp samples was determined by dissolving in 8%
185 LiCl/DMAc solution and analyzed by gel permeation chromatography (GPC) equipped with a
186 multi-angle light scattering (MALLS) detection system (Dupont, 2003). According to the NREL
187 procedure, a two-step acid hydrolysis was used to determine the hemicelluloses composition

188 (Sluiter et al., 2008).

189

190 *Quantification of Cellulose II content and crystallinity index by ¹³C CP-MAS NMR*
191 *spectroscopy*

192

193 The cellulose II content and crystallinity index of samples were quantified by the high-
194 resolution solid-state ¹³C CP-MAS NMR spectroscopy. Samples were freeze-dried and ground
195 before analysis. This method uses the unique chemical shifts created by the carbon-13 atom
196 of the AGU to distinguish between the various cellulose polymorphs quantify the degree of
197 crystallinity and cellulose-II content in pulp samples. The supramolecular structure of
198 cellulose can be examined by analyzing the signals generated by the carbon-13 atoms of the
199 anhydroglucose unit (AGU). Each carbon of the AGU induces resonance at unique chemical
200 shift ranges; atoms C-1(100-110 ppm), C-4 (80-90 ppm), C-2, C-3, and C-5 (70-80 ppm), and C-
201 6 (60-70 ppm). The signals generated by each carbon atom differ according to the type of
202 cellulose: crystalline cellulose, amorphous cellulose, cellulose I, or cellulose II. For the study
203 of crystallinity degree, the C-4 atoms are good indicators and depending on the extent of
204 crystallinity or disorder; the C-6 could also contribute to the analysis. For instance, fully
205 amorphous cellulose shows no peak at atoms C-4 and C-6, while crystalline cellulose exhibits
206 peaks at C-4 and C-6. The intensity of the peak depends on the degree of crystallinity (Park
207 et al., 2010). The crystalline index is quantified by subtracting the amorphous reference
208 spectrum from that of the sample, where the difference represents the crystallinity degree.
209 Typically, the C-4 signal, separated into two distinct peaks in cellulose, is ascribed to
210 crystalline and non-crystalline domains, assigned 89 ppm and 84 ppm, respectively.

211 For the quantification of cellulose II, the cellulose I reference spectrum is subtracted from
212 that of the study sample before analyzing the carbon atoms. According to the Larsson
213 deconvolution method, the C-1 resonance provides information on the determination of
214 small amounts of cellulose II in the sample. The onset of a peak at 106.5 ppm or the widening
215 of the C-1 signal between 100 and 110 ppm indicates the presence of cellulose II. On the
216 other hand, more significant amounts of cellulose II two can be quantified by integration or
217 deconvolution of the C-6 signal. Depending on the extent of cellulose I to cellulose II
218 conversion, the resonance at 65.6 ppm diminishes while that at 62.5 increases. For samples
219 rich in cellulose II or on the complete transition from cellulose I to cellulose II, one narrow
220 peak instead of two is observed at C-6.

221

222

223 *Crystallinity index by X-ray diffraction (XRD)*

224 The supramolecular changes resulting from the mechanical and chemical treatments applied
225 were monitored by X-ray diffraction studies. Pulp samples analyzed were ground to powder
226 by a cryogenic grinder prior to the analysis. The cellulose allomorphs contributing to the
227 crystallinity index were identified and quantified. The analysis was performed with the
228 PANalytical X'Per pro MDP diffractometer (Cu-K α). The calculation of the crystallinity index
229 was done by Segal's method.

230

$$\text{Crystallinity index} = \left(\frac{I_{cr}}{I_{cr} + I_{am}} \right) \times 100 \quad (3)$$

231 Where I_{cr} and I_{am} are the intensities of crystalline and amorphous regions of cellulose,
232 respectively.

233 *Cellulose fiber swelling tests*

234

235 The extent of cellulose fiber swelling in various solvents was determined by measuring the
236 increase in the fiber width with the help of the MORFI apparatus. The MORFI apparatus is a
237 fiber quality analyzer that measures pulp characteristics, including the fiber width. Values of
238 the variation in fiber width indicate the extent of swelling, particularly in the lateral direction.
239 To determine swelling at various soda concentrations, the pulp samples (unrefined and disc
240 refined) were not subjected to drying before the test. The pulp samples were weighted and
241 mixed with soda at a pulp consistency of 5% and mixed at intervals for 30 min. Thereafter, it
242 was diluted to a concentration of 40 mg/L with water before passing it to the MORFI
243 apparatus. The soda concentrations investigated were 0%, 2%, 4%, 6%, and 8%.

244

245 Swelling has been reported to reach a maximum at soda concentrations ranging from 10% to
246 12%. Therefore, to study the effect of various pretreatment methods on the morphology of
247 cellulose fibers, the swelling test was performed at a pulp consistency of 1%, and soda
248 concentration of 12%, while stirring at 250 rpm for 30 minutes. When the time elapsed, the
249 suspension was diluted to a concentration of 40 mg/L before being analyzed by the MORFI.
250 The samples used in this study were freeze-dried.

251

252 Also, the swelling degree of the extracted pulp was determined by reacting it with dilute CUEN
253 solution (0.16 M). This concentration was chosen to favor swelling rather than dissolution.
254 About 40 mg of pulp (frozen in storage) was dispersed in 2ml of 0.16 M CUEN and agitated at
255 150 rpm for 10 minutes. After which, the suspension was diluted to 1L and analyzed by the
256 MORFI.

