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# Alkaline Pretreatment Facilitate Mechanical Fibrillation of Unbleached Cellulose Pulps for Obtaining of Cellulose micro/nanofibrils (MFC)

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## ABSTRACT

Energy expenditure is a limiting factor for the production of cellulose micro/nanofibrils in mechanical processing. This study evaluated the effect of novel alkaline pretreatments on unbleached *Eucalyptus* sp. pulps (hardwood) and *Pinus* sp. cellulose (softwood) to facilitate the production of cellulose nanofibrils by mechanical fibrillation and reduce the energy consumed by the mill. Pretreatments with NaOH in concentrations of 5% for 2 h and 10% for 1 h and 2 h and a hybrid pretreatment with 5%/16% NaOH/ H<sub>2</sub>O<sub>2</sub> for 2 h were evaluated. The 10% pre-treatment was done at 1 h and 2 h to evaluate the effect of the less aggressive treatment (1 h). The morphology, chemical composition, turbidity of the fibers/suspensions, mechanical properties, fibrillation quality index and energy expended during the fibrillation were evaluated for each pretreatment. The less aggressive pretreatments produced micro/nanofibrils with fewer passes of the pulp through the fibrillator, which effectively facilitated extraction with lower energy consumption. The hybrid pretreatment did not show satisfactory results in reducing energy consumption, and the quality of the nanofibrils produced by this pretreatment was inferior to the others. This study showed innovation in performing novel and efficient NaOH and hybrid (NaOH/H<sub>2</sub>O<sub>2</sub>) pretreatments on commercial unbleached pulps to obtain pulp micro/nanofibrils.

## 摘要

能量消耗是机械加工中生产纤维素微/纳米纤维的限制因素。本研究评估了新型碱性预处理对未漂白桉树纸浆(硬木)和松树纤维素(软木)的影响,以促进通过机械纤维化生产纤维素纳米纤维,并减少磨机能耗。评估了浓度为5%的NaOH预处理2 h,浓度为10%的NaOH预处理1 h和2 h,以及浓度为5%/16%的NaOH/H<sub>2</sub>O<sub>2</sub>混合预处理2 h。在1小时和2小时进行10%预处理,以评估攻击性较小的治疗(1小时)的效果。对每种预处理的纤维/悬浮液的形态,化学成分,浊度,力学性能,成纤质量指数和成纤过程中消耗的能量进行了评估。不太激进的预处理产生了微/纳米原纤维,纸浆通过原纤维发生器的次数更少,从而有效地促进了提取,能耗更低。混合预处理在降低能耗方面没有显示出令人满意的结果,并且这种预处理所制备的纳米纤维的质量不如其他预处理。本研究表明,在对商业未漂白纸浆进行新型高效NaOH和混合(NaOH/H<sub>2</sub>O<sub>2</sub>)预处理以获得纸浆微/纳米纤维方面存在创新。

## KEYWORDS

Cellulose nanofibers; cell wall; energy consumption; microfibrillated cellulose (MFC); nanotechnology; turbidity

## 关键词

纤维素纳米纤维; 细胞壁; 能源消耗; 微纤化纤维素(MFC); 纳米技术; 浊度

## Introduction

Many studies have been conducted to produce new materials that have a lower environmental impact and can replace materials produced from nonrenewable sources (Wegner and Jones, 2006). Cellulose stands out in this context due to its biodegradability, abundance, negligible toxicity and renewability. Cellulose is considered one of the most abundant polymers and can be found in various sources, such as wood, cotton, hemp, and algae, and synthesized by tunicates and some bacteria (EichHorn et al. 2018; Gharekhani et al. 2015; Klemm 2006).

Cellulose fibers are nanofibril aggregates with diameters smaller than 100 nm in a matrix composed mainly of hemicelluloses and lignin. Since their first mention at the end of the 1970s, cellulose nanofibrils have been studied for applications in various industrial fields (Naderi, Lindström, and Sundström 2014). Cellulose nanofibrils have applications in paper and packaging (Matos et al. 2019), automotive applications (Kalia et al. 2014), biomedicine (Ling et al. 2018), composites (Mesquista et al. 2018), and fiber-cement composites (Fonseca et al. 2019; Tonoli et al. 2019).

Many methods are used to extract cellulose micro/nanofibrils, including mechanical (Wang et al. 2007), enzymatic (Siró and Plackett 2010), chemical (Tonoli et al. 2016) and combined chemo-mechanical (Dias et al. 2019; Martins et al. 2021) techniques. The chemo-mechanical treatment used in this work consists in combining a chemical pre-treatment with mechanical refining (Yusra et al. 2018). However, the energy spent on the fibrillation process is a limiting factor for producing nanofibrils on an industrial scale. Pretreatments are used to facilitate fibrillation and to reduce the energy expended by the process. The fibrillation requires a large amount of effort to break the hydrogen bonds between the micro/nanofibrils. When a pretreatment is applied, these bonds are partially broken before the pulp is passed through the fibrillator, making the process more efficient (Kalia et al. 2014).

Few studies are reported in the literature on fibrillation of unbleached commercial pulps. However, certain levels of hemicellulose and lignin can assist in the fibrillation process and reduce the cost of producing micro/nanofibrils due to the absence of the bleaching step, making it convenient the fibrillation of unbleached pulps (Costa et al. 2016; Ferrer et al. 2012).

The objective of this study was to investigate the influence of using alkaline pretreatments (5% NaOH for 2 h, 10% NaOH for 1 h, 10% NaOH for 2 h and 5%/16% NaOH/H<sub>2</sub>O<sub>2</sub> reacting for 2 h) to facilitate the fibrillation of high yield pulp (HYP), short fiber (SF, hardwood) and long fiber (LF, softwood) pulps to produce cellulose micro/nanofibrils and, consequently, their effect on reducing the energy consumption for mechanical fibrillation process and their nanofibril quality.

## Material and methods

### Materials

The unbleached hardwood short fiber pulp from *Eucalyptus* sp. (SF) and softwood long fiber pulp from *Pinus* sp. (LF) and high yield pulp from *Eucalyptus* sp. (HYP) (with one drying cycle) used in the present study were donated by Klabin S.A. (Paraná, Brazil). NaOH and H<sub>2</sub>O<sub>2</sub> were used in the pretreatments.

### Alkaline pretreatments

Before the pretreatments, the pulp fibers were oven-dried at 50°C for 24 h. The pulp fibers were pretreated with a 5% aqueous NaOH solution (by weight) for 2 h and then with a 10% aqueous NaOH solution (by weight) for 1 h and 2 h at 80°C, and the solutions were continuously stirred throughout the pretreatments (~800 rpm). After the pretreatments, the fibers were filtered and washed repeatedly with deionized water until a neutral pH was attained. The pretreated pulps were oven-dried at 50°C for 24 h or until a constant weight was achieved. The control treatments (C1h and C2h) were subjected to

the same procedures in water at 80°C without chemical reagent for 1 h (C1h) and for 2 h (C2h). All chemical treatments and the control treatments (C1h and C2h) were done at 80°C and drying after the treatments was at a temperature of 50°C.

