Facilitating the selection of raw materials: Evaluation of the effects of TCF and ECF bleaching sequences on different wood and non-wood pulps

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Asesoramiento en la selección de materias primas: Evaluación de los efectos de las secuencias de blanqueo TCF y ECF en diferentes pastas madereras y no madereras

Assessorament en la selecció de matèries primes: Avaluació dels efectes de les seqüències de blanqueig TCF i ECF en diferents pastes fusteres i no-fusteres

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SUMMARY

Properties of cellulosic raw materials are known to vary widely among different sources. The interest in the usage of non-conventional fibers makes necessary a better knowledge of the peculiarities of each source and their behavior under different bleaching processes. ECF and TCF bleached pulps (ISO brightness ≥ 82%) from eucalyptus, flax and sisal as well as cotton linters were analyzed. Eucalyptus showed the highest zero-span tensile strength (1.1-1.2 N.m/g), higher than that of sisal (0.85-0.95 N.m/g) and flax (0.7-0.8 N.m/g) which were also found to be linearly correlated to their viscosity regardless of the cellulose source. Sisal and eucalyptus showed the largest hemicelluloses content (≈13-16 %) while cotton linters appeared as a high-cellulose content (97.7 %) source for high-quality fibers. ECF and TCF bleaching processes produced different effects on fibers, as the latter showed a slightly lower quality than the former, difference that may not be significant if the great environmental benefit of TCF bleaching is considered. Finally, fiber surface was examined using SEM microscopy for a more complete assessment of raw materials.

Keywords: ECF; TCF; eucalyptus; cotton; sisal; flax.

RESUMEN

Es conocido que las propiedades de las materias primas celulósicas varían ampliamente dependiendo de su origen. El interés en el uso de fibras no convencionales hace necesario un mejor conocimiento de las particularidades de cada materia y su comportamiento en los diferentes procesos de blanqueo. Pastas blanqueadas ECF y TCF (blancura ISO ≥ 82%) de eucalipto, lino, sisal y línters de algodón fueron analizadas. La mayor resistencia a la tracción a mordazas juntas (1.1-1.2 N.m/g) se obtuvo en eucalipto, resistencia mayor que en sisal (0.85-0.95 N.m/g) y lino (0.7-0.8 N.m/g). Esta propiedad se correlacionaba linealmente con la viscosidad independientemente del material celulósico. El contenido más alto en hemicelulosas se obtuvo en sisal y eucalipto (≈13-16 %) mientras que alto contenido en celulosa (97.7 %) se obtuvo en los línters de algodón, lo que les hace interesantes como fibras de alta calidad. Los procesos de blanqueo ECF y TCF produjeron diferentes efectos en las fibras, dónde el proceso TCF generó fibras de menor calidad que las ECF, diferencia que puede ser atenuada si se considera el beneficio medioambiental del blanqueo TCF. Finalmente, la superficie de las fibras se examinó por microscopia SEM para mejorar el asesoramiento en la selección de las materias primas.

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Palabras clave: ECF; TCF; eucalipto; algodón; sisal; lino.

RESUM

És conegut que les propietats de les matèries primes cel·lulòsiques varien àmpliament depenent de l'origen. L'interès en l´ús de fibres no convencionals fa necessari un millor coneixement de les particularitats de cada matèria i el seu comportament en diferents processos de blanqueig. Pastes blanquejades ECF i TCF (blancor ISO ≥ 82%) d'eucaliptus, lli, sisal i línters de cotó van ser analitzades. La major resistència a la tracció a mordasses juntes (Zero-Span) (1.1-1.2 N.m/g) es va obtenir en l'eucaliptus, resistència major que en sisal (0.85-0.95 N.m/g) i lli (0.7-0.8 N.m/g). Aquesta propietat es correlacionava linealment amb la viscositat independentment del material cel·lulòsic. El contingut més alt en hemicel·luloses es va obtenir en sisal i eucaliptus (≈13-16 %) mentre que alt contingut en cel·lulosa (97.7 %) es va obtenir en línters de cotó, el què els fa interessants com a fibres d'alta qualitat. Els processos de blanqueig ECF i TCF van produir diferents efectes a les fibres, on el procés TCF va generar fibres de menor qualitat que les ECF, diferència que pot ser atenuada si es considera el benefici mediambiental del blanqueig TCF. Finalment, la superfície de les fibres es va examinar per microscòpia SEM per tal de millorar l'assessorament en la selecció de les matèries primes.

