Obtaining Soluble-grade Cellulose Pulp from *Agave tequilana* Weber var. Azul Bagasse

Manuel Alberto Gallardo-Sánchez,[a] José Anzaldo Hernández,[b] Rogelio Ramírez Casillas,[b] José Inés Escalante Vázquez,[c] Daniel Escobar Hernández,[c] J. Félix Armando Soltero Martínez,[d] Salvador García Enríquez,[b,*] and Emma Rebeca Macías Balleza [d,*]

Natural lignocellulosic biomass is a valuable feedstock for soluble-grade cellulose (α-cellulose > 90%) with advantageous features such as abundance, high strength, rigid structure, low weight, and it is biodegradable. The bagasse from *Agave tequilana* Weber var. azul is the main agroindustrial waste from the tequila industry and poses an environmental threat. However, due to its high cellulose content, *Agave tequilana* bagasse is an excellent candidate for the extraction and utilization of its components. In this study, alkaline cooking, followed by five stages of bleaching, was employed to obtain soluble-grade cellulose pulp. The obtained soda pulp material had a Kappa number (KN) of 23 ± 3, viscosity (μ) of 11.53 to 10.18 cp, degree of polymerization (DP) of 830 to 750, brightness of 87.5%, and percentage of alpha-cellulose (α) of 81 ± 3 at 94 ± 3%. The obtained material was characterized using X-ray diffraction, Fourier-transform infrared spectroscopy, and scanning electron microscopy to compare its properties with published information. The waste of *A. tequilana* Weber var. azul produced pulp with a high percentage of alpha cellulose and a high crystallinity degree. This methodology is novel and simple for the production of soluble-grade cellulose pulp, a raw material for the production of cellulose nanocrystals.

Contact information: a: Departamento de Ingeniería de Proyectos; b: Departamento de Madera Celulosa y Papel, c: Departamento de Química; d: Departamento de Ingeniería Química, Centro Universitario de Ciencias Exactas e Ingenierías, Universidad de Guadalajara, Blvd. Marcelino García Barragán #1421, Esq Calzada Olímpica, Guadalajara, Jalisco, 44430 México;
* Corresponding authors: salgaren@hotmail.com; emmarebecamacias@hotmail.com

INTRODUCTION

The bagasse of *Agave tequilana* Weber var. azul is a fibrous, highly moist feedstock (80%), mainly composed of cellulose (70 to 80%), lignin (15 to 20%), and hemicelluloses (5 to 10%) (Ponce-Reyes *et al.* 2014). Because the bagasse is hard and difficult to transport, use, and process, it is considered a waste that is being disposed in inadequate areas, causing several environmental concerns such as changes in soil fertility and phytosanitary problems. In addition, the waste is rich in residual sugars, which makes it an ideal substrate for microbial fermentation and pest proliferation, especially insects and rodents, causing an extremely bad odor and potential health hazards (Rodríguez Macías *et al.* 2010; Salcedo Luna *et al.* 2010; Satyanrayana *et al.* 2013). Although there are alternative uses to bagasse, such as a composting material and as an element in the manufacture of handicrafts, fill mattresses, and production of light bricks, the bagasse waste generated is much higher than its alternative uses (Granados Sánchez 1993; Colunga García-Marín 2007).

On the other hand, the increasing demands for greener technologies and products have led researchers to study the feasibility of biodegradable and renewable raw materials obtained from a variety of botanical species and agroindustrial wastes (Ramires and Dufresne 2011). In this sense, the present work aims to re-utilize the bagasse of *Agave tequilana* Weber var. azul as a raw material for the production of soluble-grade cellulose, in a way that decreases its environmental impact and contributes to the preservation of the environment. Besides, tequila bagasse possesses several advantages in comparison to alternative lignocellulosic feedstock, as it is considered a waste material with a higher content of cellulose and α-cellulose (Iñiguez-Covarrubias *et al.* 2001; Balam-Cocom *et al.* 2006).

Cellulose is the most abundant renewable plant material produced on earth, with an estimated annual production of 7.5×10^{10} tons (Bolio-López *et al.* 2011; Carchi 2014). Cellulose is approximately one-third of plant tissue as it is widely distributed in the plant cell walls, particularly stems, trunks, and woody parts. Cellulose is exclusively composed of β-glucose molecules and its chemical formula is $(C_6H_{10}O_5)_n$. It is a solid, white, odorless, and tasteless polymer, and insoluble in water, alcohol, and ether (Kalia *et al.* 2011; Mariano *et al.* 2014). In most natural fibers, the holocellulose content, which comprises the cellulose and hemicellulose, is in the range 60 to 80%, complemented with 5 to 20% of lignin (phenolic reticulated polymer responsible for thickening and stiffening of the plant), and up to 5% of pectin and water. In addition, the fibers contain low percentages of wax, also known as extractives or low molecular weight sugars (Morán *et al.* 2008).

