

Optimizing Cellulose Microfibrillation With NaOH Pretreatments for Unbleached Eucalyptus Pulp

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Eucalyptus pulp**

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ABSTRACT

This study aimed to assess the effect of drying unbleached *Eucalyptus* cellulose fibers after the application of pretreatments in order to optimize the microfibrillation process, as well as to evaluate the efficiency of NaOH pretreatments in reducing energy consumption for production of microfibrillated cellulose (MFC). Pretreatments with 0 wt% (untreated), 5 wt% and 10 wt% NaOH were evaluated. The length and width of the fibers pretreated with NaOH decreased significantly, mainly with hasher pretreatments. The removal of hemicellulose from the fiber cell wall was an important factor concerning the degree of fibrillation of the fibers. Pretreating fibers with 5 wt% NaOH for 2 h increased the water retention value (WRV), in addition to presenting the lowest energy consumption for fibrillation, promoting energy savings of up to 48%. Pulps that were not dried after the NaOH pretreatments incurred in easier microfibrillation and lower energy consumption when comparing to the dried pulp, which shows the negative impact of drying on the fibers to obtain the MFC.

Keywords: Energy consumption. Nanocellulose. Nanofibrils. Nanofibers. Pretreatments.

INTRODUCTION

Cellulose is a biopolymer that stands out for several reasons, such as its abundance, renewability, and nontoxicity to the environment and biodegradability after disposal. Technology advancements in the industrial sector have brought the possibility of producing several materials, such as cellulose, at the nanometric scale (Liu 2018). Nanostructured cellulose can be obtained from several sources, such as bacterial cellulose (Gatenholm and Klemm 2010), or from lignocellulosic materials spread into cellulose nanofibrils (CNFs) (Osong et al. 2016), cellulose nanocrystals (CNCs) (Sehaqui et al. 2011), and microfibrillated cellulose (MFC) (Guimarães Junior et al. 2018).

Microfibrillated cellulose (MFC) is a fibrillated material with fibrils with average diameter of less than 100 nm and a length that can reach more than 10 μm (Abdul Khalil et al. 2012). This material has a high specific surface area due to the large amount of individual micro/nanofibrils, which increases bonding with each other or with other matrices, forming high-strength films (Guimarães Junior et al. 2018). Several industrial sectors and researchers are developing applications for MFC, such as those reported elsewhere for pharmaceutical (Mohd Amin et al. 2012), food, paint and cosmetics (Nikolajski et al. 2012), films and coating (Matos et al. 2019), and fiber-cement composite (Fonseca et al. 2019) fields, as well as bacterial nanocellulose for medical uses (Klemm et al. 2011).

MFC can be obtained by mechanical, chemical or enzymatic methods (Rol et al. 2019). The most common method for producing MFC involves a mechanical approach. However, the high energy consumption of the operation is the main limiting factor for scaling up this procedure. Therefore, pretreatments of cellulosic pulp are necessary to

optimize the process. When submitting cellulose pulp to pretreatment, hydrogen bonds are weakened, which makes the process more efficient (Durães et al. 2020).

Previous studies have tested alkaline pretreatments of cellulosic pulp using sodium hydroxide (NaOH) at different concentrations to obtain MFC. Wang et al. (2014) stated that pretreatments with high alkaline concentrations impair the MFC acquisition process due to the conversion of cellulose I into cellulose II (mercerization). According to the authors, this process generates greater aggregation through the interdigitation of MFC in cell walls, which significantly hinders its individualization. Dias et al. (2019) studied alkaline pretreatments of bleached *Eucalyptus* sp. and showed that the use of 5% NaOH for 2 h was the most effective to obtain MFC and reduce energy consumption during the fibrillation process. Thus, alkaline pretreatments associated with mechanical methods are considered a viable alternative to reduce operational energy consumption.

However, if pulp fibers are dried, some cellulose chains can irreversibly bond, modifying their structure and properties, such as reducing the capacity to retain water. This process is usually called hornification. Regarding this process, Ballesteros et al. (2017) studied the water retention values of bleached and unbleached *Eucalyptus* and *Pinus* fibers after successive hornification cycles. According to the authors, when the cell wall of the fibers is subjected to the drying process, the cellulose fibrils increase the degree of physical cross-linking between themselves, which decreases the pore sizes and the water holding capacity of the fibers. When fibers retain less water in their structure, the MFC is less exposed and, consequently, more difficult to obtain (García-Iruela et al. 2019).

Studies related to the drying of fiber have already been reported (Zimmermann et al. 2016; Silva et al. 2021). However, there is still a lack of information about the

microfibrillation process of unbleached *Eucalyptus* kraft pulp, whereas more data could help optimize the fibrillation process and facilitate the scaling up of MFC production.

Given the above considerations, the present study aimed to investigate the drying effect on unbleached *Eucalyptus* cellulosic fibers after applying NaOH pretreatments to optimize the microfibrillation process, as well as assessing the efficiency of pretreatments to reduce the energy consumption for production of microfibrillated cellulose (MFC).

METHODOLOGY

Materials

Unbleached *Eucalyptus* sp. Kraft (E) pulp from Klabin S.A. (Paraná/Brazil) was used as the source for MFC. Sodium hydroxide (NaOH) was purchased from Êxodo Científica (Sumaré/Brazil).

Alkaline pretreatment

The cellulosic pulp was dried in an air circulation oven at 50°C for 24 h prior to the pretreatments. Then, the fibers were pretreated with 5 wt% NaOH solution for 2 h and 10 wt% NaOH for 1 h at 80°C while under continuous agitation at 800 rpm. Afterwards, the fibers were subjected to repeated sifting and washing with deionized water until neutral pH was reached. The pH was monitored by pH indicator strips.

After the pulp was pretreated and thoroughly washed, it was divided into two samples: pulp oven-dried at 50°C for 24 h and wet pulp (refrigerated at $5 \pm 3^\circ\text{C}$ until grinder fibrillation). As a control, pulp without pretreatment was immersed in water until fibrillation. The pulps were subjected to continuous stirring (~ 800 rpm) at 80°C for 1 h and 2 h. All treatments were coded to be easily assessed throughout the manuscript (Table 1).

Table 1 - Experimental design and coding of samples.

Fiber	Drying before grinding	Pretreatment	Code
Eucalyptus (E) Unbleached	Dried	Not pretreated	E0-D
		5 wt% NaOH for 2 h	E5-D
		10 wt% NaOH for 1 h	E10-D
	Not dried	Not pretreated	E0-ND
		5 wt% NaOH for 2 h	E5-ND
		10 wt% NaOH for 1 h	E10-ND

Fiber characterization

The pulps were chemically characterized before and after alkaline pretreatments. The levels of lignin and soluble monosaccharides were analyzed in the procedure, with lignin being evaluated following the Tappi UM 250 standard (1976) and monosaccharides according to Wallis and Wearne and Wright (1996). An ion chromatography system (Dionex ICS 5000, Sunnyvale, CA, USA) was used.