Paraules clau: ECF; TCF; eucaliptus; cotó; sisal; lli.

INTRODUCTION

Nowadays global cellulose market offers a wide variety of fibers obtained from diverse sources bleached throughout different sequences[1,2]. Each fiber source has unique characteristics, hampering the decision of which raw material suits best the different applications, always seeking for optimal processability and product quality. Wood fibers are by far the main cellulose source for worldwide pulp and paper industry [3]. However, non-wood fibers sources are gaining increasing attention due to the fact that they are usually derived from annual crops, offer high-quality fibers and in many cases they are obtained as by-product, improving biomass utilization [4].

Among woody fibers, hardwoods such as eucalyptus, birch or poplar provide short fibers of thick walls and a narrow lumen compared to softwoods, such as pine, spruce or fir. Generally, hardwoods yield less-resistant papers but offer a better formation, smoothness, bulk and opacity [4]. Eucalyptus has been increasingly used for papermaking since 1960's and is currently becoming one of the most important fiber sources worldwide [5]. It was predicted that by 2015, market pulp production would have reached 70 million tons, with about 35 million coming from hardwoods and more than 50% of this coming from eucalyptus [6].

On the other hand, non-wood plants are a heterogeneous group of organisms providing fibers with a great morphological and chemical diversity. Flax fibers, for example, are derived from plants usually harvested for both the production of fibers and seeds (raw material of the linseed oil) [7]. Flax fibers have been used since ancient time for the manufacture of linen, being nowadays the greatest flax producers Canada, China, India, and United States [7]. Flax pulp usually consists of two different types of fibers, namely: "bast fibers", obtained from the bark which are long and strong (10–55 mm long and 12–30 μm thick), and "core fibers," obtained from the log or xylem, which are shorter and stiffer (0.05 to 0.5 mm long and 10-30 μm in thick). The usage of both fractions responds basically to an economical reason, as bast fibers are up to four times more expensive than core fibers [8].

Another example of non-wood fibers could be found in sisal, which provides fibers with a great potential for several applications. Traditional uses for sisal included manufacture of natural ropes, cordage and sacking, although the apparition of synthetic materials and the lack of technological development has diminished the typical sisal markets [9]. In papermaking terms, sisal presents a high tear resistance, alpha cellulose content, porosity, bulk, absorbency and folding endurance, making it an interesting choice for specialty papers [10]. Also, sisal has been reported to have better physical properties than softwood kraft fibers [11].

Cotton linters are another sort of non-wood fiber presenting the peculiarity of not undergoing a cooking process. They constitute a byproduct of the textile industry, being the short fiber that cannot be used in the textile process and presenting a very high cellulose content [12]. The ginning process used for cotton fibers extraction leaves linters attached to seed coat. Because of this, another mechanical process is then necessary for their removal. As extracted from seeds, cotton linters also contain other compounds such as pectin, proteinaceous matter, waxes, ashes and minor soluble polysaccharides. These compounds are usually removed by boiling into a diluted caustic solution under nitrogen in order to obtain pure cellulose fibers [13]. In 2010, 42 million metric tons of cotton was produced, which lead to the production of 2.5 million metric tons of cotton linters [14] Traditional products made from cotton linters are: absorbent cotton, special papers or derivatives such as cellulose nitrate or acetate [12]. Due to their characteristics, cotton linters have also shown to be a promising raw material for the production of nanocellulose [15,16].

Simultaneously, environmental concerns affecting the pulp and paper industry, increased interest in removing chlorine from bleaching processes, compounds known to be highly polluting. Firstly, ECF (elemental chlorine free) sequences and subsequently TCF (totally chlorine free) sequences were developed decades ago in order to reduce this environmental impact[17,18]. In this work, pulps obtained from eucalyptus, sisal and flax bleached through ECF or TCF bleaching sequences linters were analyzed. For comparative purposes, cotton linters were also characterized as an example of fibers not produced by a pulping process. The purpose of this analysis was to both acknowledge the specific characteristics of each raw material and also to assess the effects of different bleaching sequences on these fibers.