257

258 *Solubility test of cellulose in aqueous NaOH*

259

260 The solubility test in aqueous NaOH was performed according to the method proposed by
261 (Isogai & Atalla, 1998). One gram (1 g) of freeze-dried cellulose was dispersed in 26.9 g of
262 water, and 2.5 g NaOH was added, making approximately 8.5% NaOH solution. The
263 suspension was thoroughly mixed and cooled to -10 °C and held until completely frozen. The
264 suspension was allowed to thaw at room temperature, after which 20.6 g of deionized water
265 was added to dilute it to 5% NaOH. The gel-like suspension was then filtered to separate the
266 undissolved residue. The filtration was conducted in a 50 ml sintered glass (G2). Before
267 drying, the undissolved residue was washed sequentially with 5% NaOH, 1% NaOH, water,
268 10% acetic acid, water, and acetone. The solubility was expressed as the % of the dissolved
269 cellulose fibers.

270

271 *Fock reactivity*

272 Fock reactivity was performed based on the modified protocol proposed by Tian et al. (2013)
273 (Tian et al., 2013). The Fock reactivity is determined in stages; Xanthation, regeneration, and

274 quantification of converted cellulose. The pulps used for the experiment were freeze-dried
275 with a moisture content of about 6%.

276

277 Results and discussions

278 Effect of refining and soda concentration on the swelling of cellulose fibers

279

280 The high water- absorption and retention capacity of mechanically refined cellulose could
281 improve the degree of swelling of the cellulose fibers in aqueous solvents. This is of particular
282 interest as swelling is the first step in the dissolution process. To investigate this, the degree
283 of swelling of unrefined and refined cellulose in caustic soda solution of various