### **Hybrid pretreatment with NaOH/H<sub>2</sub>O<sub>2</sub>**

Before the pretreatments, the pulp fibers were oven-dried at 50°C for 24 h. The pulp fibers were then pretreated with 5%/16% (by weight) aqueous NaOH/H<sub>2</sub>O<sub>2</sub> solution at 80°C for 2 h with continuous stirring (~400 rpm). Only the 2 h time was used because the concentration of H<sub>2</sub>O<sub>2</sub> was low and 1 h of reaction would not be sufficient for the treatment. After the pretreatments, the fibers were filtered and washed repeatedly with deionized water until a neutral pH was attained. The pretreated pulps were oven-dried at 50°C for 24 h or until constant weight was achieved.

### **Yield calculation of cellulose pulp material after the pretreatments**

The yield of cellulose pulp material after the pretreatments was calculated using Equation (1). This calculation was made based on the pre-treatment mass and is valid for LF, SF and HYP pulps.

$$Y = \frac{fm}{im} \quad (1)$$

*fm* (grams) represents the final mass (after pretreatments) and *im* (grams) the initial mass.

### **Fiber characterization**

The chemical composition of the pulps was estimated before and after the pretreatments. The soluble lignin and monosaccharide contents were evaluated. The amount of soluble lignin was evaluated by following the Tappi UM 250 standard (1976). The monosaccharide content was determined according to the method established by Wallis, Wearne, and Wright (1996). A Dionex ICS 5000 ion chromatography system was used.

The mean length, length-weighted mean length, weight-weighted mean length, width and curl were measured using a fiber image analyzer (Valmet FS5, Finland).

### **Production of micro/nanofibrils by mechanical fibrillation**

The pretreated and untreated cellulose pulps were suspended for 6 days in deionized water at a ratio of 2.0% by weight for SF and HYP and 1.5% by weight for LF to cause the pulp fibers to swell. The concentrations were different due to the different fiber sizes; LF contains longer fibers, which can block fibrillation; therefore, LF fibers need to be well dispersed in water. Then, the fibers were mechanically fibrillated using a SuperMassColloider grinder (Masuko Sangyo MKCA6-2), which was equipped with two grinding stones (MKCA6-80) operated at 1,500 rpm, and the fibers were fibrillated with 30 passes through the equipment starting with the distance of the stones at point 0 and opening up to 150 μm with an increase in the number of passes (Guimarães et al. 2015; Scatolino et al. 2017). Although the concentration of the LF suspensions was lower (1.5% w/w), the opening of the stones was greater from the onset of fibrillation compared to the SF and HYP suspensions. Aliquots were collected after every 5 passes through the equipment and used for the light microscopy and transmission electron microscopy (TEM) analyses. For the TEM analyses, samples were collected after 15 and 30 passes for measurements of micro/nanofibril diameters. Suspension concentrations were corrected according to the need for each type of analysis.

### **Light microscopy**

A Nikon Eclipse E200 optical light microscope was used to initially analyze the fibrillation degree of the pretreated and untreated fibers after different numbers of passes through the equipment (0, 5, 10, 15, 20, 25 and 30 passes). The samples were prepared by diluting the fibers in deionized water (0.75% w/w) and staining them with safranin-ethanol (1.00% v/v) to provide contrast.

### **Transmission electronic microscopy-TEM**

The morphology of the cellulose nanofibrils was investigated with a Tecnai G2-12 microscope using an accelerating voltage of 80 Kv. The sample preparation method and equipment settings followed the suggested in Tonoli et al. (2016) and Dias et al. (2019). The nanofibril suspensions obtained after 15 and 30 passes through the grinder were prepared by adding uranyl acetate to improve the contrast of the samples. Suspension droplets containing the dye were deposited on Formvar-coated (thermo-plastic resin) copper grids (400 mesh) and dried before visualization by TEM. To measure the diameters of the nanofibrils, ImageJ software was used, and 200 individual structures were measured per pretreatment.

### **Turbidity**

The pretreated and untreated nanofibril pulps were diluted to concentrations of 0.25% by weight, placed in test tubes and kept at rest for 1.5 h prior to decanting the material (adapted from Winter et al. 2010). The supernatant obtained after resting (1.5 h) was analyzed using an Alfakit Plus turbidimeter.

### **Mechanical properties of micro/nanofibrils films**

Micro/nanofibrils films obtained with 30 passes were produced according to Guimarães Júnior et al. (2015). The micro/nanofibril suspensions were diluted to the proportion of 1% w/w and poured 40 mL of suspension into 15 cm diameter acrylic petri dishes. Suspensions were dried in a circulation oven at 45°C for 48 h to form the films.

The mechanical properties of tensile strength, maximum elongation at break and Young's modulus, were determined with a texture analyzer (Stable Microsystems, model TATX2i, England). The films with 100 mm x 15 mm nominal dimensions were pulled at a speed of about 1 mm/s, starting with an initial separation of 50 mm between claws. The tensile properties of the samples were determined based on the ASTM D 882-02 standard (ASTM, 2002). Young's modulus was estimated from the tangent of the initial linear function of the stress-strain curve, considered as an elastic region. To measure the thickness of the films, a digital micrometer of rapid advance (0–30 mm) with a resolution of 0.001 mm was used, where 10 random measurements were made for each specimen.

### **Energy consumed during fibrillation**

The energy consumed during fibrillation was determined by considering the mean current measured by the grinder ammeter at each pass during fibrillation, the equipment voltage and the fibrillation time per ton of fibrillated material at a 2.0% concentration for the HYP and SF pulp and a 1.5% concentration for the LF. The energy consumed during fibrillation was calculated using Equation (2).

$$EC = \frac{(Px t)}{m} \quad (2)$$

EC represent the energy consumption (kW.h/t); *P* is the power (in kW, voltage x electric current), *t* is the time (in hours) spent during fibrillation; *m* is the mass of the material (in tons).

**Fibrillation quality index**

The simplified fibrillation index (Q.I.) was adapted by Desmaisons et al. (2017) according to Equation (3).

$$Q. I. = 0.30x_1 + (-0.03x_2) - 0.07x_3^2 + 2.54 x_3 - 5.35ln(x_4) + 59.9 \tag{3}$$

Where *x*<sub>1</sub> represents the fraction on the nanoscale (%), determined by quantifying the content of nanofibrils with a diameter less than 60 nm, measurements of up to 200 elements were performed on MET images); *x*<sub>2</sub> represents the turbidity of the diluted suspensions (in NTU); *x*<sub>3</sub> is Young’s modulus (in GPa); and *x*<sub>4</sub> the fraction of non-deconstructed fibers determined by an index of 1 (more deconstructed) to 10 (less deconstructed) in the light microscopy images).