The average length, weighted average length, width and curvature were measured using a fiber image analyzer (Valmet FS5, Finland). The curvature index measures the degree of curvature of the fiber and is defined as follows: $(\text{contour fiber length} / \text{projected fiber length} - 1) \times 100$ (Alimadadi et al. 2018).

The water retention value (WRV) of the pulp was calculated according to the Scandinavian test method SCAN - C 62:00 (2000), dispersing them in water with a fiber content of 0.5 wt% after boiling for 5 min. The water suspension was filtered by a Heraeus Megafuge 16R centrifuge (Thermo Fisher Scientific, Waltham, MA, USA), at $3,000 \times g$ for 15 min to dehydrate, and the wet pulps were weighed immediately after. After drying in an oven at 110°C for 5 h, the weight of the pulp was determined again. WRV was calculated based on Eq. (1):

$$\text{WRV (g/g)} = \frac{W_0 - W_1}{W_1} (1)$$

where W_0 and W_1 are the weights of wet and oven-dried pulps, respectively.

Pulp mechanical fibrillation

The cellulose pulps with and without pretreatment were soaked in deionized water at a concentration of 2 wt% for 6 days to maximize the swelling of the fibers. After this procedure, the fibers were subjected to mechanical fibrillation using a Super MassColloider fibrillator (Masuko Sangyo MKCA6-2) with 5 passes at 1,500 rpm (Tonoli et al. 2016; Lago et al. 2020).

Light microscopy (LM) of pulp fibers

A Nikon Eclipse E20 light microscope was used to analyze the fibrillation levels of the pretreated fibers and without pretreatments after 5 passes through the equipment. The samples were diluted in deionized water (0.75 wt%) and stained with ethanol-safranin (1% v/v) to enhance the contrast of the images.

Transmission electron microscopy (TEM) of MFC

The morphology of the MFC was analyzed by a Zeiss EM 109 microscope with an accelerated voltage of 80 kV. The sample preparation and equipment settings followed the information reported by Tonoli et al. (2016). Uranyl acetate was added during sample preparation to improve the contrast of the samples. A few drops of the suspension with the dye were added to copper grids (400 mesh) with formvar film (thermoplastic resin) and dried before visualization by TEM. To measure MFC diameters, ImageJ software (Schindelin et al. 2012; Claro et al. 2019) was used, with 200 individual structure measurements for each pretreatment.

Energy consumption (EC) during fibrillation

The EC to fibrillate the pulps was calculated considering the average amperage used for each cycle (dispersion passage through the fibrillator), the equipment tension and the fibrillation time per ton of micro/nanofibrillated material, with a consistency of

2.0 wt% (Eq. 2). The EC was calculated until the moment of gel formation, corresponding to the successful fibrillation of the pulps.

$$EC = (P \times h)/m \text{ (2)}$$

where EC is the energy consumption (kW.h.ton⁻¹); P is the power (in kW, voltage x electric current); h is the time (in hours) spent during fibrillation; and m is the mass (in tons) of the cellulose material processed in the grinder.

RESULTS AND DISCUSSION

Chemical characterization of the pulps

Table 2 shows the chemical composition of unbleached Kraft pulp from *Eucalyptus* sp. (E) before and after chemical pretreatments. It is important to note that the chemical characterization of dried and not dried pretreated pulps was the same because alkaline pretreatments of the cellulosic pulps were the same in both cases. It is clear that all chemical pretreatments performed resulted in a relative increase of the glucose content as a probable consequence of the decreased content of hemicellulose, mainly xylose (Castro et al. 2020). The higher the NaOH concentration and pretreatment time of the fibers were, the greater the relative amount of cellulose and lower the xylose content (Bufalino et al. 2015).

Table 2 - Average values, in percentage, and standard deviation of the chemical composition of unbleached *Eucalyptus* sp. pulp.

Pulp	Glucose	Arabinose	Galactose	Xylose	Mannose	Insoluble lignina	Soluble lignina
E0	64.0 ± 0.4	0.08 ± 0.1	0.24 ± 0.1	12.0 ± 0.1	0.24 ± 0.1	16.0 ± 0.1	2.0 ± 0.1
E5	69.0 ± 4.1	0.06 ± 0.1	0.15 ± 0.1	7.0 ± 0.5	NA**	15.0 ± 0.1	3.0 ± 0.1
E10	72.0 ± 0.4	0.06 ± 0.1	0.13 ± 0.1	5.0 ± 0.1	0.26 ± 0.1	15.0 ± 0.1	3.0 ± 0.1

* Result valid for both dried and not dried pulp after pretreatment. **NA = not available.

An 8% increase in the relative glucose content was found for the E10 samples.

With harsher pretreatment, the relative xylose content decreased. After E10

pretreatment, the initial xylose content of 12% decreased to around 5%. This effect happens because xylose is more present on outer layers than in the corresponding internal layers (Dahlman et al. 2003), and the pretreatment reaches the fibers more superficially.

Morphological properties and water retention values (WRVs) of fibers

Table 3 shows the morphological properties of cellulosic fibers before and after chemical pretreatments. It is possible to observe that there was a small decrease in the weighted average width of the fibers.

Table 3 - Average values and standard deviation of the morphological properties of the fibers obtained by the fiber analysis equipment, for the *Eucalyptus* pulp with and without pretreatment before mechanical fibrillation.

Pulps	Weighted average length (mm)	Width (μm)	Curvature (%)	WRV (g/g)
E0-D	0.9 ± 0.1	20.6 ± 0.1	6.8 ± 0.3	3.2 ± 0.1
E5-D	0.8 ± 0.1	19.5 ± 0.1	19.9 ± 0.3	3.4 ± 0.1
E10-D	0.8 ± 0.1	19.7 ± 0.1	30.4 ± 0.2	2.3 ± 0.1
E0-ND	0.7 ± 0.3	20.9 ± 0.1	5.9 ± 0.3	3.4 ± 0.1
E5-ND	1.0 ± 0.4	19.7 ± 0.1	16.9 ± 0.4	3.6 ± 0.1
E10-ND	0.6 ± 0.3	19.9 ± 0.2	29.7 ± 0.3	2.9 ± 0.1

Regarding the fiber length, a small reduction was observed in all oven-dried pretreated fibers, especially those that were subjected to more intense pretreatments with NaOH. The decreased fiber length may be related to the increase in the curvature of the fibers, which may have influenced the measurement values. The curvature of the fibers can also mask length results due to changes during the analysis (Martin-Sampedro et al. 2014).

The WRVs of dried and not dried fibers are presented in Table 3. The WRV is the most commonly used index to assess the swelling of cellulose fibers (Olejnik et al. 2017). The WRVs found for E5-D and E5-ND indicate that there was no reduction in water retention by the fibers. According to Klemm et al. (2006), the alkaline

environment contributes significantly to the swelling of the fibers, which makes the microfibrils more exposed and, consequently, easier to bind with water. Regarding the E10 fibers, the WRVs found were below those of the E5 fibers, for both dried and not dried. These results corroborate the findings of Dias et al. (2019), where the higher concentration of NaOH promoted an increase in the removal of fiber cell wall components, mainly hemicellulose, which have a large number of hygroscopic sites capable of forming hydrogen bonds (Pacaphol and Aht-Ong 2017).