284 concentrations was determined at room temperature. Swelling degree was measured on the
285 MorFi analyzer from the change in fiber width when the pulp was placed in the caustic soda
286 solution according to a method developed by (Arnoul-Jarriault et al., 2016). The properties
287 of the unrefined and refined pulps before the swelling test are shown in Table 1. In this
288 instance, the pulp used was not dried before the swelling test.

289

290

291 **Table 1. Properties of bleached mixed hardwood pulp before swelling.**

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300

Samples	Unrefined pulp	Refined pulp (Disc pilot) ^(a)
Fiber length (μm)	685 \pm 13	544 \pm 6
WRV %	103 \pm 1.8	233 \pm 2.8
SSA (m^2/g)	0.4	0.6
DPv	1293 \pm 32	1087 \pm 28

The pulp was refined at a net power of 8kW until an SR° 85

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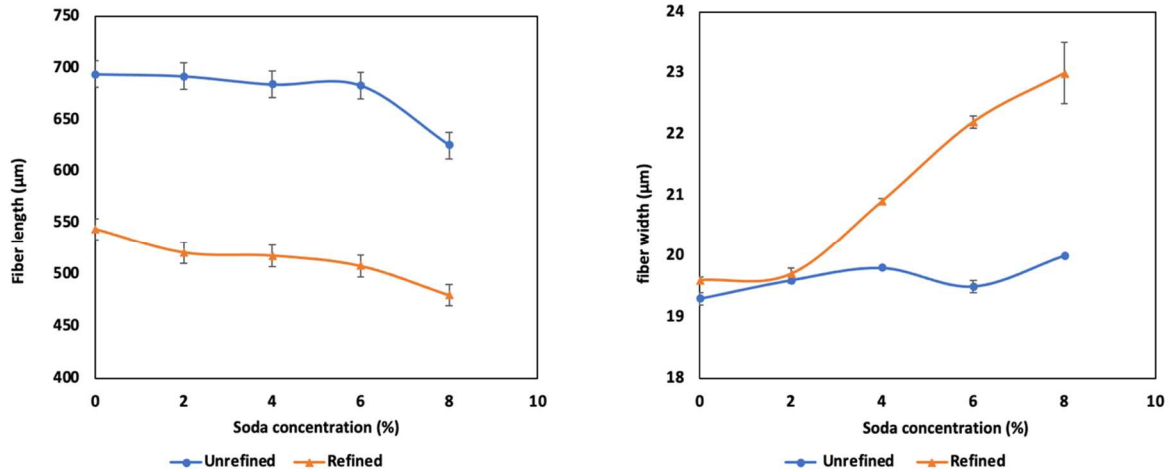
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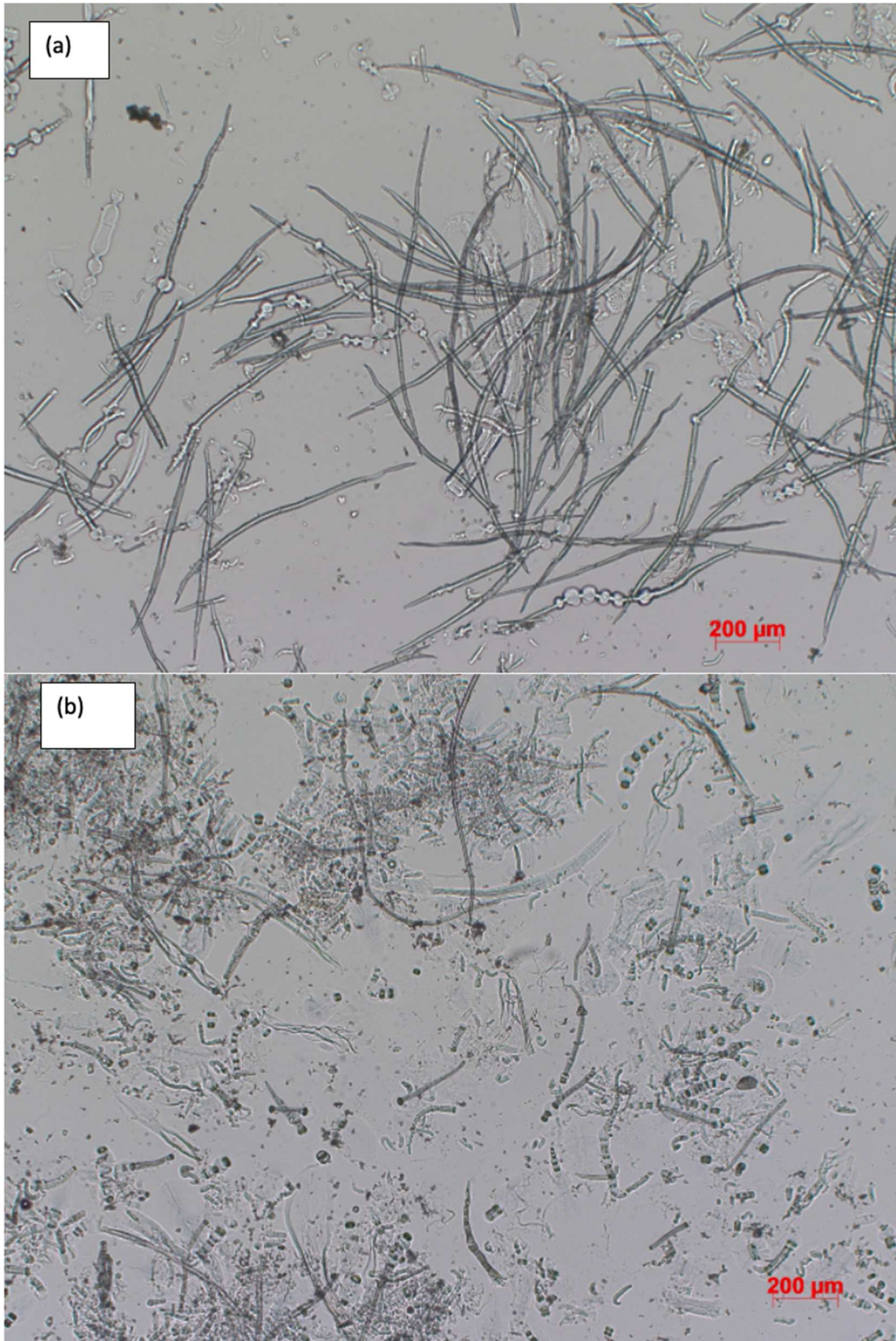
As expected, a change in the pulp properties was observed with refining. Upon refining, a decrease in the fiber length and degree of polymerization was recorded, and the WRV and SSA doubled as well. These changes in morphology could explain the improved swelling of the refined pulp compared to the unrefined pulp in soda solution, as seen in Figure 1, where the evolution of the fiber length and width with increasing soda concentration is shown. The refined pulp experienced more swelling than the unrefined pulp. Also, the swelling increased with increasing soda concentration, and the fiber length decreased slightly. The slight loss in fiber length with the increase of swelling is a general trend observed in studies of swelling (Arnoul-Jarriault et al., 2016; Gomes et al., 2020).