**Results and discussion**

**Chemical characterization of the pulps**

The pulp yield for the HYP, SF and LF pretreated samples is shown in Table S1. A mass loss occurred due to the removal of lignin and hemicelluloses, which was confirmed by the chemical characterization. Hemicelluloses are removed by thermal pretreatments (Brito et al. 2008). The pulps that underwent the hybrid pretreatment exhibited the largest decreases in insoluble and soluble lignin content, as hydrogen peroxide is capable of bleaching cellulose pulps (Owolabi et al. 2017). Even for control treatments C1h and C2h, there was a decrease of mass after heating in water and filtration. An important aspect that should be considered is the possibility of material loss in the washing step of the pulp after the pretreatments.

Table 1 shows the chemical composition of the HYP, SF and LF samples before and after the chemical pretreatments. All the chemical pretreatments performed caused a relative increase in the glucose content, which is probably a consequence of the decrease in the relative hemicelluloses content, especially the xylose content. The higher the NaOH pretreatment concentration and time, the higher the cellulose content and the lower the xylose content in the fibers.

**Table 1.** Values of mean and standard deviation of the chemical composition of the pulps HYP, SF and LF. ND = not detected.

Pulp	Glucose (%)	Arabinose (%)	Galactose (%)	Xylose (%)	Manose (%)	Insoluble lignin (%)	Soluble Lignin (%)
HYP ST	51.0 ± 0.1	0.20 ± 0.10	0.68 ± 0.00	11.0 ± 0.1	0.47 ± 0.00	23.0 ± 0.0	3.0 ± 0.0
HYP 5% 2 h	58.0 ± 0.2	0.17 ± 0.00	0.67 ± 0.00	7.0 ± 0.2	0.45 ± 0.00	23.0 ± 0.0	3.0 ± 0.0
HYP 10%1 h	59.0 ± 1.1	0.14 ± 0.00	0.63 ± 0.00	6.0 ± 0.1	0.51 ± 0.00	23.0 ± 0.0	3.0 ± 0.0
HYP 10%2 h	58.0 ± 0.2	0.17 ± 0.00	0.67 ± 0.00	7.0 ± 0.2	0.45 ± 0.00	23.0 ± 0.0	3.0 ± 0.0
HYP H <sub>2</sub> O <sub>2</sub> /NaOH	56.0 ± 0.4	0.13 ± 0.00	0.43 ± 0.00	6.0 ± 0.0	0.81 ± 0.00	20.0 ± 0.1	4.0 ± 0.0
HYP C1 h	45.7 ± 1.0	0.30 ± 0.00	0.90 ± 0.10	10.4 ± 0.3	0.59 ± 0.00	23.6 ± 0.0	3.1 ± 0.0
HYP C2 h	48.8 ± 0.5	0.30 ± 0.00	0.89 ± 0.10	10.5 ± 0.1	0.83 ± 0.00	24.1 ± 0.0	3.2 ± 0.0
SF ST	64.0 ± 0.4	0.08 ± 0.00	0.24 ± 0.00	12.0 ± 0.0	0.24 ± 0.00	16.0 ± 0.0	2.0 ± 0.0
SF 5% 2 h	69.0 ± 4.1	0.06 ± 0.00	0.15 ± 0.00	7.0 ± 0.5	ND	15.0 ± 0.0	3.0 ± 0.0
SF10% 1 h	72.0 ± 0.4	0.06 ± 0.00	0.13 ± 0.00	5.0 ± 0.0	0.26 ± 0.00	15.0 ± 0.0	3.0 ± 0.0
SF 10% 2 h	74.0 ± 0.6	0.06 ± 0.00	0.08 ± 0.00	5.0 ± 0.1	0.27 ± 0.00	15.0 ± 0.0	3.0 ± 0.0
SF H <sub>2</sub> O <sub>2</sub> /NaOH	64.0 ± 1.9	N.D.	0.20 ± 0.00	7.0 ± 0.3	0.61 ± 0.00	12.0 ± 0.1	2.0 ± 0.0
SF C1 h	56.8 ± 0.8	0.16 ± 0.00	0.53 ± 0.00	10.6 ± 0.1	0.55 ± 0.10	16.1 ± 0.0	3.2 ± 0.0
SF C2 h	58.0 ± 0.6	0.16 ± 0.00	0.54 ± 0.00	10.8 ± 0.1	0.55 ± 0.00	16.4 ± 0.0	3.4 ± 0.0
LF ST	68.0 ± 0.3	0.85 ± 0.00	0.35 ± 0.00	8.0 ± 0.3	5.05 ± 0.00	10.6 ± 0.0	0.4 ± 0.0
LF 5% 2 h	78.0 ± 0.0	0.58 ± 0.00	0.25 ± 0.00	5.0 ± 0.0	5.11 ± 0.03	11.0 ± 0.0	0.3 ± 0.0
LF 10% 1 h	80.0 ± 0.1	0.54 ± 0.00	0.21 ± 0.00	4.0 ± 0.1	4.97 ± 0.4	10.0 ± 0.1	0.2 ± 0.0
LF 10% 2 h	80.0 ± 0.3	0.24 ± 0.00	0.25 ± 0.00	4.0 ± 0.0	4.91 ± 0.00	11.0 ± 0.0	0.2 ± 0.0
LF H <sub>2</sub> O <sub>2</sub> /NaOH	78.0 ± 0.2	0.58 ± 0.00	0.25 ± 0.00	9.0 ± 0.0	5.00 ± 0.1	12.0 ± 0.1	0.8 ± 0.1
LF C1 h	65.6 ± 0.9	0.85 ± 0.00	0.69 ± 0.00	7.2 ± 0.2	5.42 ± 0.50	10.5 ± 0.0	0.4 ± 0.0
LF C2 h	66.6 ± 0.9	0.80 ± 0.00	0.62 ± 0.00	7.8 ± 0.1	5.10 ± 0.00	9.4 ± 0.0	0.4 ± 0.0

**Table 2.** Mean and standard deviation values of the morphological properties of the fibers obtained by the fiber analysis equipment, for the pulp HYP, SF and LF with and without pretreatments before fibrillation.