Compared to the not dried fibers, the dried samples had decreased WRVs. According to Ballesteros et al. (2017), the drying and subsequent wetting of the fibers tends to reduce the WRV due to the collapse and stiffening of the fiber surface generated by the hornification process. In addition, the number of pores on the fiber surface decreases due to the greater crosslinking of cellulose fibrils, which further reduces the WRVs (Mo et al. 2019).

Morphology of fibers and MFC

Light microscopy of pulp fibers

Figure 1 presents the curvature of dried and not dried fibers. The images in Figures 1a, 1c, and 1e show the oven-dried fibers after the chemical pretreatments, while those in Figures 1b, 1d, and 1f show the fibers that were not dried after the chemical pretreatments.

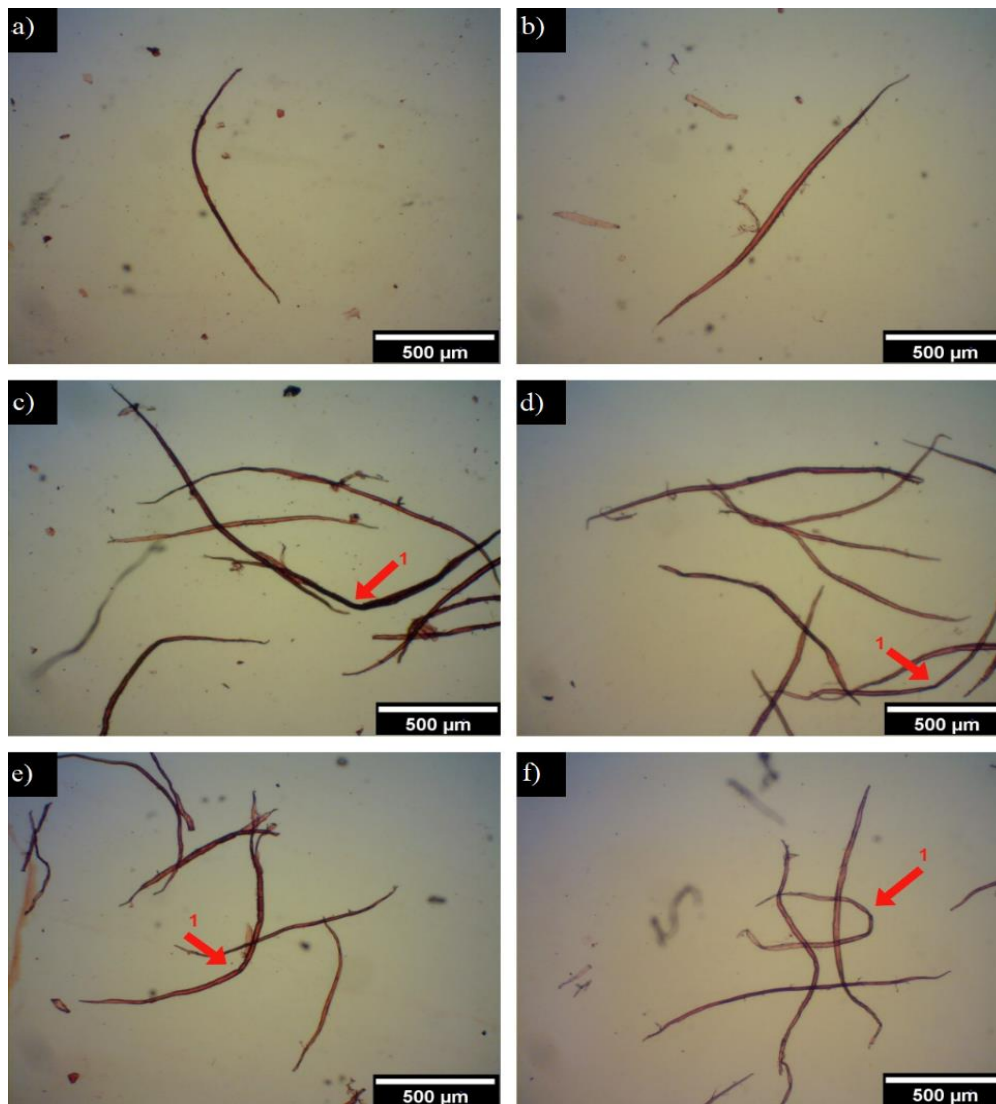


Fig. 1 Light microscopy images of unbleached *Eucalyptus* fibers after chemical pretreatments: a) E0-D b) E0-ND; c) E5-D; d) E5-ND; e) E10-D; f) E10-ND. Arrow 1: Curved fibers after chemical pretreatments

Fibers that were subjected to chemical pretreatments presented a considerable increase in curvature when compared to the untreated fibers. Pulps that were subjected to pretreatments in higher alkaline concentrations (10% NaOH) had even greater curvature, with curvature values of $30.4 \pm 0.2\%$ for E10-D and $29.7 \pm 0.3\%$ for E10-ND (Table 3).

The increase in curvature mainly resulted from the greater removal of hemicellulose and lignin from the fiber cell wall, and with higher concentrations of NaOH, the curvature value of the fibers increased (Tarrés et al. 2017). Fibers that were

oven-dried after the pretreatments had a higher curvature than the not dried fibers. The hornification of the fibers is responsible for the closer proximity of the cellulosic chains (Oksanen et al. 2009; Luo et al. 2018) which contributes to the shrinkage and bending of the fibers.

Transmission electron microscopy (TEM) of MFC

Figure 2 shows the MFC morphology observed by TEM. The MFC produced from the E0 fibers (Figs. 2a and 2b) was less individualized than that from the fibers subjected to pretreatments with NaOH. The E5 fibers were easily converted to MFC, presenting an average diameter of 26 ± 14 nm for E5-D (Fig 2c) and 29 ± 15 nm for E5-ND (Fig 2d). Due to the intense removal of hemicellulose from the cell wall of the fibers, the E10 fibers presented less individualized MFC, regions with aggregation and fibers that were not fibrillated, which is not desired in this process. This fact indicates the importance of hemicellulose during the fibrillation process (Durães et al. 2020). According to Chaker et al. (2013), hemicellulose hinders the formation of irreversible hydrogen bonds between nanofibrils, acting as a physical barrier that prevents direct contact and further aggregation (Figure 3).