314
 315 **Figure 1. Swelling behavior of unrefined and refined pulp (Disc pilot) at various soda concentration**
 316

317 Figure 2 shows optical microscopy images of unrefined and refined pulps after 2 min in 0.25
 318 M CUEN. It can be seen that the short fibers, which are more populated in the refined pulp,
 319 swell more homogeneously than long fibers. Swelling and ballooning were well observed in
 320 the unrefined pulp. The dissolution by ballooning is associated with a restriction in the outer
 321 fiber wall (primary (P) and secondary (S1) layers). Other dissolution pathways involve the
 322 dissolution by the unwinding of the helical cellulose structure in the secondary layer (S2, S3)
 323 and the dissolution by fragmentation, both resulting from more homogeneous swelling. Also,
 324 homogeneous swelling can be made possible by the absence of the P and S1 layers or by the
 325 use of strong solvents that resist the effect of the outer layers (Navard & Cuissinat, 2006).

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Figure 2. State of unrefined (a) Valley beater refined pulp (SR° 85) (b) after a stay of 2 min. in 0.25M CUEN solution

Compared to the unrefined pulp, the restrictions in the outer layer of the refined pulp are minimized by the refining action, leading to dissolution with less ballooning and more homogeneous swelling.

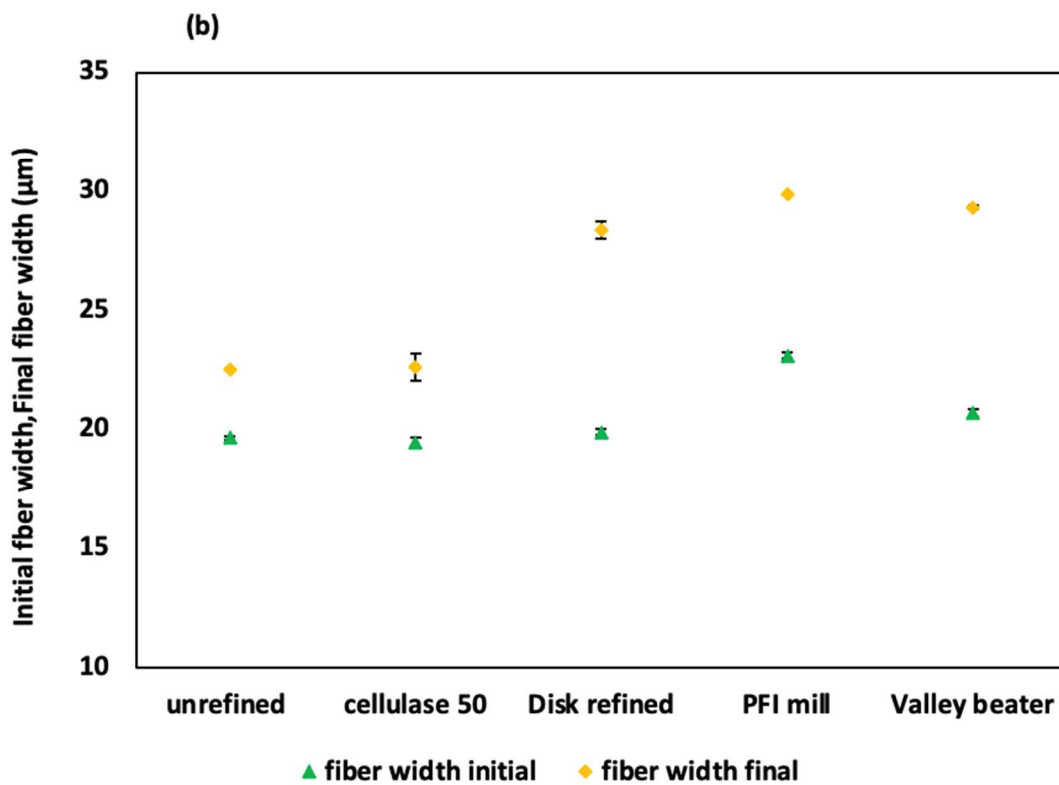
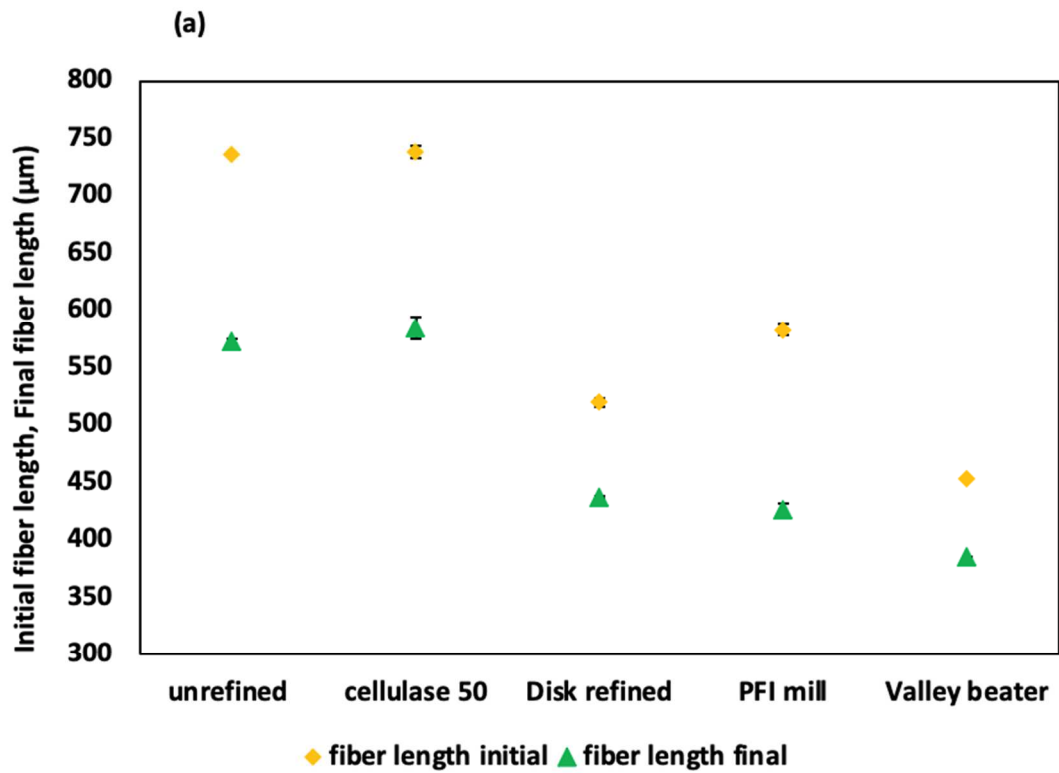
337

338 **1.1. Influence of the pretreatment strategy on the swelling of cellulose fibers in 12%**
339 **NaOH solution**

340

341 In order to better understand the influence of mechanical pretreatment on cellulose swelling
342 in NaOH solvent, freeze-dried cellulase treated pulp (50 U/g pulp) and pulp refined to the
343 same degree (°SR-85) by different technologies (PFI, Valley beater, and Disc pilot), were
344 treated with 12% NaOH at 1% pulp consistency for 30 min at room temperature. As shown
345 in Figure 3 a, a decrease in fiber length was observed for all the samples regardless of the
346 treatment strategy employed. Likewise, the degree of swelling represented by the gain in
347 fiber width (Figure 3 b) increased for all the samples but more substantially for the refined
348 pulps.

349



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Figure 3. Effect of pretreatment strategy on swelling in 12% soda (cellulase 50: represents pulp treated with cellulase at a dosage of 50 U/g pulp) (a) variation in fiber length (b) variation in fiber width

356 Under these conditions (12% caustic soda, 1% pulp consistency, with continuous stirring for
 357 30 minutes), the variation in width for the disc-refined pulp was 42% against 17% shown
 358 earlier in Figure 1 (obtained under the following conditions; 8% caustic soda, 5% pulp
 359 consistency, with intermittent stirring for 30 minutes). The considerably higher swelling
 360 obtained in the second case (Figure 3 b) was obviously due to the different operating
 361 conditions during the swelling process. Firstly, it is known that in cellulose pulps, swelling in
 362 the interfibrillar and intrafibrillar areas reaches a maximum between NaOH concentrations of
 363 10 and 12% (Richter & Glidden, 1940). In addition, the lower pulp consistency (1% versus 5%)
 364 and better mixing enhanced the swell test performance.

365
 366 The cellulase-treated pulp did not swell as much as the mechanically refined pulp. The higher
 367 swelling of the mechanically refined pulp could be attributed to the external and internal
 368 fibrillation effect of the refining action, which causes a kind of peeling off of the fiber wall
 369 layer, creating new surfaces which ultimately improve accessibility.