Cellulose pulp can be obtained from mechanical, chemical, thermo-mechanical, chemo-mechanical and biological processes from wood or other plants (natural fibers). The traditional pulping process renders relatively low yields of approximately 40 to 60% of the original material for plant leaves (Jiménez Muñoz *et al.* 2014). There are three standard chemical processes for making pulp, the sulfite, kraft, and soda processes and the yield of pulp is dependent on the chemical composition of the source, ranging between 40 and 55 for different kinds of wood (May 1980). Soluble-grade cellulose pulp is cellulose without contaminant molecules, such as lignin, and hemicelluloses, and it is commonly obtained through a series of processes consisting of pulping followed by bleaching. The whole process consists of several stages, where an isothermal bath at constant temperature in order to hydrolyze the hemicelluloses and facilitate its extraction (60 to 80 ℃) for a certain period of time (2 to 4 h) (Ponce-Reyes *et al.* 2014; Robles *et al.* 2015). The bleaching procedures are applied depending on the Kappa number (KN) obtained from the pulp under the TAPPI T236 om-06 standard (2006), which determines the lignin content of the pulp. A higher KN indicates a higher lignin content. Chlorine dioxide (ClO_2) is one of the bleach reagents used to separate and eliminate residual lignin and some sugars of low molecular weight from cellulose in the pulp (Robles *et al.* 2015). Other common reagents include sodium hydroxide (NaOH), which extracts the residual lignin from the pulp after the ClO_2 stage and removes the hemicelluloses; alternatively hydrogen peroxide (H_2O_2) can help to whiten cellulose by eliminating those residues that could not be extracted by the ClO_2 and NaOH stages of treatment (Casillas *et al.* 2019).

Second, is necessary to evaluate the molecular chain degradation of cellulose, which is the soluble grade-cellulose, performing a viscosity test (μ) and the degree of polymerization (DP) following the TAPPI T230 om-13 (2013) standard, the DP values for "technical cellulose pulp" are suitable in the range of 200 to 1000 (Peng *et al.* 2011). This procedure is performed prior and after the bleaching process to determine possible internal structure damage of cellulose caused by chemical

degradation. Besides, is also necessary to obtain the percentage of α-, β-, and γ-cellulose using the TAPPI T203 cm-09 (2009) standard. The α-cellulose is one of the molecular structural components that cannot be degraded *via* NaOH due to its high molecular weight. A degree of polymerization greater than 500 and α-cellulose content greater than 90% are the principal characteristics of dissolving pulp (Casillas *et al.* 2019). β-cellulose is the structural part with the lowest molecular weight, and possess an amorphous structure. However, β-cellulose is responsible for molecular chain flexibility. In contrast, gamma-cellulose is hemicelluloses and residual low molecular weight sugars that do not belong directly to the molecular structure but are attached to it physically, so they do not represent any direct property of cellulose (Libby 1968; Hubbe *et al.* 2008).

　　　　Many reports in the literature describe obtaining cellulose pulp from various types of agave. Leaves of *Agave angustifolia* were used to obtain cellulose pulp (cellulose 97% and the DP was not reported); this pulp was recycled to produce cellulose nanocrystals (CNC) (Rosli *et al.* 2013). Nanoparticles of *Agave sisalana* fiber were produced with bleached cellulose pulp; this cellulose had a DP of 1035 and 90% of cellulose (Siqueira *et al.* 2010). Bagasse of *Agave tequilana* Weber var. azul was the source to get CNF and CNC, in the process, the cellulose pulp was obtained, but α-cellulose and DP were not reported (Siqueira *et al.* 2010). Nevertheless, bagasse of *Agave tequilana* Weber var azul was used to obtain cellulose pulp, and among the reported characteristics of this pulp, there was a DP of 173 and 89 % of α-cellulose (Lomelí *et al.* 2018). However, a method to obtain only pure soluble-grade cellulose, α-cellulose, without drastically decreasing of the DP value, from the bagasse of *A. tequilana* Weber var. azul has not yet been described.