Pulp	Weighted average length (mm)	Mass weighted average length (mm)	Width ( $\mu\text{m}$ )	Curl (%)
HYP ST	0.8 $\pm$ 0.0	1.0 $\pm$ 0.0	20.7 $\pm$ 0.1	4.3 $\pm$ 0.0
HYP 5% 2 h	0.7 $\pm$ 0.1	0.9 $\pm$ 0.1	19.4 $\pm$ 0.0	8.5 $\pm$ 0.1
HYP 10% 1 h	0.6 $\pm$ 0.0	0.8 $\pm$ 0.0	20.3 $\pm$ 0.0	20.2 $\pm$ 0.0
HYP 10% 2 h	0.6 $\pm$ 0.0	0.8 $\pm$ 0.1	20.1 $\pm$ 0.1	20.2 $\pm$ 0.3
HYP NaOH/H <sub>2</sub> O <sub>2</sub>	0.6 $\pm$ 0.1	0.9 $\pm$ 0.1	19.0 $\pm$ 0.0	8.3 $\pm$ 0.1
HYP C1 h	0.6 $\pm$ 0.0	0.9 $\pm$ 0.0	19.0 $\pm$ 0.0	6.6 $\pm$ 0.2
HYP C2 h	0.6 $\pm$ 0.0	0.9 $\pm$ 0.0	19.0 $\pm$ 0.0	5.8 $\pm$ 0.1
SF ST	0.9 $\pm$ 0.1	1.1 $\pm$ 0.0	20.6 $\pm$ 0.0	6.8 $\pm$ 0.1
SF 5% 2 h	0.8 $\pm$ 0.1	1.0 $\pm$ 0.1	19.5 $\pm$ 0.0	19.9 $\pm$ 0.3
SF 10% 1 h	0.8 $\pm$ 0.0	0.9 $\pm$ 0.0	19.7 $\pm$ 0.0	30.4 $\pm$ 0.0
SF 10% 2 h	0.8 $\pm$ 0.0	0.9 $\pm$ 0.0	19.4 $\pm$ 0.1	33.1 $\pm$ 0.2
SF NaOH/H <sub>2</sub> O <sub>2</sub>	0.8 $\pm$ 0.0	1.0 $\pm$ 0.0	18.8 $\pm$ 0.0	17.0 $\pm$ 0.1
SF C1 h	0.8 $\pm$ 0.0	1.0 $\pm$ 0.0	19.5 $\pm$ 0.0	8.0 $\pm$ 0.4
SF C2 h	0.8 $\pm$ 0.0	1.0 $\pm$ 0.0	20.0 $\pm$ 0.0	9.3 $\pm$ 0.9
LF S/T	2.1 $\pm$ 0.0	2.8 $\pm$ 0.1	29.1 $\pm$ 0.1	8.0 $\pm$ 0.0
LF 5% 2 h	2.0 $\pm$ 0.0	2.7 $\pm$ 0.0	27.2 $\pm$ 0.1	15.7 $\pm$ 0.3
LF 10% 1 h	1.9 $\pm$ 0.0	2.6 $\pm$ 0.0	27.8 $\pm$ 0.0	25.8 $\pm$ 1.4
LF 10% 2 h	1.8 $\pm$ 0.0	2.6 $\pm$ 0.0	27.0 $\pm$ 0.0	37.7 $\pm$ 2.1
LF NaOH/H <sub>2</sub> O <sub>2</sub>	1.8 $\pm$ 0.1	2.6 $\pm$ 0.1	25.2 $\pm$ 0.1	23.4 $\pm$ 0.1
LF C1 h	ND	ND	ND	ND
LF C2 h	ND	ND	ND	ND

The xylose content of all the pulps decreased as the pretreatment became more aggressive. Intermediate hemicelluloses content may facilitate the mechanical fibrillation process and may lead obtaining SF micro/nanofibrils easier than obtaining from LF fibers (Syverud et al. 2011).

### Fiber/nanofibril morphology

The nanofibril suspensions were analyzed under a light microscope. The light microscopy images were obtained to determine the fibrillation efficiency and to monitor the micro/nanofibrils obtained during the passes through the fibrillator. Figures S1-3 show the pulp obtained without pretreatment and after the pretreatments. In the 15th pass, the 5% NaOH for 2 h and 10% NaOH for 1 h pretreatments reduced the amount of whole fibers and increased the amount of fiber fragments due to the passes through the fibrillator.

For the untreated SF, many intact fibers were observed, even with 30 passes (Figures S3(a,b)). Therefore, the fibrillated control SF was not as successful as the pulp that underwent the pretreatments, demonstrating the efficiency of the pretreatments.

Table 2 shows the mean and standard deviation values of the cellulose fiber morphological properties before and after the chemical pretreatments. The fiber-weighted mean length, weight-weighted mean length and width slightly decreased after the pretreatments were applied. Additionally, the fibers curled considerably after the different pretreatments, and the higher concentration and reaction time (2 h) caused greater curl, especially for the SF and LF.

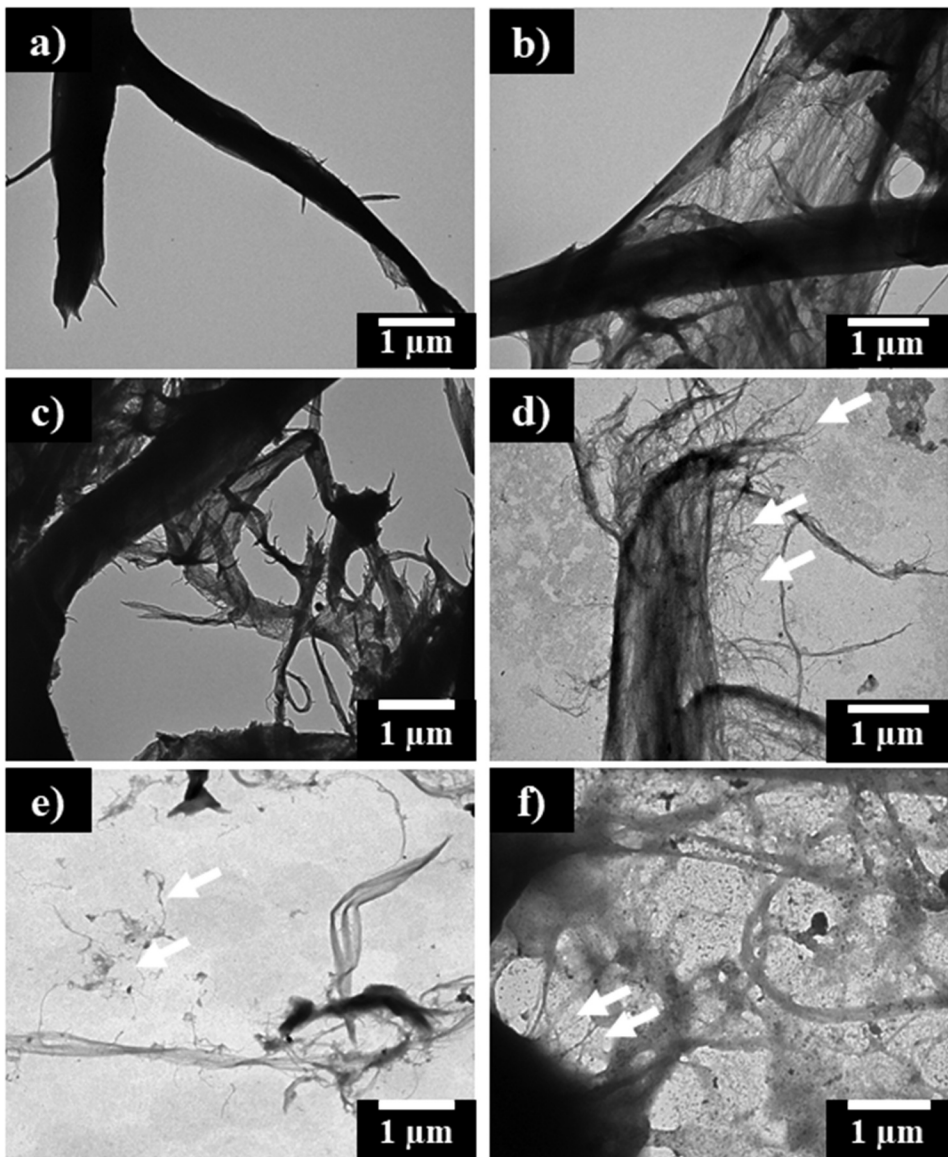
The decrease of the fiber lengths for all the pulps depended on the NaOH concentration. The more concentrated the NaOH solution, the greater the reduction of the length. The decreased length may be related to the increased fiber curl, which hindered and influenced the measurements (Blomstedt et al. 2007). The use of NaOH is responsible for the fiber swelling, which causes the fibers to deform (Dias et al. 2019; Durães et al. 2020). The HYP pretreated with 10% NaOH for 1 h and 2 h contained fibers with significant different curl values. This type of pulp contains many metal residues resulting from the pulping process, and chelating agents or higher H<sub>2</sub>O<sub>2</sub> concentrations must be used to prevent these metals from binding to oxygen radicals (Li et al. 2015). The reaction time only influenced the final properties of the LF, and the curl was greater when the reaction proceeded for 2 h.