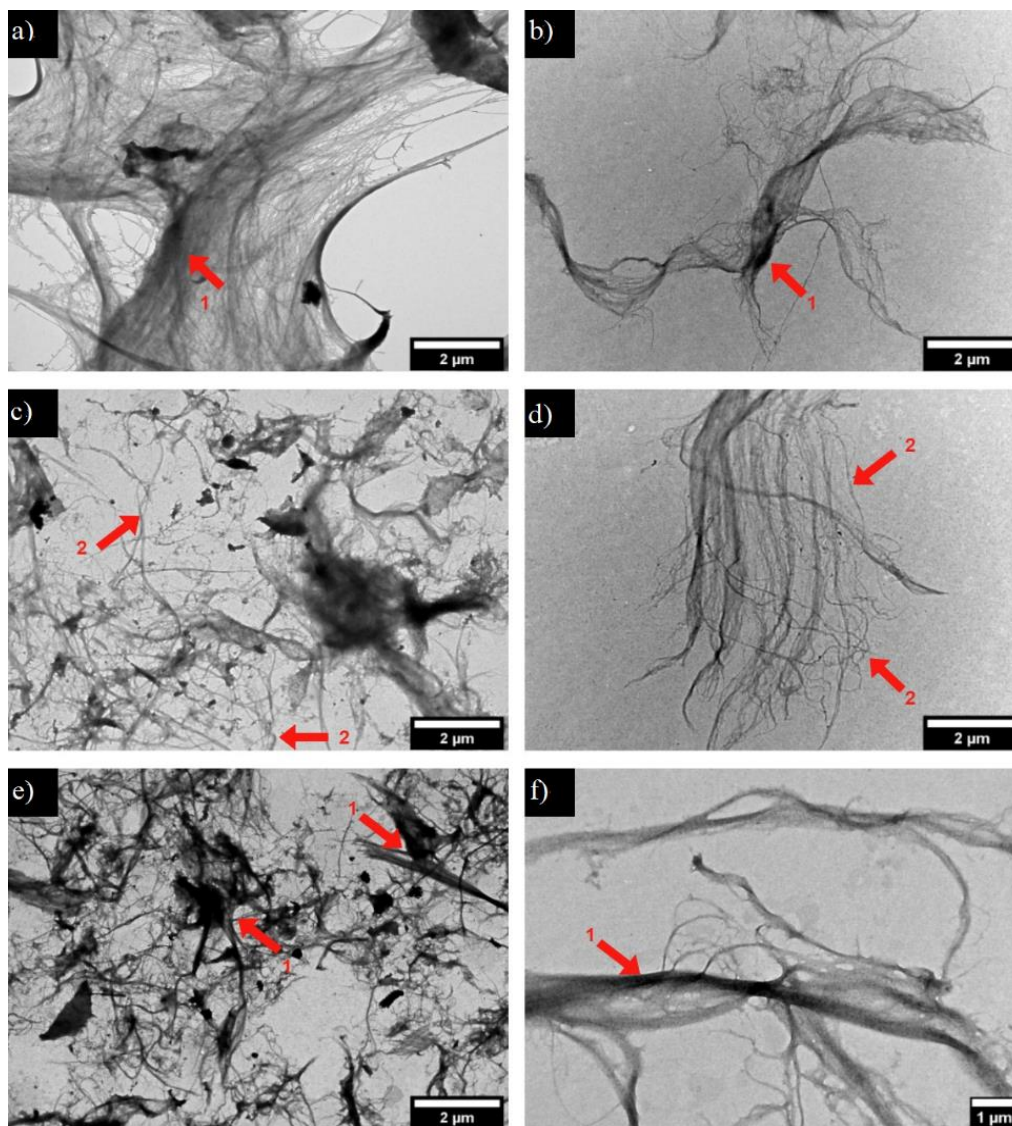


Fig. 2 Transmission electron microscopy (TEM) images of unbleached *Eucalyptus* fibers with and without pretreatment, showing the general aspect of MFC obtained with 5 passes through the fibrillator: a) E0-D; b) E0-ND; c) E5-D; d) E5-ND; e) E10-D; and f) E10-ND. Arrow 1: Fibrils and microfibrils with preserved structure and still with large dimensions after chemical pretreatments and mechanical fibrillation; Arrow 2: Well individualized micro/nanofibrils after chemical pretreatments and mechanical fibrillation