370 According to (Navard & Cuissinat, 2006), the outer layers of the cellulose fiber wall (primary
 371 and S1 layers) are more resistant to dissolution than the inner layers. Their conclusion was
 372 based on observations (ballooning effect) made when cotton and wood fibers were dissolved
 373 before and after detachment of the outer layers by enzymatic treatment. As mechanical
 374 refining disrupts the surface of the fibers (external fibrillation), this could explain the
 375 increased swelling recorded for refined pulps. On the other hand, with reference to what is
 376 claimed in the literature (Köpeke et al., 2008; H. Li et al., 2018; J. Li et al., 2018; Miao et al.,
 377 2015), better swelling of the cellulase degraded pulp was expected. It could be that the
 378 cellulase dosage was not sufficient to see an effect. In fact, the DP was still above 1000, which
 379 is much higher than in most of these other studies.

380 The swelling behavior of the pulps, determined by the increase in fiber width, was consistent
 381 with the modification of pulp properties brought about by the pretreatment, in particular,
 382 the water retention value, the specific surface area, the crystallinity index (CI), and the
 383 average fiber length (Table 2).

384
 385 **Table 2. Difference in the morphology of bleached mixed hardwood pulps (unrefined, refined, and cellulase**
 386 **treated)**
 387

Pulp Samples	Unrefined	Valley beater	PFI	Disc pilot	Cellulase
Fiber length (µm)	685±13	430±22	544±0.7	544±6	681
SSA (m ² /g)	0.4	1.3	1.0	0.6	-
WRV (%)	103±1.8	268±9	237±1.8	233±2.8	105±1
CI (%)	75	64	68	72	76
Fine % (wt)	20±2.2	70±7.2	37±4	-	-
DPv	1293±32	1192±47	1221±0.5	1087±28	1021±1

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1.2. Effect of xylan extraction strategy on swelling of cellulose fibers in 0.16 M CUEN

Cupri-ethylenediamine (CUEN) solution (0.5M) is a known solvent for cellulose fibers. It is commonly used to determine the viscosity of cellulosic pulp, which indicates the chain length (degree of polymerization). It was found that dilution of the CUEN solution to 0.16 M swells the fibers without dissolution, which facilitates the examination of the swelling behavior of dissolving pulps. Actually, a positive correlation between the Fock reactivity and the degree of swelling of various dissolving pulps determined by measuring the variation in the width of the fibers treated in dilute CUEN solution was obtained (Arnoul-Jarriault et al., 2016). In the present study, unrefined and refined pulp extracted with 6 and 10% soda were treated in 0.16M CUEN to assess the influence of the hemicelluloses elimination treatments on the swelling degree of the cellulose fibers. According to the results shown in Table 3, it appeared that treatments involving mechanical refining had better swelling than without refining. The pulp extracted with 10% soda had less swelling compared to pulp extracted with 6% soda, which could be associated with the formation of cellulose II and the fibril aggregation that occurs with the removal of hemicelluloses.

Table 3. Reactivity of cellulose fibers assessed by determining the variation in fiber width in 0.16 M Cupri-ethylenediamine solution.

Pulp samples	Fiber length (μm)			Fiber width (μm)		
	Initial	Final	Variation (%)	Initial	Final	Variation (%)
^(a) UR-10CCE	623±2.8	636±1.4	2.1±0.7	16.2±0.1	16.8±0.1	4±0.2
^(b) PFI-10CCE	490±0.7	448±0.7	-9±0.3	23.4±0.1	27±0.4	15±2.1
^(c) VB /6CCE	499±1	485±1.4	-3±0.6	22.6±0.1	24.9±0.1	10±1.1
^(d) VB 120 min-6CCE	434±0.7	407±3	-6±0.5	22.5±0.1	27.9	24±0.4
^(e) VB 120 min-10CCE	378±4	368±0.7	-3±1.3	23.8±0.1	27.1±0.1	14±0.4
^(f) VB 180 min-6CCE	339±1.4	340±1.4	0.3±0.8	26	31.7±0.1	22±0.2
^(g) VB 180 min-10CCE	320±0.7	319±1.4	-0.3±0.2	27.5±0.4	32±0.7	16±1.3

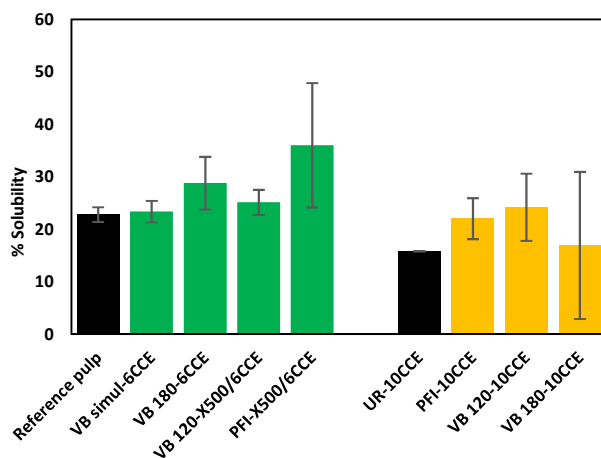
- 415 (a) Unrefined pulp extracted with 10% NaOH
 416 (b) PFI refined pulp (17,500 revolutions; SR° 85) extracted with 10% NaOH
 417 (c) Valley beater refined simultaneously with CCE (at 6% NaOH for 60 min)
 418 (d) Valley beater refined pulp (120 min; SR° 85) extracted with 6% NaOH
 419 (e) Valley beater refined pulp (120 min) extracted with 10% NaOH
 420 (f) Valley beater refined pulp (180 min) extracted with 6% NaOH
 421 (g) Valley beater refined pulp (180 min) extracted with 10% NaOH
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423 To investigate the effect of refining severity of extracted pulp on the swelling degree, the
 424 width variation of Valley beater refined for 120 min and 180 min were examined. Even though
 425 the fiber morphology of the pulp differed considerably prior to the extraction treatment,
 426 similar swelling (variation in width) was obtained for both pulps (VB 120 min and VB 180 min)
 427 extracted at 6% and 10% soda concentrations. This could be explained by the fibril
 428 aggregation occurring during the dewatering process, which was probably reinforced for the
 429 severely refined pulp (VB 180 min). This indicates that although refining improves swelling,
 430 the influence of cellulose II and fibril aggregation that occurs with dewatering cannot be
 431 neglected. Therefore, to limit this effect, lower soda concentrations could be used for the