　　　　In this sense, in the present work it is proposed to utilize agroindustrial wastes, bagasse of *Agave tequilana* Weber var. azul, as raw material for the production of soluble-grade cellulose by means of a novel methodology consisting of a chemical cooking followed by a five–stage bleaching process, suggesting the use of this material as a possible solution to environmental problems.

EXPERIMENTAL

Materials

　　　　Bagasse from *Agave tequilana* Weber var. Azul was kindly donated by Mundo Agave (Tequila, Mexico). Sodium hydroxide (NaOH, 97% purity), potassium permanganate (KMnO$_4$, 0.1 N, 97% purity), sulfuric acid (H$_2$SO$_4$, 97% purity), potassium iodide (KI, 97% purity), sodium chlorite (NaClO$_2$, 97% purity), hydrochloric acid (HCl, 37% purity), and hydrogen peroxide (H$_2$O$_2$, 30% purity) were acquired from Golden Bell Reactivos (Zapopan, México). Anthraquinone (97% purity) and cupriethylenediamine (CED, 1 M, 97% purity) were obtained from Sigma-Aldrich (Toluca, México). Potassium dichromate solution (K$_2$Cr$_2$O$_7$, 0.5 N, 96% purity) and ferrous ammonium sulfate ((NH$_4$)$_2$Fe(SO$_4$)$_2$·6H$_2$O, 0.1 N, 9% purity) were obtained from HYCEL Reactivos Químicos (Zapopan, México). Sodium thiosulfate (Na$_2$S$_2$O$_3$, 0.1 N, 96% purity) was from Karal Reactivos Analíticos (León, México).

Methods

Obtaining and characterizing cellulose pulp

The bagasse of *Agave tequilana* Weber var. azul was washed until the mellow was removed and the sugars and parenchymal cells were not detected, and then dried at room temperature. Next, the bagasse was cooked using a solution of 20% NaOH, 0.1% anthraquinone, at a hydromodule ratio of 5:1, for 90 min at 170 ℃ in a rotating stainless steel reactor. The resulting pulp was washed and filtered using a stainless steel mesh (0.40 mm).

The characterization of the cellulose pulp was determined from the Kappa number (KN) under the TAPPI T236 cm-06 (2006) standard. The viscosity (μ) and degree of polymerization (DP) were determined under the TAPPI T230 om-13 (2013) standard. The amounts of α-, β-, and γ-cellulose were determined by the TAPPI T203 cm-09 (2009) standard. The reported values are the average of at least two independent measurements.

Scanning electron microscopy (SEM)

The morphology of the untreated fibers and treated fibers were analyzed *via* scanning electron micrographs for several samples, using a TESCAN MIRA 3 high-resolution microscope (Micra Nanotecnología, Ciudad de México, México) at 10 kV accelerating voltage and a working distance of 15 mm. The samples were coated with a sputter layer of gold beforehand (SPI-module sputter coater; Micra Nanotecnología, Ciudad de México, México).

Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of the untreated fibers and treated fibers were measured with a spectrophotometer (Spectrum GX; Perkin Elmer, Guadalajara, México) using the attenuated total reflectance technique (ATR). The spectra were obtained from the average of 16 scans with a resolution of 4 cm^{-1}, in the frequency range of 4000 to 700 cm^{-1}.

X-ray diffraction (XRD)

X-ray diffraction of untreated fibers and treated fibers was completed using an X-ray diffractometer (EMPYREAN; PANanalytical, Ciudad de México, México) at 45 kV and 40 mA, with an angle of incidence of 5° to 70°, a step of 0.2 and a time per step of 30 s, using CuKα radiation in a Ni filter and a graphite monochromator. The percentage of crystallinity was calculated using the Rietveld method (Snyder 1993), with the MAUD program (University of Trento, MAUD version 2.1, Trento, Italia).

Obtaining soluble grade cellulose pulp

The cellulose pulp was subjected to a five-stage bleaching process consisting of: (1) the addition of chlorine dioxide until the concentration of ClO_2 was 15% of the KN value obtained just after the alkaline cooking ([ClO_2] = 0.15 KN), (2) alkaline extraction of residual lignin with NaOH, the NaOH concentration should be 60% of the ClO_2 concentration used in step 1 ([NaOH] = 0.6 [ClO_2]), (3) addition of 2.5% H_2O_2 and the addition of 2% NaOH in aqueous solution, (4) addition of 2% ClO_2 with a consistency of 10% m/v in an isothermal bath at 60 ° C for 1 h, and (5) an alkaline extraction with 10% NaOH at 25 °C for 2 h for the elimination of hemicelluloses. In all stages, the pulp was washed, centrifuged, and homogenized.