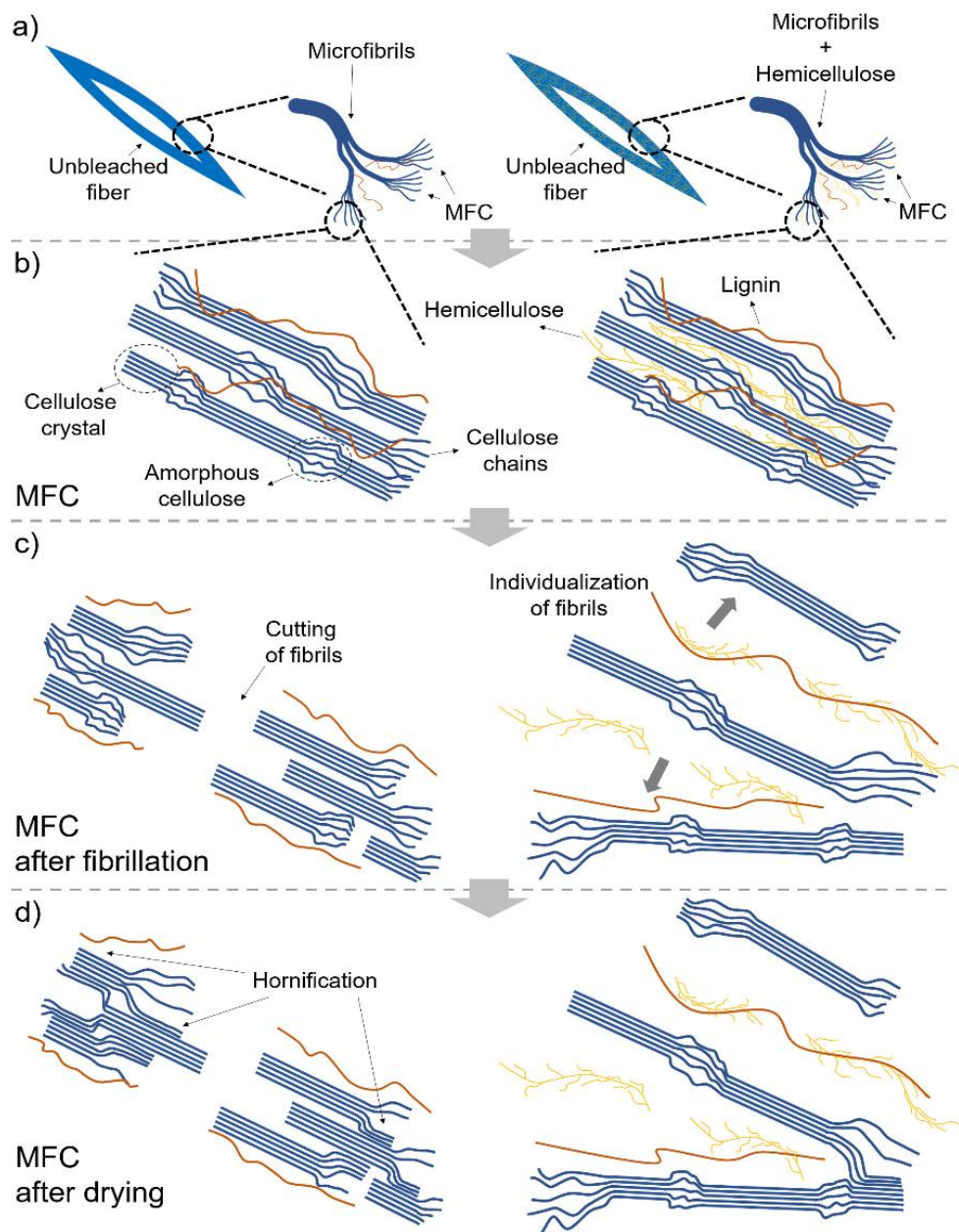


Fig. 3 Description of the importance of hemicellulose during fibrillation and the hindrance caused by the hornification process. a) depicts the unbleached fibers and their deconstruction into MFC; b) is a close up into the microstructure and composition of the MFC still inserted into the fiber; c) shows the individualization process happening more easily when hemicellulose is present. The proximity of cellulose bundles without hemicellulose is stiffer, incurring in cutting of fibrils besides individualization; d) depicts the hornification process and subsequent structural change happening after drying the fibrillated MFC

Figure 4 shows the MFC distribution according to the diameter classes for pulps with and without pretreatment, as well as dried and not dried pulps. Most of the MFC obtained showed diameters that ranged from 15 to 30 nm. The MFC content for not

dried fibers with average diameters below 45 nm was approximately 74% for E0-ND, 86% for E5-ND and 82% for E10-ND. However, fibers that were dried presented larger particles, with average diameters below 45 nm representing 72% for E0-D, 84% for E5-D and 78% for E10-D. Not dried fibers presented smaller MFC diameters than dried fibers. The hornification of the fibers during oven-drying implies the close proximity of the cellulose chains and the reduced number of pores in the fiber microstructure, which decreases the amount of individualized micro/nanofibrils in the MFC suspension (Duan et al. 2015).

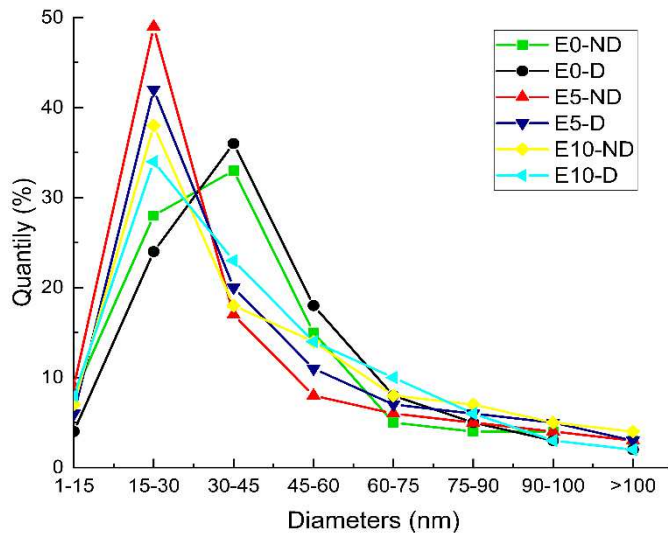


Fig. 4 Distribution of diameters of MFC obtained from unbleached *Eucalyptus* pulps with and without pretreatment. D = Dried; ND = Not Dried

Energy consumption for obtaining MFC

Figure 5 shows the evolution of energy consumption during fibrillation with the increase in the number of passes through the mechanical grinder fibrillator.

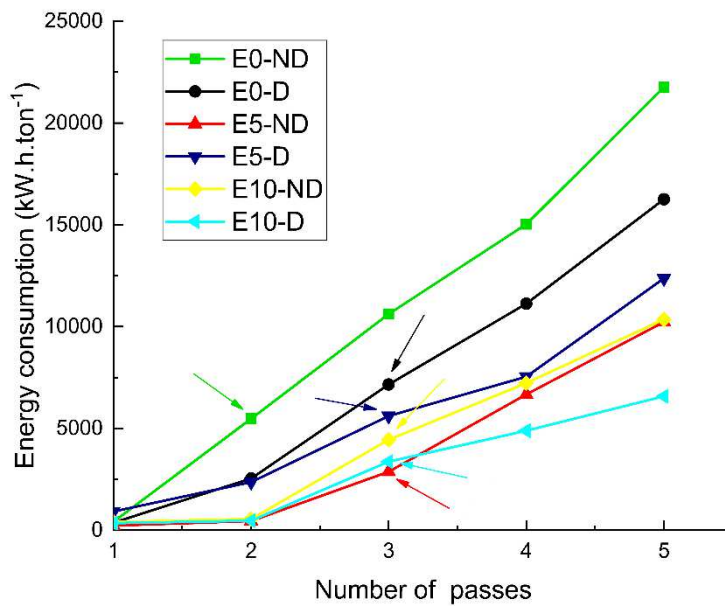


Fig. 5 Evolution of accumulated energy consumption with the increase in the number of passes through the grinder mechanical fibrillator for unbleached *Eucalyptus* pulps with and without pretreatment. The arrows indicate the passage at which the pulps have gelatinous aspect. D = Dried; ND = Not Dried

All of the pretreated samples reached a gelatinous appearance on the 3rd pass, exception for E10-ND pulp, that was able to achieve it on the 2nd pass. This viscosity of the suspension is due to cellulose's ability to retain water in its internal and external structures, and MFC, with more exposed micro/nanofibrils, is able to retain significantly more water than the pulp (Ioelovich 2008).

The E10 pretreatments, both dried and not dried, were not as effective in the fibrillation process. As previously noted in Dias et al. (2019), this harsher pretreatment removes most of the hemicellulose present in the fibers. The presence of these monosaccharides in the pulp contributes to increased fibrillation since the carboxylic groups of the hemicellulose contribute to electrostatic repulsion between MFC chains in water (Iwamoto et al. 2008).

Pretreatment E5-D was proved to be efficient in reducing energy consumption, promoting savings of up to 22% compared to E0-D fibers (Table 4). However, fibers

E5-ND demonstrated greater efficiency in the process, reaching a savings of up to 48% compared to E0-ND fibers. The procedures conducted prior to fibrillation that preserve most of the hemicellulose in the cell walls of the fibers are more efficient in the fibrillation process (Dias et al. 2019).

Table 4 - Average values of energy consumption for gel formation in the fibrillation process for the different pretreatments of unbleached *Eucalyptus* sp. pulp.