432 hemicelluloses extraction to prevent the transformation of the crystal lattice of native
433 cellulose to cellulose II and the use of integrated dissolution processes (in the pulp mill) that
434 omit the drying step.
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436 2. Influence of conditions of xylan extraction on dissolution 437 performance of cellulose fibers 438

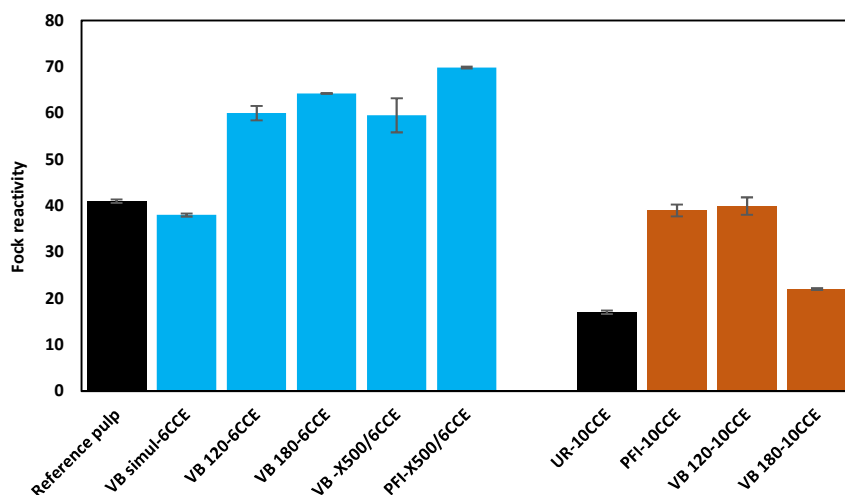
439 The dissolution performance of some purified pulps was assessed by the solubility of the
440 freeze-dried samples in 8.5% NaOH at -10°C and Fock reactivity (See methodology for details).
441 The solubility of the pulp in 8.5% soda was determined according to the method proposed by
442 (Isogai & Atalla, 1998), but the freezing temperature was kept at -10°C, which was a level
443 where the cellulose solubility was found close to optimum. From the result obtained,
444 illustrated in Figure 4, the solubility of the untreated and treated pulps was under 40%, which
445 was consistent with results reported in the literature for kraft pulps of a similar degree of
446 polymerization. The influence of mechanical refining and soda concentration on the solubility
447 of the cellulose fibers is seen. Increasing the soda concentration of the hemicelluloses
448 extraction from 60 g/L to 100 g/L decreases the solubility of the resulting pulp. This was not
449 particularly surprising because of the transformation of the native cellulose to cellulose II at
450 high alkali charge and a possibility of aggregative interactions between the cellulose fibrils
451 that occur when hemicelluloses are removed. The lowest solubility (16%) was obtained for
452 the unrefined pulp extracted with 10% soda, while the highest (36%) was obtained when
453 mechanical refining was coupled with sequential xylanase and 6% CCE treatments.
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457 **Figure 4. Performance of xylan extraction treatment on the solubility of the resulting cellulose fibers in 8.5% NaOH at -10°C.** {Reference pulp is the starting pulp without any treatment, VB 120 represent Valley beater (120 min), VB 180 represent Valley beater (180 min), 6CCE and 10CCE represents the soda concentration of the CCE treatment (60 and 100 g/L NaOH respectively, X500 represents the xylanase dosage (500 U/g pulp))
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462 When the Fock reactivity of the purified pulp was determined, a trend similar to that observed
463 for solubility in 8.5% NaOH was observed (Figure 5). Higher Fock reactivity was recorded for
464 the pulp extracted with 6% soda compared to those extracted with 10% soda. Values of Fock
465 reactivity in the range of 60-70 % were determined for refined pulp extracted at 6% soda
466 concentration, with and without an additional sequential xylanase treatment.



467 **Figure 5. Performance of xylan extraction treatment on the Fock reactivity of the resulting cellulose fibers.**
 468 {Reference pulp is the starting pulp without any treatment, VB 120 represent Valley beater (120 min), VB 180
 470 represent Valley beater (180 min), 6CCE and 10CCE represents the soda concentration of the CCE treatment
 471 (60 and 100 g/L NaOH respectively, X500 represents the xylanase dosage (500 U/g pulp))

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 475 A lower reactivity to xanthation was recorded for the pulp purified by performing
 476 simultaneous refining and CCE at 6% alkali load. This might be explained by the less
 477 destructive effect of the simultaneous refining/CCE (shorter treatment time) reported
 478 previously (Ngene et al., 2022) and also by the presence of some cellulose II peaks detected
 479 by X-ray analysis, as illustrated in Appendix (Figure A1). For the pulps extracted with 10%
 480 soda, higher Fock reactivity was obtained for refined pulp compared to the unrefined pulp.
 481 In fact, the Fock reactivity was substantially increased except for the (VB 180-10 CCE), where
 482 extreme mechanical refining was applied before the CCE treatment. Since the Fock test was
 483 performed on dried cellulose fibers, the poor reactivity to xanthation might be explained by
 484 two occurrences: Firstly, the effect of external fibrillation of both fines and fibers brought
 485 about by mechanical refining, which intensifies aggregation on drying (hornification); and
 486 secondly, the impact of cellulose II which facilitates fibril densification and aggregation on
 487 dewatering. Apparently, refining aids the transformation of more regions of the crystal lattice
 488 of native cellulose to cellulose II during subsequent CCE, as shown by the diffractograms in
 489 the Appendix (Figure A2) and the results obtained by solid-state NMR spectroscopy (¹³C-
 490 CP/MAS-NMR) shown in the Appendix (Figure A3 and Table A3).