The increased curl of the fibers is also related to the removal of hemicelluloses. When the pulp is subjected to more concentrated alkaline pretreatments for longer reaction times, the removal of hemicelluloses is more aggressive and increases the fiber curl (Dias et al. 2019; Li et al. 2016).

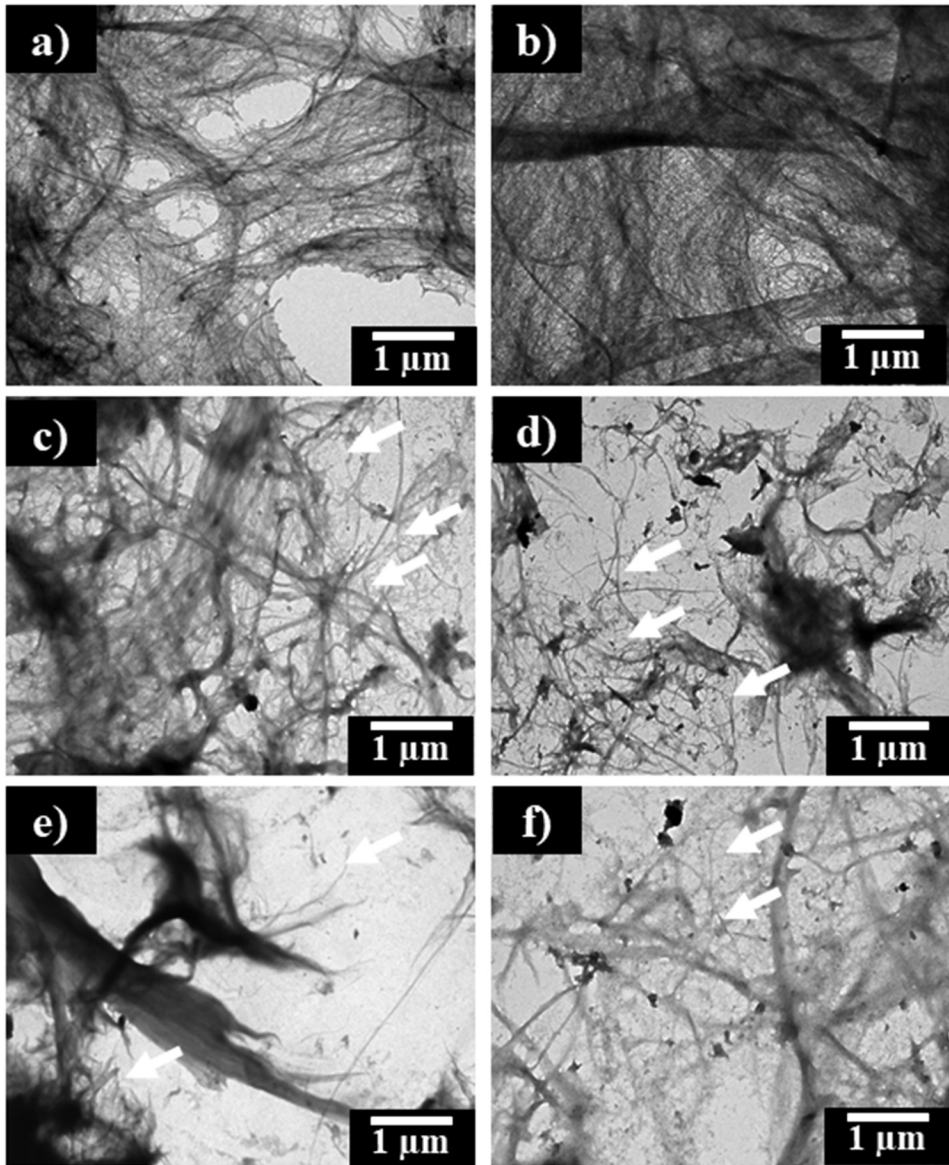
The removing of lignin was significant only for the hybrid treatment due to the presence of H<sub>2</sub>O<sub>2</sub>. Peroxide (H<sub>2</sub>O<sub>2</sub>) in alkaline media is used to bleach lignin-rich pulps (Su et al. 2015).

### TEM

Figures 1–3 show the morphology of the nanofibrils obtained from the untreated and treated HYP, SF and LF.