Pulps	Number of passages*	Energy consumption* (kW h ton ⁻¹)	Energy savings (%)
E0-D	3	7.159	-
E5-D	3	5.612	22.0
E10-D	3	3.367	53.0
E0-ND	2	5.476	-
E5-ND	3	2.871	48.0
E10-ND	3	4.440	19.0

*until gel formation

A superior performance was achieved in reducing the energy consumption for obtaining MFC from the fibers that were not dried after pretreatment, with the exception of fibers E10-D and E10-ND. The fiber swelling of not dried samples allowed a greater reduction in energy consumption than that of oven-dried fibers (Ireana Yusra et al. 2018). Thus, not dried fibers with mild alkaline pretreatment E5-ND have been proven to be the ideal path to produce MFC with a relatively low energy consumption.

CONCLUSIONS

This study sought to evaluate the effect of chemical pretreatments to optimize the process of obtaining MFC. In addition, it was evaluated the effect of drying the pretreated unbleached *Eucalyptus* fibers before grinding to obtain MFC.

E5-ND fibers were more easily fibrillated with reduced energy consumption, being influenced mainly by the hornification and swelling processes of the fibers. Morphological analyses have also shown that the E5-ND samples were more effective in producing MFC. E10-D and E10-ND pretreatment produced an intense removal of

the fiber cell wall components responsible for water retention in the structure, reducing fiber swelling, which compromised fibrillation.

The E5-ND fibers presented a very significant reduction in energy consumption, reaching approximately 48% savings. Even though the E10-D fibers showed a 53% reduction in energy consumption, the pretreatment was not effective in obtaining MFC. Thus, removing part of the hemicellulose appears to facilitate the fibrillation process, while intense removal of this component impairs the obtention of MFC.

This study helps improve the methodology for obtaining MFC. It was shown that oven-drying fibers after pretreatment is detrimental to lowering the energy consumption and improving the MFC obtaining process, which is desired when scaling up the production.

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Figures

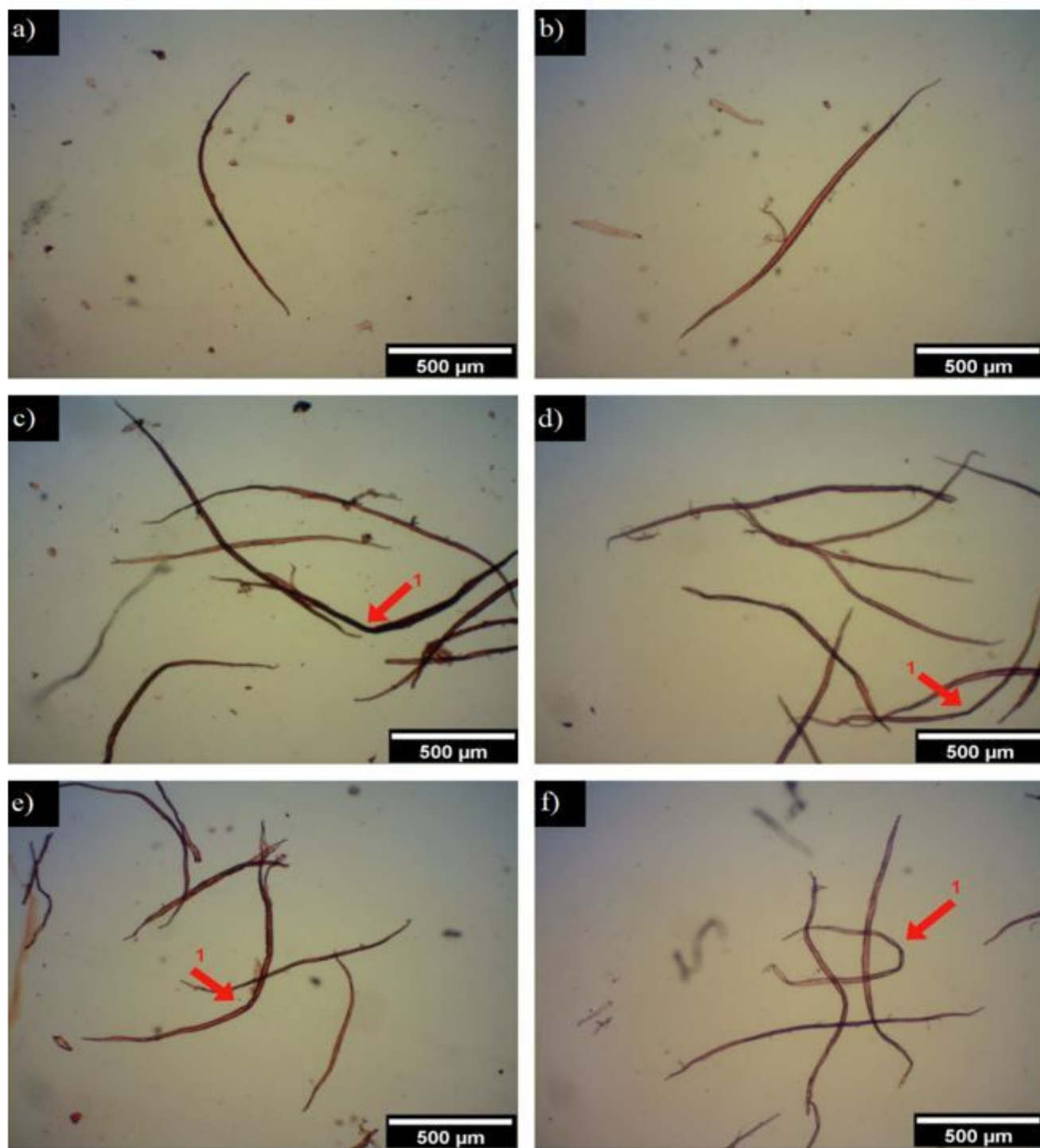


Figure 1

Light microscopy images of unbleached Eucalyptus fibers after chemical pretreatments: a) E0-D b) E0-ND; c) E5-D; d) E5-ND; e) E10-D; f) E10-ND. Arrow 1: Curved fibers after chemical pretreatments