MATERIALS AND METHODS

Raw materials

Commercial TCF and ECF bleached pulps from sisal (*Agave sisalana*), flax (*Linum usitatissimum*), eucalyptus (*Eucalyptus globulus*) and cotton linters (*Gossypium sp.*) were analyzed.

Sisal and flax fibers were obtained through a NaOH cooking process bleached through DPo (ECF) or QPo (TCF) sequences and provided by Celesa (Spain). Eucalyptus fibers were obtained through a kraft process, bleached through ODEoD (ECF) or OOQ(PoP) (TCF) sequences and provided by Ence (Spain). Cotton linters were provided by Celsur (Spain). Prior to analysis, cotton linters were pre-beated in a valley mill for 90 minutes in order to reduce their average length.

Pulp properties

ISO brightness, Kappa number (KN) and viscosity of samples was determined in accordance to ISO 3688:1999, ISO 302:2004 and ISO 5351:2010, respectively. HexA content of samples was determined through UV detection following the procedure described by Chai et al., 2001 [19,20]. Two hydrolysis for sample and four oxidations of each hydrolysis were performed giving rise to eight measures of HexA content.

Carbohydrate composition of samples was determined using high performance liquid chromatography (HPLC) following a modified version of TAPPI T 249 cm-09 method [21]. Chromatographic analysis was performed using a 1100 Agilent HPLC instrument furnished with a BIO RAD Aminex HPX-87H ion-exchange column. Data was collected by the refractive index detector (RID). Operating conditions were as follows: 0.6 mL/min, mobile phase H_2SO_4 6 mM and temperature 60 °C. Concentrations were calculated by interpolation into calibration curves run from standards of glucose, xylose, ramnose and arabinose. Because the column fails to resolve xylose, mannose and galactose, their combined content is expressed as xylose.

Pulp refining and handsheet properties

Fibers drainage resistance (Schopper-Riegler degree, °SR) and their water retention value (WRV) were measured in accordance to ISO 5267-1:1999 and ISO 23714:2014, respectively.

Fibers zero-span tensile index was determined according to ISO 15361:2000 in a Zero-span 1000 Pulmac tester. For analysis, strips obtained from paper sheets prepared in a laboratory Rapid-Köthen lab former (ISO 5269-2:2004) were previously soaked in distilled water for 5 seconds.

Fiber morphology

Fiber length was determined in accordance to TAPPI T 271 om-02 method in a Kajaani fiber analyzer (FS300, Metso automation, Finland).

RESULTS AND DISCUSSION

Chemical characterization

The chemical composition of the initial raw materials used (before obtaining the pulp) was different in each wood (eucalyptus) or non-wood (sisal, flax and cotton) plant [22]. The highest pentosane content was for eucalyptus and sisal (15-35%), followed by bast flax fibers (2-6%) and cotton. Concerning lignin, eucalyptus had the higher content (18-25%) followed by sisal (7-10%), bast flax fibers (1-6%) and cotton. In cotton linters pentosane content and lignin were insignificant, being this material of high cellulose content (~96%). Cellulose content was also high in bast flax fibers (higher than 60%), followed by sisal (53-64%) and eucalyptus (38-49%).

Raw materials were characterized after pulping and bleaching processes, and because of this, all observed brightness values were greater than 82% ISO (Figure 1A). Also, it was observed that ECF sequences led to higher brightness values than TCF. Concerning kappa number (Figure 1B), TCF bleached samples presented higher values than ECF ones, which could be explained by their content in HexA (also indicated in figure). Although lignin content of these pulps was very low, it is well known that HexA could interfere into KN determination increasing its value[23]. HexA, formed during alkaline cooking, result highly attacked by chlorine-derived reagents during ECF bleaching[24], which does not happen during TCF processes. Among samples, TCF bleached eucalyptus and sisal showed a high content in hexenuronic acids, while flax content was lower and cotton linters lacked of them.