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 496 **2.1. Correlation of swelling behavior of cellulose fibers in CUEN, with solubility in 8.5% NaOH at -10°C and Fock reactivity.**

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 499 The standard method for determining the reactivity of cellulose fibers in the laboratory is the
 500 Fock test. It is a long, tedious process that involves the use of several toxic chemicals.
 501 Consequently, some alternatives have been proposed in the literature (Arnoul-Jarriault et al.,

2016; Ceccherini, 2019). These methods investigated the swelling behavior and rheological properties of cellulose fibers in CUEN. One of these methods was developed in our laboratory, and a correlation was obtained with the Fock test. The influence of mechanical refining pretreatment and alkali loading used for the CCE stage on the dissolution performance of bleached mixed hardwood kraft paper pulp was assessed by three methods; (i) swelling behavior in 0.16 M CUEN determined by the MorFi apparatus (Arnoul-Jarriault et al., 2016) (ii) solubility in 8.5% soda at -10°C (Isogai & Atalla, 1998) and (iii) Fock reactivity (a modified protocol by Tian et al. (2013)). Correlation between swelling in CUEN and dissolution performance was determined.

Table A2 presented in the Appendix shows the values obtained in (%) for the variation in width, solubility in 8.5% NaOH, the Fock reactivity, the crystallinity index (CI), the xylan content, and the degree of polymerization of some purified pulp. We did not find a logical connection between the influence of the crystallinity index and the degree of polymerization on the overall performance of the cellulose fiber during dissolution. The pulp with the highest CI and DPv (VB 180-10CCE) had a low Fock reactivity (22%), but an even lower value (17%) was obtained for the extracted unrefined pulp with similar DPv and CI. In (Figure 6 a, b, and c), the correlation between the Fock reactivity and the other methods (solubility in 8.5% NaOH at -10 °C and variation in width) was illustrated. This result shows that both methods can be used in the laboratory to assess the reactivity of cellulosic fibers to dissolution in the viscose process. Solubility measurement in 8.5% NaOH at -10 °C is simple, and no special equipment is required other than a cooling bath. One disadvantage of using this method is the difficulty of filtering the heterogeneous gel-like substance obtained after freezing and thawing. Swelling measurement in CUEN solution is also simple. However, it requires the use of the Morfi fiber analyzer.

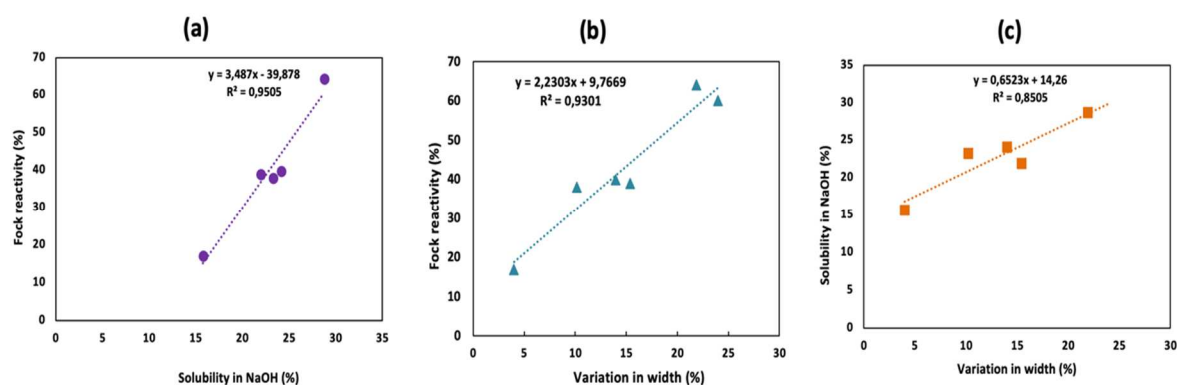


Figure 6. Correlation between different methods of assessing cellulose fiber reactivity in aqueous solvent systems

3. Influence of crystallinity index and xylan content on the reactivity of extracted cellulose fibers

According to the literature, cellulose dissolution may be affected by its degree of polymerization (DP) and crystallinity index (CI) (Duan et al., 2016b; Ferreira et al., 2020; M.

540 loelovich, 2009; Isogai & Atalla, 1998; Liu et al., 2019; Miao et al., 2015). These characteristics
541 varied slightly depending on the purification treatment employed in our study. In this section,
542 we investigated the existence of a possible correlation with the Fock reactivity. The influence
543 of the crystallinity index (CI) on the dissolution index (Fock) is seen in Figure 7. Here, for
544 better comparison, the refined samples presented were all refined by the Valley beater, and
545 the only other condition was the NaOH concentration used for the CCE. Based on the result,
546 a correlation between the Fock reactivity and the CI is seen particularly when the CCE
547 treatment was carried out at 6% NaOH. At this soda concentration, there was no influence
548 of cellulose II on the outcome of the result. So, it can be seen that the soda treatment alone
549 results in a slight decrease in the CI (UR 6CCE), which is further decreased when mechanical
550 refining was applied prior to the CCE (VB 120-6CCE). Increasing the severity of the refining
551 also led to more decrease in the CI (VB 180-6CCE). This loss in CI from 75% in (UR 6CCE) to
552 63% in (VB 180-6CCE) resulted in a corresponding gain in the Fock reactivity from 41% (UR
553 6CCE) to 64% in (VB 180-6CCE).