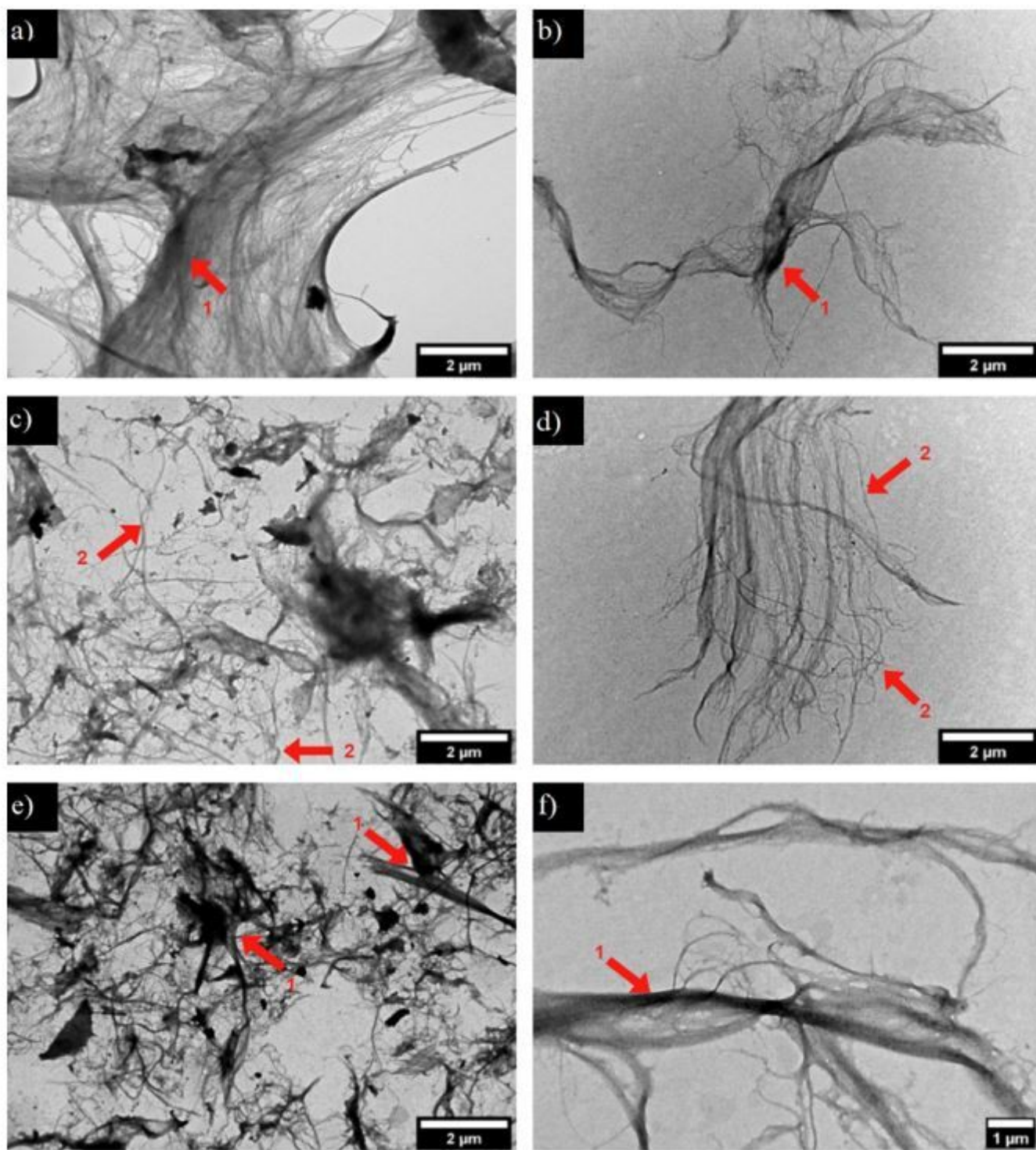


Figure 2

Transmission electron microscopy (TEM) images of unbleached Eucalyptus fibers with and without pretreatment, showing the general aspect of MFC obtained with 5 passes through the fibrillator: a) E0-D; b) E0-ND; c) E5-D; d) E5-ND; e) E10-D; and f) E10-ND. Arrow 1: Fibrils and microfibrils with preserved structure and still with large dimensions after chemical pretreatments and mechanical fibrillation; Arrow 2: Well individualized micro/nanofibrils after chemical pretreatments and mechanical fibrillation

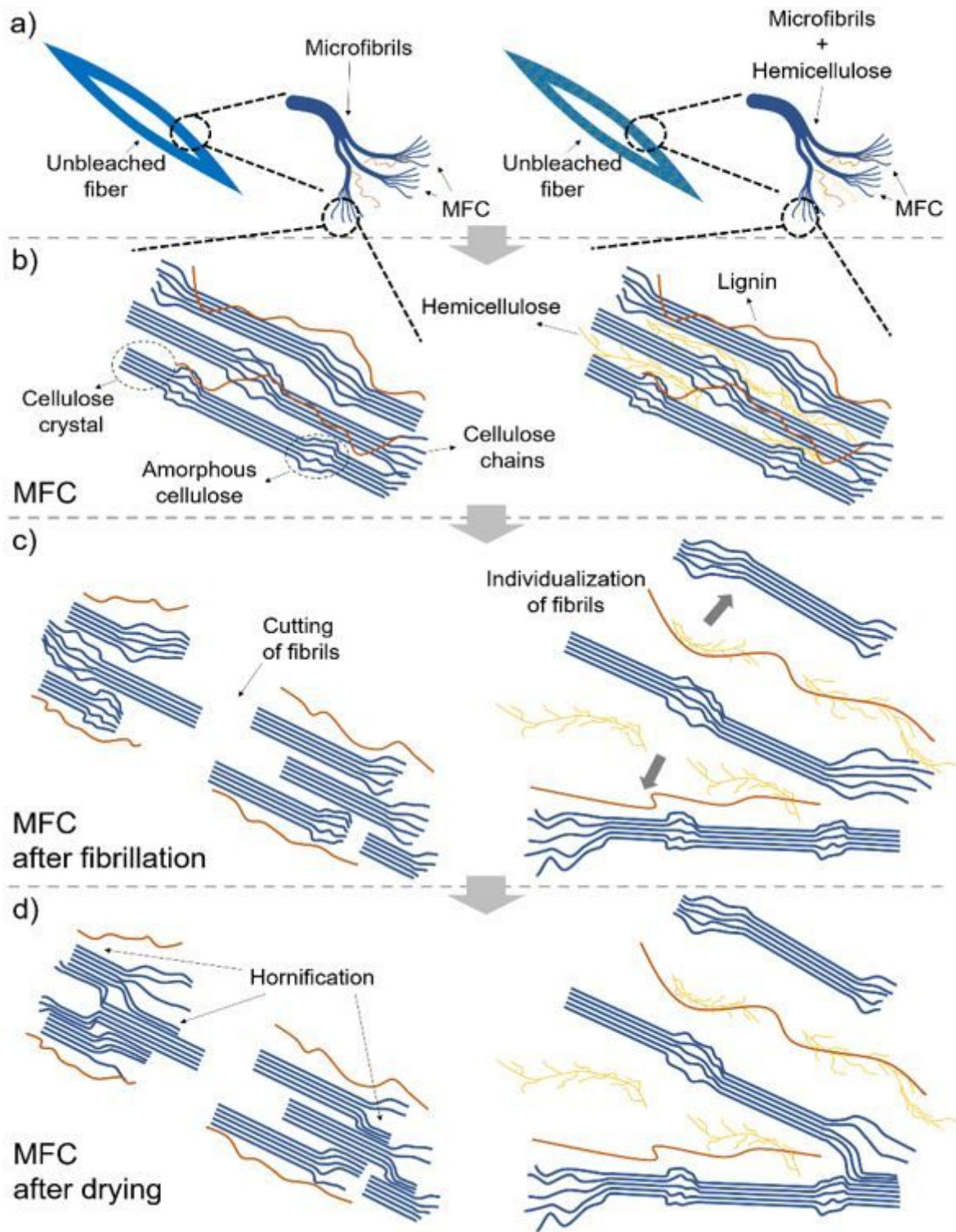


Figure 3

Description of the importance of hemicellulose during fibrillation and the hindrance caused by the hornification process. a) depicts the unbleached fibers and their deconstruction into MFC; b) is a close up into the microstructure and composition of the MFC still inserted into the fiber; c) shows the individualization process happening more easily when hemicellulose is present. The proximity of cellulose

bundles without hemicellulose is stiffer, incurring in cutting of fibrils besides individualization; d) depicts the hornification process and subsequent structural change happening after drying the fibrillated MFC