Carbohydrate composition of pulps is a key factor determining their behavior in further papermaking steps, but also in other processes such as the manufacture of cellulose derivatives. As could be predicted by HexA (which are contained into hemicelluloses), sisal and eucalyptus accounted for the higher hemicelluloses content, while flax showed a significantly lower value (Table 1). Surprisingly, cotton linters showed to have a small content in hemicelluloses (2%). Cotton is well known to produce high-cellulose content fibers, and these hemicelluloses are assumed to proceed from seed cloak rests dragged during linters extraction. Finally, carbohydrate composition was also found to be different depending on the bleaching process. ECF

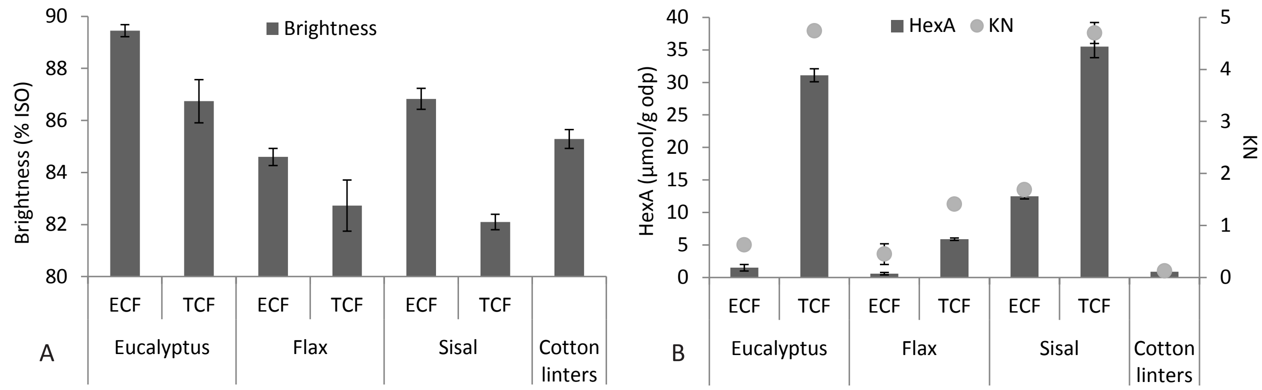

Fig. 1 *ISO brightness (A), Kappa number (KN) and hexenuronic acid content (HexA) (B) of samples.*

bleached samples showed a content in hemicelluloses 3 points lower compared to TCF, indicating that hemicelluloses suffered a greater chemical attack during ECF bleaching.

Table 1. *Carbohydrate composition of pulps*

% of sugar (w/w)		Glucan	Xylan	Rhamnan	Glucuronic Acid	Acetyl
Eucalyptus	ECF	84.8 ± 1.3	14.8 ± 1.1	0.1 ± 0.1	0.3 ± 0.1	-
	TCF	83.6 ± 0.4	15.9 ± 0.1	0.2 ± 0.1	0.3 ± 0.1	-
Flax	ECF	96 ± 0.7	3.2 ± 0.3	-	0.8 ± 0.1	-
	TCF	95.3 ± 0.9	3.7 ± 0.8	-	1 ± 0.1	-
Sisal	ECF	86.6 ± 0.5	12.8 ± 0.2	-	0.6 ± 0.1	-
	TCF	82.7 ± 0.6	16.1 ± 0.3	0.2 ± 0.2	0.7 ± 0.1	0.3 ± 0.2
Cotton linters		97.7 ± 0.3	2 ± 0.2	0.1 ± 0.1	0.1 ± 0.05	0.1 ± 0.1

Physical characterization

Fibers viscosity is a characteristic frequently used as an indicator of cellulose integrity, as it is directly correlated to its degree of polymerization (DP). Figure 2A shows viscosity values of samples, where it can be observed that cotton linters showed the largest value whereas flax accounted for the smallest. It is widely described that TCF sequences produce a slightly larger cellulose degradation than ECF [25], fact that corresponds with the obtained results. Conservation of cellulose integrity is important due to its implication on fibers mechanical performance. In this direction, wet zero-span tensile strength is an indicator of the maximum tensile load assumable by a single fiber. Observation of zero-span strength values of fibers (Figure 2A) revealed a tendency to correlate to cellulose viscosity (Figure 2B), highlighting the relation between cellulose DP and fibers mechanical performance. The only sample skipping this correlation was cotton linters (black dot in chart), which were not obtained through a pulping process, and thereafter should be considered separately. Data also indicated that non-wood fibers such as sisal could have equivalent mechanical resistance as that of eucalyptus fibers and that TCF process slightly diminished this resistance compared to ECF bleaching.