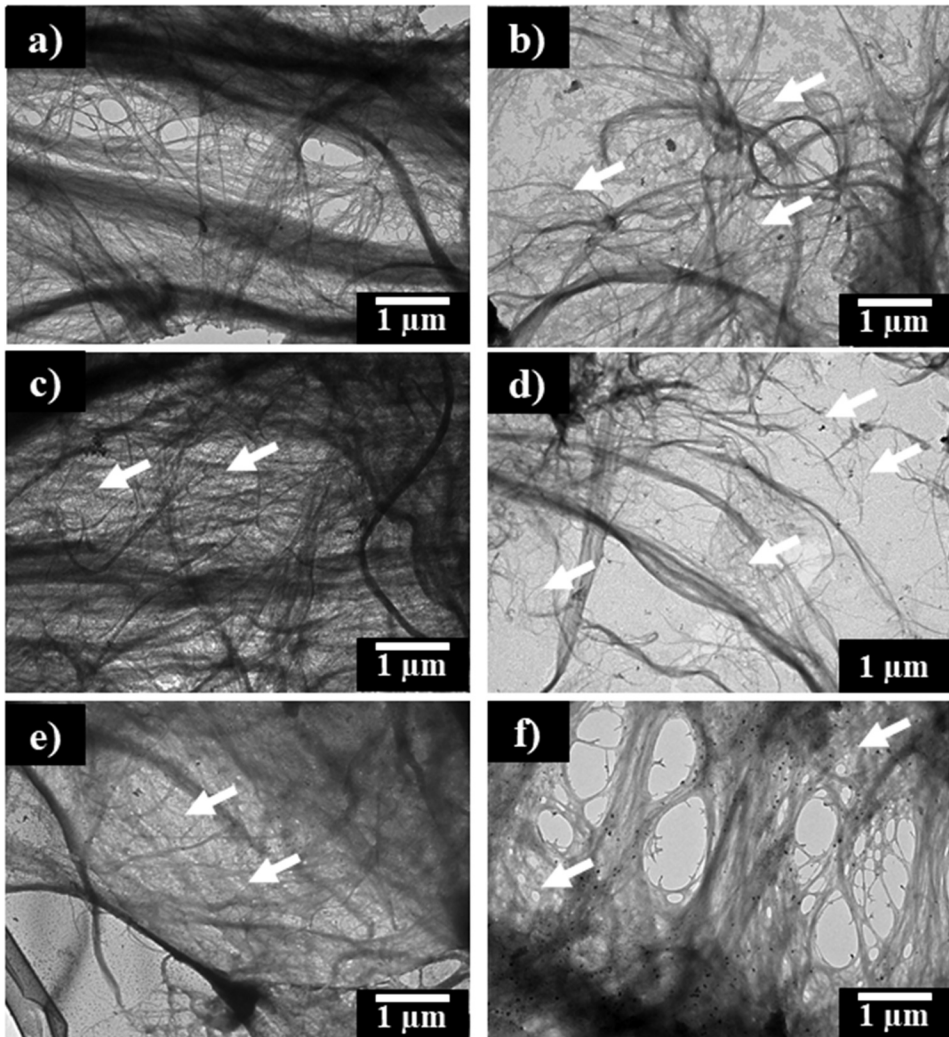


**Figure 1.** Typical HYP transmission electron microscope (MET) images without pretreatment (ST) and treated of the nanofibrils obtained with 15 passes (15x) and 30 passes (30x) through the fibrillator: a) ST 15x; b) ST 30x; c) 5% NaOH 2 h 15x; d) 5% NaOH 2 h 30x; e) 10% NaOH 1 h 15x; f) 10% NaOH 1 h 30x. Arrows show the extracted micro/nanofibrils.



**Figure 2.** Typical images from the SF transmission electron microscope (MET) without pretreatment (ST) and treated of the nanofibrils obtained with 15 passes (15x) and 30 passes (30x) through the fibrillator: a) ST 15x; b) ST 30x; c) 5% NaOH 2 h 15x; d) 5% NaOH 2 h 30x; e) 10% NaOH 1 h 15x; f) 10% NaOH 1 h 30x. Arrows show the extracted micro/nanofibrils.

Figure 4 show the distribution of the nanofibril diameters in the untreated (ST) and pretreated HYP, SF and LF. The SF nanofibrils have larger diameters than the HYP and LF nanofibrils. The obtained nanofibril diameters were concentrated at values of 30–45 nm. The content of nanofibrils with mean diameters lower than 45 nm was approximately 43% for the ST HYP, 53% for the ST SF and 62% for the ST LF and approximately 62%, 68% and 71% for the HYP, SF and LF treated with 5% NaOH for 2 h. For the 10% NaOH pretreatment performed for 1 h, the HYP, SF and LF contained 30%, 71% and 68% nanofibrils with

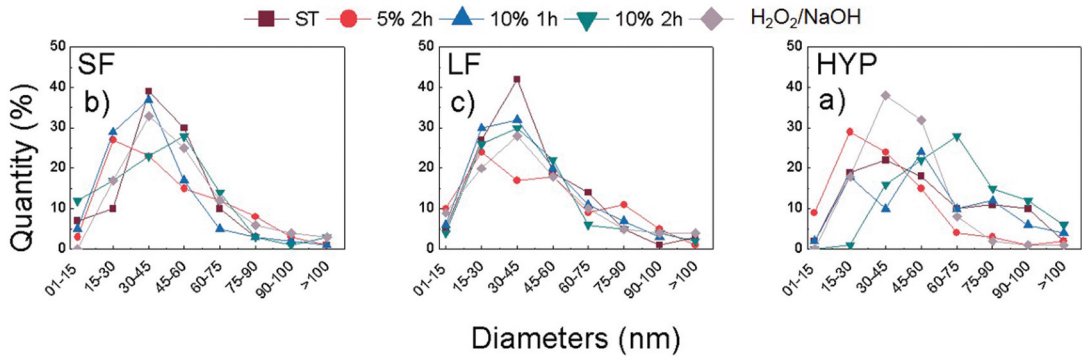


**Figure 3.** Typical images of the LF transmission electron microscope (TEM) without pretreatment (ST) and treated of the nanofibrils obtained with 15 passes (15x) and 30 passes (30x) through the fibrillator: a) ST 15x; b) ST 30x; c) 5% NaOH 2 h 15x; d) 5% NaOH 2 h 30x; e) 10% NaOH 1 h 15x; f) 10% NaOH 1 h 30x. Arrows show the extracted micro/nanofibrils.

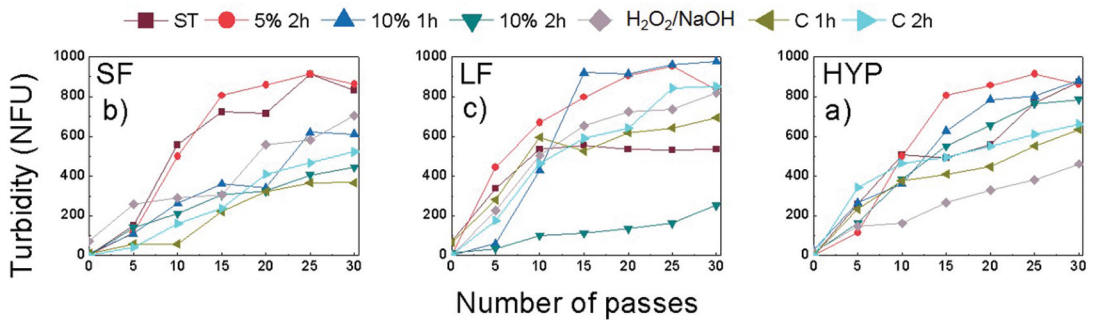
diameters less than 45 nm, respectively. For the HYP and LF pretreated with 10% NaOH for 2 h, there was still much fibrillated material (18% and 8%, respectively) with diameters greater than 100 nm.