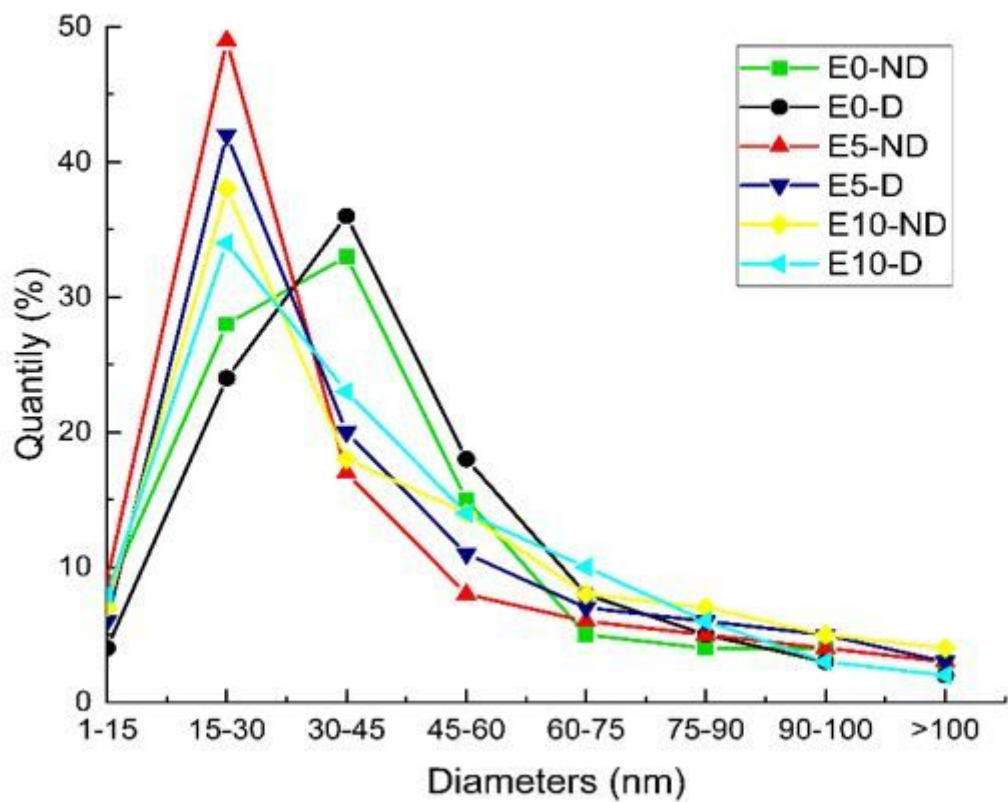


Figure 4

Distribution of diameters of MFC obtained from unbleached Eucalyptus pulps with and without pretreatment. D = Dried; ND = Not Dried

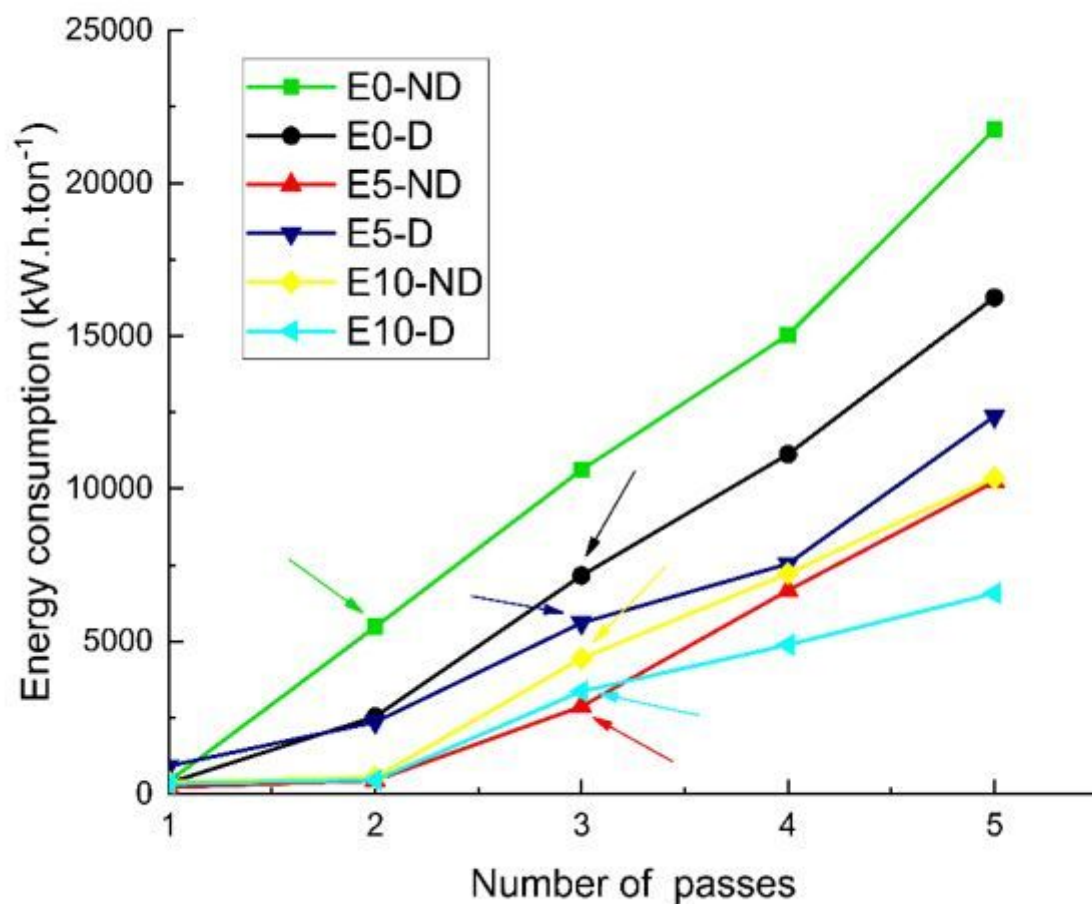


Figure 5

Evolution of accumulated energy consumption with the increase in the number of passes through the grinder mechanical fibrillator for unbleached Eucalyptus pulps with and without pretreatment. The arrows indicate the passage at which the pulps have gelatinous aspect. D = Dried; ND = Not Dried