Concerning other physical properties, fiber water-binding capacity showed some differences depending on their origin (Table 2). ECF-bleached fibers presented a tendency (especially visible in eucalyptus) to have smaller water retention values than when bleached without chlorine, possibly due to the smaller content in hemicelluloses, compounds with a well-known tendency for water intake. Moreover,

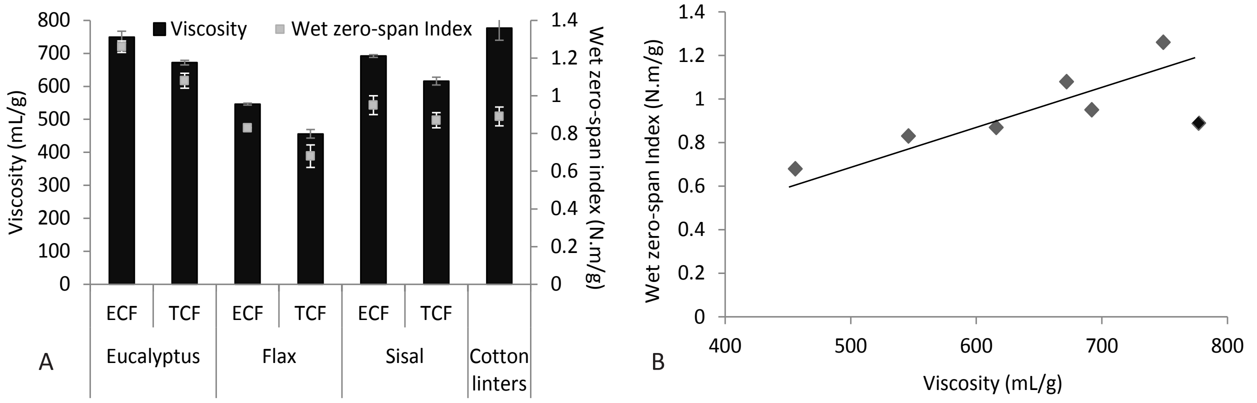

Fig. 2 *Viscosity (bars, left axis) and wet zero-span tensile index (points, right axis) (A) and correlation between both variables (B).*

fibers drainage resistance, as °SR degrees, is usually taken as an indicator of fibers beating degree. Table 2 also indicates °SR degrees of pulps, highlighting the high value showed by flax fibers, and by cotton linters, due to the pre-refining process to which linters were submitted prior to characterization, the same happening with WRV.

Lastly, fiber length (Table 2) showed significant differences between sources, while it did not show any affectation by different bleaching sequences. Differences between two calculations (nominal and length-weighted), especially notorious in flax pulp but also in sisal and cotton linters, were caused by the morphological heterogeneity among fibers. Nominal calculation favors the shorter fibers as they usually outnumber the longer ones. Because of this, length-weighted length, L (l), usually provides a more realistic value of average fiber longitude. As can be observed, eucalyptus provided the shortest fibers, while all non-woods were longer, with the biggest values showed by sisal and cotton linters. The fiber length will affect the physico-mechanical properties of the final papers, since short fibers will provide papers with higher density whereas more resistant papers will be obtained with long fibers.

Table 2. *Water retention value (WRV), Schopper-Riegler drainage resistance (°SR), nominal fiber length (L(n)) and length-weighted fiber length (L(l))*

		WRV	°SR	L(n) (mm)	L(l) (mm)
Eucalyptus	ECF	1.12 ± 0.03	20 ± 1	0.65 ± 0.1	0.82 ± 0.03
	TCF	1.36 ± 0.02	16 ± 1	0.6 ± 0.05	0.79 ± 0.04
Flax	ECF	0.95 ± 0.05	27 ± 1	0.45 ± 0.04	1.45 ± 0.13
	TCF	1.08 ± 0.01	33 ± 2	0.42 ± 0.05	1.31 ± 0.15
Sisal	ECF	0.91 ± 0.01	15 ± 1	1.4 ± 0.15	1.91 ± 0.1
	TCF	0.99 ± 0.01	16 ± 1	1.48 ± 0.12	2.16 ± 0.16
Cotton linters		1.38 ± 0.02	47 ± 2	1.08 ± 0.09	1.95 ± 0.1