*Soluble-grade cellulose pulp characterization*

After the bleaching process, the brightness percentage was determined under the TAPPI T452 om-08 (2008) standard, by making sheets for physical tests, under the TAPPI T205 SP-02 (2002) standard. The brightness was determined in a chromatic analyzer Elrepho 3000 series (Datacolor International, Lawrenceville, NJ, USA). The lightness value "*L*" and the color channels "*a*" and "*b*" from the chromaticity spectrum and the percentages of brightness at 440 and 460 nm of wavelength were obtained. The percentage of brightness was interpolated to 457 nm.

The viscosity and degree of polymerization were determined using the TAPPI T230 om-13 (2013) standard, and the percentage of α-cellulose was obtained according to the TAPPI T203 cm-09 (2009) standard.

RESULTS AND DISCUSSION

Alkaline Cooking and Bleaching Process

After pulp cooking, a yield of 40% of pulp in bagasse was achieved. After the bleaching processes, this value decreased to 30%, with respect to the amount of initial bagasse used. This effect was due to the elimination of hemicelluloses present in the pulp, which represent 15% of the total bagasse weight. Figure 1 shows the pulp before and after the bleaching treatment, where a change of color from brown to white is noticed.
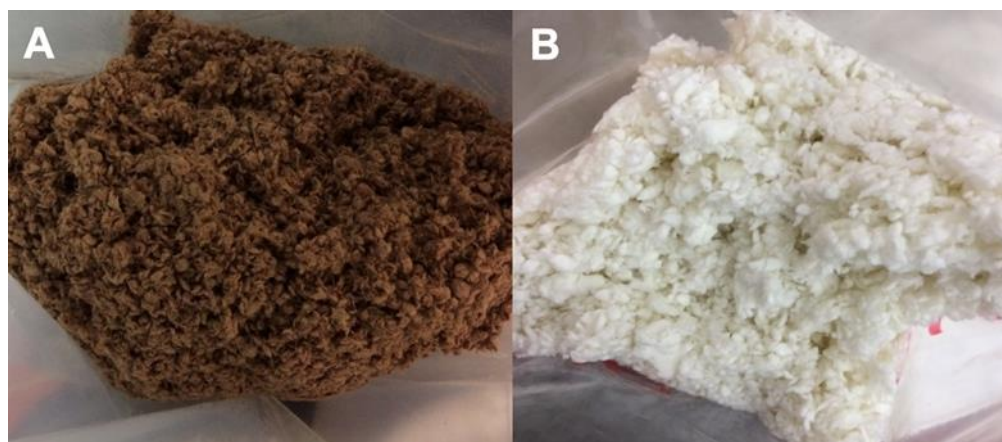
Fig. 1. Pulp photographs: A) before and B) after the bleaching process

For the unbleached cellulose pulp, a remarkably high KN of 23 ± 3 was obtained, indicating a high lignin content in the pulp (Iakovlev *et al.* 2014; Jaouadi *et al.* 2015). The analysis of the viscosity and DP before and after the bleaching process yielded values of 11.53 cp, 830, and 10.18 cp, 750, respectively. The decrease in DP indicated that the molecular structure of cellulose did not suffer severe chemical attack during the bleaching process. The percentage of α-cellulose increased considerably after the bleaching process, from 81% ± 3 to 94% ± 3, indicating that soluble-grade cellulose was obtained.

Several authors have reported obtaining soluble-grade cellulose from the bagasse of *Agave angustifolia* and *Agave sisalana* by cooking with a 4% NaOH solution, at temperatures ranging from 70 to 80 °C for 2 h in a digester. Then, a bleaching treatment was performed using 1.7% (w/v) $NaClO_2$ from 70 to 80 °C for 4 h (Rosli *et al.* 2013). In this case, the authors used agave leaves, the most rigid part of the plant, and obtained a material with α-cellulose of 97%. In the current case, the