### ***Turbidity of the supernatant obtained from the fiber/nanofibril suspensions***

Figure 5 show the evolving turbidity values of the supernatant obtained from the fibrillated cellulose fiber suspensions before (ST), after the pretreatments every 5 passes of the suspension through the fibrillatory.



**Figure 4.** Diameter distribution of fibrillated material obtained from untreated (ST) and pre-treated HYP, SF and LF pulps.



**Figure 5.** Relationship between the supernatant turbidity of the micro/nanofibril suspensions and the number of passes in the fibrillator for HYP, SF and LF without pretreatment (ST) and with the different pretreatments.

The turbidity of the supernatant increases due to the higher content of dispersed nanofibrils. The more turbid the supernatant, the more nanofibrils are dispersed in it. Because they are lighter, the nanofibrils are well dispersed in the supernatant, and the non-nanoscale material is decanted (Mckee et al. 2014).

The pulps pretreated with 5% NaOH exhibited higher supernatant turbidity values for all the pulps evaluated. Pretreatments that use alkaline conditions to modify the fiber cell walls dissolve hemicelluloses and lignin, which explains why some pulps are turbid despite not being passed through the fibrillator (Xiao, Sun, and Sun 2011).

The HYP fiber suspensions did not form gels with fibrillation; however, the presence of micro/nanofibrils was confirmed by the light microscopy and TEM analyses.

For the SF, as previously mentioned, the best pretreatment according to the supernatant turbidity result was also the 2 h 5% NaOH pretreatment. The light microscopy images (Figure S2) show the evolution of fibrillation with an increasing number of passes.

The increase in turbidity of the LF pulps occurred mainly in the samples pretreated with 5% NaOH, between the 5th and 10th passages in the fibrillator. The significant increase in turbidity occurred for the suspensions that passed through the fibrillator between 10 and 15 times.

### **Mechanical properties of nanofibrils films**

Table 3 show the stress-deformation resistance and modulus of elasticity for cellulose micro/nanofibrils films. Despite the HYP pulps showing low fibrillation, the micro/nanofibrils from the alkaline pretreatments of these pulps presented films with tensile strengths of up to 45 MPa and Young module up to 2.7 GPa.

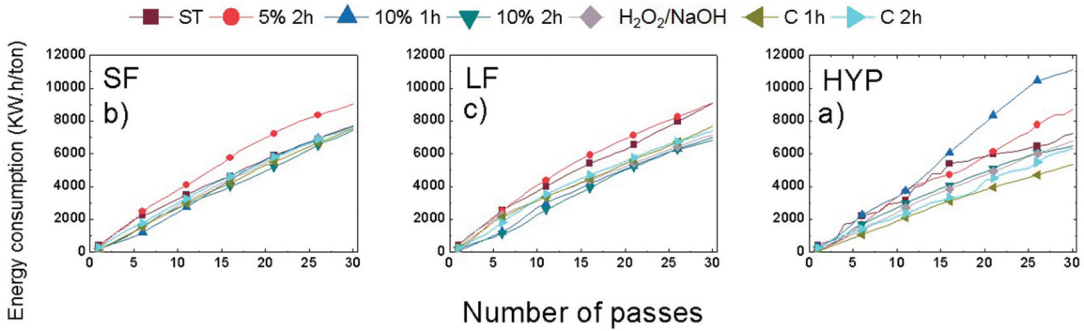
**Table 3.** Stress-deformation resistance and modulus of elasticity for cellulose micro/nanofibrils films. The micro/nanofibrils obtained from C 1 h, C 2 h and ST pulps did not form films.

Pretreatment	Tensile Strength (MPa)	Modulo Young (GPa)
HYP ST	-	-
HYP 5% 2 h	37,09 ± 2,33	2,73 ± 0,52
HYP 10% 1 h	45,73 ± 2,49	2,82 ± 0,09
HYP 10% 2 h	40,86 ± 8,84	2,61 ± 0,22
HYP H <sub>2</sub> O <sub>2</sub> /NaOH	34,15 ± 3,84	3,11 ± 0,44
HYP C 1 h	-	-
HYP C 2 h	-	-
SF ST	42,17 ± 5,20	2,40 ± 0,74
SF 5% 2 h	37,96 ± 2,86	2,50 ± 0,07
SF 10% 1 h	25,83 ± 0,71	1,64 ± 0,27
SF 10% 2 h	34,29 ± 3,08	2,21 ± 0,42
SF H <sub>2</sub> O <sub>2</sub> /NaOH	20,5 ± 4,25	2,69 ± 0,91
SF C 1 h	36,71 ± 0,92	2,31 ± 0,30
SF C 2 h	41,91 ± 5,59	2,08 ± 0,78
LF ST	24,59 ± 0,91	1,37 ± 0,41
LF 5% 2 h	30,46 ± 3,24	1,72 ± 0,49
LF 10% 1 h	35,3 ± 8,39	1,73 ± 0,67
LF 10% 2 h	17,91 ± 4,89	1,19 ± 0,08
LF H <sub>2</sub> O <sub>2</sub> /NaOH	20,79 ± 8,69	1,30 ± 0,69
LF C 1 h	54,25 ± 19,75	4,55 ± 1,16
LF C 2 h	48,86 ± 3,15	2,98 ± 0,72

Pretreatments in SF and LF pulps reduced the tensile strength values (22 Mpa) and Young's modulus (1.8 GPa), while the pulps without treatment or treated with hot water (C 1 h and C 2 h) reached values of up to 55 Mpa in tensile strength and 4.5 GPa in Young's modulus for LF and in SF up to 43 Mpa in tensile strength and Young's modulus of 2.5 GPa. The removal of lignin occurs with high concentrations of pre-treatments and is essential to improve mechanical properties. However, pre-treatments did not reach high concentrations sufficient for significant removal to occur. The presence of lignin decreases the bond strengths between micro/nanofibrils by reducing the tensile strength values compared to bleached pulps with reference values of 75–150 GPa (Visanko et al. 2017). The lignin influences the interconnections of the finest fibrils, causing coiling and decreasing the tensile strength and modulus of elasticity (Jiang et al. 2019). On the other hand, sodium hydroxide caused the removal of hemicelluloses, disrupting the structure of the hemicelluloses and the fiber, influencing the tensile strength and Young's modulus (Rambabu et al. 2016).