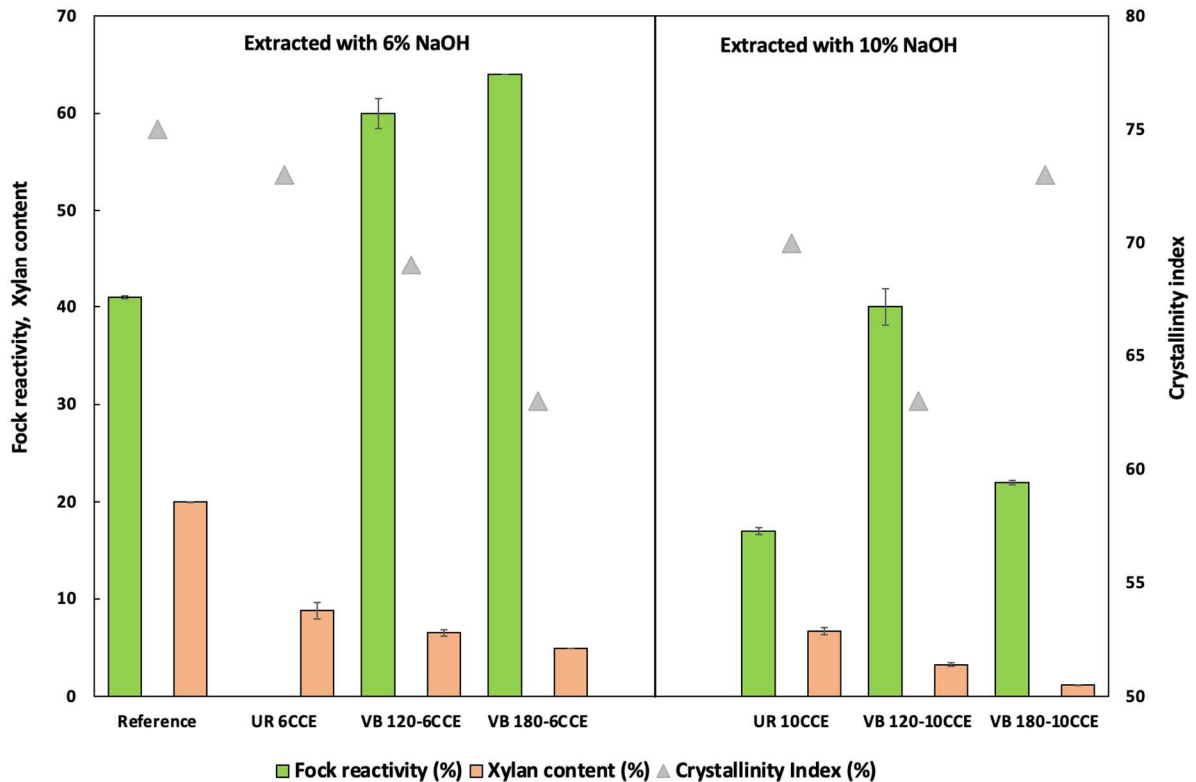
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555 On the other hand, the relationship between the crystallinity index and Fock reactivity was
556 not apparent when the extraction was carried out with 10% NaOH because of the influence
557 of cellulose II, and other modifications at the supramolecular level, particularly fibril
558 aggregation and co-crystallization. As shown in Figure 7, performing the CCE at 10%, NaOH
559 decreased both the Fock reactivity and crystallinity index, but the effects associated with the
560 presence of cellulose II outweighed the benefit of the loss in crystallinity index. In the case of
561 refined pulp extracted with 10% NaOH (VB 120-10CCE), the crystallinity index experienced a
562 further decrease without a corresponding increase in the Fock reactivity when compared to
563 the reference pulp. Upon further increase of the severity of the refining treatment prior to
564 the CCE at 10% NaOH (VB180-10CCE), a substantial gain from 63% to 73% in the crystallinity
565 index brought about by aggressive fibril aggregation was observed. Even though strong soda
566 treatment and extreme refining, when applied individually, decrease crystallinity index.
567 Coupling both treatments seemed to increase the crystallinity index, which could be
568 detrimental to cellulose dissolution, particularly if drying is applied.

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 573 **Figure 7. Effect of the crystallinity index (CI) on the Fock reactivity {Reference pulp is the starting pulp without**
 574 **any treatment, UR represents unrefined pulp, VB 120 represent Valley beater (120 min), VB 180 represent**
 575 **Valley beater (180 min), 6CCE and 10CCE represents the soda concentration of the CCE treatment (60 and 100**
 576 **g/L NaOH respectively)}**

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 580 **Conclusions**

581
 582 Fiber swelling is a prerequisite for dissolution. Thus, the swelling capacity in 12% NaOH and
 583 dilute cupric ethylenediamine (CUEN) solution was determined. From the result, high purity
 584 pulp produced from a coupling of mechanical refining prior to CCE had better swelling than
 585 unrefined subjected to similar chemical treatments. Also, Solubility studies performed on the
 586 extracted pulp showed that treatments in which mechanical refining was applied had better
 587 solubility in 8% NaOH at -10°C and high Fock reactivity than unrefined pulp. Refined pulp
 588 extracted with 6% soda had the best result with Fock reactivity ranging from 60-70%, which
 589 exceeds those obtained for prehydrolysis kraft dissolving pulp (PHK). Higher caustic soda
 590 charge (10%) did not lead to better Fock reactivity because of the transformation of cellulose
 591 I to cellulose II, which was also facilitated by the refining. The presence of cellulose II is a
 592 problem because of the creation of a denser fibril network in cellulose fibers upon dewatering
 593 and drying. A good correlation was found between swelling measurements, solubility in
 594 NaOH, and Fock reactivity. This would make it possible to consider replacing the realization
 595 of tedious Fock measurements, made problematic due to the use of CS₂.
 596 Finally, the results showed that the crystallinity index was influenced by mechanical refining
 597 and the strength of the NaOH used in the hemicelluloses extraction process. This was
 598 particularly interesting because we found a correlation between the Fock reactivity and the
 599 crystallinity index when extraction was performed with a low soda concentration (6%).
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Graphical abstract