Flax pulp fractionation

As previously reported, flax fibers are composed by two well-differentiated fractions, short core fibers (0.39 mm) and long bast fibers (1 mm) [8]. For a better characterization of this raw material, we proceeded to their separation and characterization. Core fibers accounted only for ≈ 30% of total fiber mass, while bast fibers represented the largest amount (≈ 70%). Table 3 shows carbohydrate composition and HexA content of both fractions, where remarkable differences in composition between them can be observed. Core fibers showed a higher hemicelluloses and HexA content, highlighting the quality difference between fractions. Surprisingly, we observed that hemicelluloses and HexA content in unfractionated pulp was different than the content of each fraction after fractionation (proportionally weighted). The reason for this difference was thought to be caused by separation procedure in the Bauer McNett equipment, process in which fines fraction is lost and thereafter pulp composition modified.

Table 3. *Carbohydrate composition and HexA content of flax fiber fractions*

	Flax TCF	
% of sugar (w/w)	Core fibers	Bast fibers
Glucans	92.2 ± 0.9	95.6 ± 0.5
Xylan	7.1 ± 0.4	3.8 ± 0.2
Arabinan	-	-
Rhamnan	0.05 ± 0.01	0.05 ± 0.01
Glucuronic Acid	0.6 ± 0.3	0.3 ± 0.1
Acetyl	-	0.2 ± 0.2
HexA (μmol g^{-1} odp)	3.6 ± 0.3	2.4 ± 0.4

SEM microscopy

Images of fibers (Figure 3) suggested the presence of cleaner fiber surfaces in ECF fibers (left pictures) compared to TCF (right), *i.e.* TCF fibers presented a larger amount of small fibrils on their surface. Possibly, greater hemicelluloses elimination produced by ECF bleaching (previously commented) enhanced the cleaning of fibers surface. Among fiber sources, flax pulp showed a higher amount of thin elements forming the network observable in Figure 3C and D and not present in other samples. Considering the higher °SR value presented by these pulps (Table 2), these smaller elements could be consequence of a beating process to which fibers are occasionally submitted before commercialization. This evidence is also shown by Figure 3G, which represents cotton linters, beated before analysis.

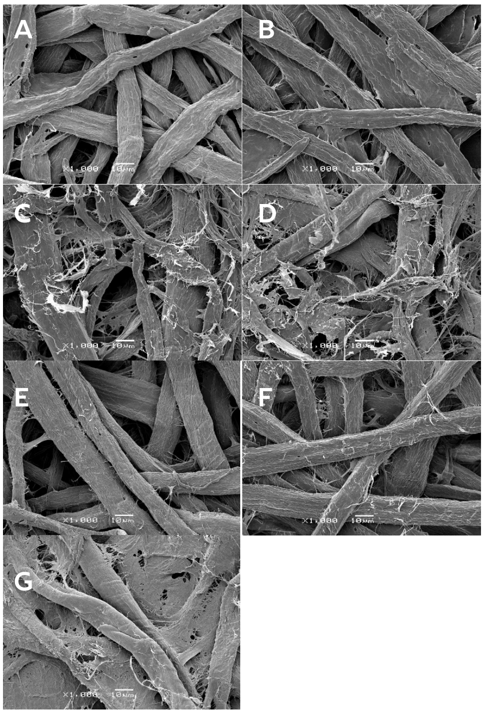

Fig. 3 *SEM micrographs of cellulose fibers. Images correspond to: Eucalyptus ECF (A), TCF (B); Flax ECF (C), TCF (D); Sisal ECF (E), TCF (F) and Cotton linters (G).*

CONCLUSIONS

Information provided in this work could allow a more informed choice of a raw material for each specific purpose, either in papermaking processes or for the procurement of cellulose derivatives. Generally, fibers properties showed significant differences between sources, including a correlation found between their viscosity and mechanical performance. Cotton linters appeared as a high-cellulose content source for high-quality fibers (97.7%). Also, we observed that TCF fibers from wood (eucalyptus) or non-wood (sisal, flax) materials showed a slightly lower quality compared to their ECF counterparts. TCF fibers showed a lower brightness (between 2-4 % ISO) and a higher kappa number (up to ≈ 4 points), HexA content (up to ≈ 30 μmol/g odp) and hemicelluloses content (up to ≈ 3 % higher). However, the enormous environmental benefits provided by completely eliminating chlorine from bleaching processes could compensate this quality loss, making TCF fibers a good choice for several applications.

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