### **Energy consumed for nanofibril production**

During the fibrillation process hydrodynamic forces are generated that depend on the suspension concentration, fiber size, and the gap between the stones (Wang and Cheng 2009). In addition, increasing the number of passes of the suspension through the fibrillator breaks the hydrogen bonds of the fibers generating micro/nanofibrils with smaller diameters (Pakutsah and Aht-ong 2020). The HYP pulp was difficult to fibrillate, and the suspension became more liquid with increasing numbers of fibrillation and pretreated HYP pulps did not form gels. HYP fibers bind to water, but since they are very thin, they cannot form a strong gel with lower viscosity flowing rapidly between the disks of the equipment (He et al. 2018). Therefore, in this case, the distance between the grinding stones needed to be decreased so that the micro/nanofibrils could be extracted. The LF are longer than the SF, and because they were longer, the LF were more difficult to disperse, causing pulp accumulation in the grinder gap at the beginning of the passes, which hindered the micro/nanofibril extraction process (Gunawardhana et al. 2017). Figure 6 show the evolving cumulative energy consumed by increasing the number of passes through the grinder.



**Figure 6.** Evolution of accumulated energy consumption with the increase in the number of passes through the fibrillator grinder for the HYP, SF and LF pulps in different pretreatments. The arrows indicate the point of gel formation. HYP pulps did not form gel.

The best results found were produced from the SF by subjecting the pulp to pretreatments with 5% NaOH in 2 h and 10% NaOH for 1 h. Fewer passes were required to obtain these gels compared to the gel obtained by the other pretreatments, and consequently, less energy was consumed. Removal of hemicellulose affects the gel-forming structure due to water retention and increased molecular weight of cellulose, causing higher viscosity (Afsahi et al. 2018; Pääkkönen et al. 2016). Although the pretreatment with 10% NaOH for 2 h apparently resulted in a lower energy expenditure, the fibers were not well fibrillated as well.

At the beginning of fibrillating the pulps pretreated with 5% NaOH for 2 h and 10% NaOH for 1 h, the distance between the grinding stones was 20  $\mu\text{m}$ . However, after the gels formed with 10 passes through the fibrillator, the suspension remained as a gel, and the distance between the grinding stones had to be gradually increased.

The pulp drying process causes the cellulose to bind irreversibly, reducing its water retention capacity. This effect is called hornification and it makes the fibrils less exposed in the fibrillation process (Ballesteros et al. 2017; Martins et al. 2021).

Table 4 shows the energy consumed to achieve gel formation in the pretreated and untreated HYP, SF and LF. For the pulps that did not form gels, the energy consumption was calculated for 15 passes. When comparing the energy consumption required for the pulps to form gels, the energy consumed for the HYP process was higher because more passes were needed to fibrillate this pulp. The SF consumed the lowest energy during the fibrillation of the pulps.

The use of unbleached pulps is feasible and preferable in relation to bleached pulps due to economic reasons, because it is less costly, due to lower environmental impacts because it does not have the bleaching stage. Furthermore, some chemical properties are due to the presence of lignin, leading to less hydrophilicity, greater tensile strength and a higher fibrillation index compared to bleached pulps (Hassan et al. 2018, 2020).

### Fibrillation quality index

It was observed that the alkaline pretreatments of NaOH 5% 2 h and NaOH 10% 1 h for the pulps SF, LF and HYP were more effective (IQ = 66–74) in relation to the pulp without treatment (IQ = 63–65) for optimization of the mechanical fibrillation process. These pretreatments made it possible to reduce the number of passes in the fibrillator equipment and consequent energy savings of 30 to 60% compared to untreated pulp. Pretreatment NaOH 10% 2 h caused greater withdrawal of hemicelluloses, making it difficult to obtain micro/nanofibrils, generating a lower fibrillation quality index (IQ = 65) compared to pretreatment of NaOH 5% 2 h (IQ = 74). For the HYP pulp the energy consumption did not reduce, but the extraction of micro/nanofibrils of the fibers occurred more

**Table 4.** Average energy consumption values for gel formation in the fibrillation process and information about the fibrillation process for the different conditions of the HYP, SF and LF pulps. The energy savings were calculated in comparison with the pulps without pretreatment (ST).

Pretreatment	Number of passages for gel formation	Energy consumption for gel formation (kW.h/t)	Economy (%)
HYP ST	15*	3.731	-
HYP 5%2 h	15*	4.900	+ 31
HYP 10%1 h	15*	4,147	+ 11
HYP 10%2 h	15*	3,869	+ 3
HYP H2O2/NaOH	15*	2,810	24
HYP C1 h	15*	2,942	21
HYP C2 h	15*	3,728	1
SF ST	13	3,553	-
SF 5%2 h	8	2,850	20
SF 10%1 h	9	2,119	40
SF 10%2 h	14	3,345	5
SF H2O2/NaOH	14	3,921	+ 10
SF C1 h	15*	3,883	+ 9
SF C2 h	12	2,864	20
LF ST	11	3,239	-
LF 5%2 h	7	2,349	28
LF 10%1 h	10	2,640	18
LF 10%2 h	15*	3,551	+9
LF H2O2/NaOH	13	3,289	+1
LF C1 h	14	3,548	+9
LF C2 h	12	3,708	+14

\* Gel formation did not occur. They were calculated with the values obtained with 15x based on the optical microscopy images that already showed nanofibrils.

+ Pretreatments that had an increase in energy consumption.

efficiently in the pretreated (IQ = 57–69) than the HYP pulp without treatment (IQ = 52). The hybrid pretreatment was the one that most improved the quality index (IQ = 69) of the HYP pulp, generating energy savings of approximately 30%.

## Conclusions

Subjecting these pulps to the pretreatment with 5% NaOH for 2 h generated nanofibrils that were better dispersed and had smaller diameters, produced supernatants with higher turbidity values than those generated by leading the pulps to the other pretreatments and the goal of reducing the energy consumed by nanofibril production was achieved. The energy consumption was lower for the pulps subjected to this pretreatment, as fewer passes were required in the mechanical fibrillator grinder. Therefore, partially removing hemicelluloses (using pretreatments with 5% NaOH for 2 h and 10% NaOH for 1 h) facilitates the extraction of more dispersed nanofibrils with smaller diameters. HYP, SF and LF submitted to the hybrid pretreatment did not facilitate fibrillation.

This study demonstrated that submitting HYP, SF and LF to alkaline pretreatments can facilitate nanofibril production at industrial scale. This study also contributes to developing more efficient methods used to obtain cellulose nanofibrils for different applications.

## Highlights

- Obtaining cellulose micro/nanofibrils in pre-treated high-yield pulps.
- Obtaining cellulose micro/nanofibrils from unbleached commercial pulps.
- Pre-treatments reduced the energy consumption of unbleached pulps.
- Reduction of energy consumption by up to 40% in unbleached pulps
- Efficacy of alkaline pretreatments on commercial unbleached pulps to increase fibrillation index.

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## Disclosure statement

No potential conflict of interest was reported by the author(s).

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