value was lower because the agave came from waste residues. In the same way, *Agave salmiana* soluble-grade cellulose was obtained with 5% NaOH using similar reaction conditions previously reported. The bleaching treatment consisted of a solution of 11% H_2O_2 at 50 °C for 90 min (Chávez-Guerrero *et al.* 2017); cellulose pulp without lignin and hemicelluloses was obtained from *Agave tequilana* Weber var. azul, after addition of 5 M NaOH at 80 °C for 3 h in a rotating digester (Ponce-Reyes *et al.* 2014). In other reports, 1.8 M NaOH (1:20 w/v) at 120 °C for 90 min was used (Robles *et al.* 2016), obtaining an approximate pulp yield of 40% by weight, using bleaching treatments with H_2O_2 (3 M), $NaClO_2$ (0.2 M), and ClO_2 (2 to 3% by weight) at temperatures between 60 and 75 °C for 2 to 3 h in an isothermal bath. In some cases, the addition of anthraquinone (AQ) helps NaOH penetrate the fiber structure and subsequently to more easily extract the lignin and low molecular weight sugars (Hubbe *et al.* 2008; Robles *et al.* 2015). In all these cases, the production of pulp with yields of α-cellulose higher than 90% have not been reported, with the exception of Rosli *et al.* (2013). The best purity has been 89%, but with DP values less than 300 (Lomelí-Ramírez *et al.* 2018). In this work, the authors combined the processes mentioned earlier to obtain soluble-grade α-cellulose with purity above 90%.

Pulp Brightness Process

Table 1 shows the values of the chromaticity parameters and the percentage of brightness for wavelengths of 440 and 460 nm, after extrapolating to 457 nm and averaging, as stipulated by the TAPPI T452 om-08 (2008) standard. A brightness value of 87.5% was obtained, similar to the results reported in the literature (Andrade and Colodette 2014; Jaouadi *et al.* 2015). The obtained results give the material a high-added value, as special chemical methods were not employed, in comparison to other reports, where a near brightness of 90% was reported.

Table 1. Chromaticity Parameters

Sample	*L*	*a*	*b*	Brightness (%)	
				440 nm	460 nm
1	92.1	-0.45	2.94	87.31	88.62
2	91.97	-0.44	2.72	86.64	87.92
3	91.37	-0.44	2.79	85.23	86.54

SEM Analysis

Figure 2a shows a scanning electron micrograph of the longitudinal section of the agave bagasse fiber, which looks similar to many vegetable fibers (Esmeraldo *et al.* 2010; Ferraz *et al.* 2011; Carvalho *et al.* 2010). The longitudinal arrangement of a large number of fibrils in tube form is easily observed, with diameters of approximately 200 μm. Material is mixed between the fibers, which could be lignin, hemicelluloses, and extractives. The latter could be amorphous waxes and low molecular weight sugars (Bessadok *et al.* 2008; Satyanrayana *et al.* 2013). The fibers showed a space between them, and in some cases, pores that function as channels that can increase and retain the volume of water (Rodríguez Macías *et al.* 2010; Singha and Rana 2010). Defects in the surface were also visible, demonstrating that it is not a homogeneous surface. Some shapes and structural parts of other fibers are not perfectly cylindrical, as commonly occurs during the sugar extraction process to which the agave bagasse is subjected during the process of the production of tequila (Bessadok *et al.* 2008; Robles *et al.* 2018). Figure 2b shows the micrograph of the pulp after alkaline cooking. The fibrils that were observed in Fig. 2a are already

separated, which indicates that the cooking process was completed successfully. Another important feature is that the fibers are no longer rigid, which means that the extractives and a large portion of lignin were removed. The fiber diameters were approximately 18 ± 5 μm, which was consistent with the reported values of previous works for different agaves. *Agave tequilana* showed fiber diameters from 16 to 45 μm, *A. angustifolia* from 9 to 110 μm, and *A. salmiana* from 20 to 30 nm (Rosli *et al.* 2013; Espino *et al.* 2014; Chávez-Guerrero *et al.* 2017). Figure 2c shows the micrograph of the bleached pulp. It can be seen that the fibrils were, in turn, composed of smaller fibers with diameters between 5 ± 3 μm. This indicated that residual lignin and hemicelluloses that remained after the cooking process were eliminated, as the fibers were less rigid than they had been before cooking (Fig. 2b). It can be understood that these small fibers contain the molecular structure of cellulose, where α-, β-, and γ-celluloses are found. Similar works with plants from the same family as *Agave tequilana* demonstrated that an aggressive hydrolysis of bleached pulp must be performed to break the amorphous regions (β- and γ-celluloses) of the cell wall, leaving only the crystalline region (α-cellulose) (Siqueira *et al.* 2011; Espino *et al.* 2014).
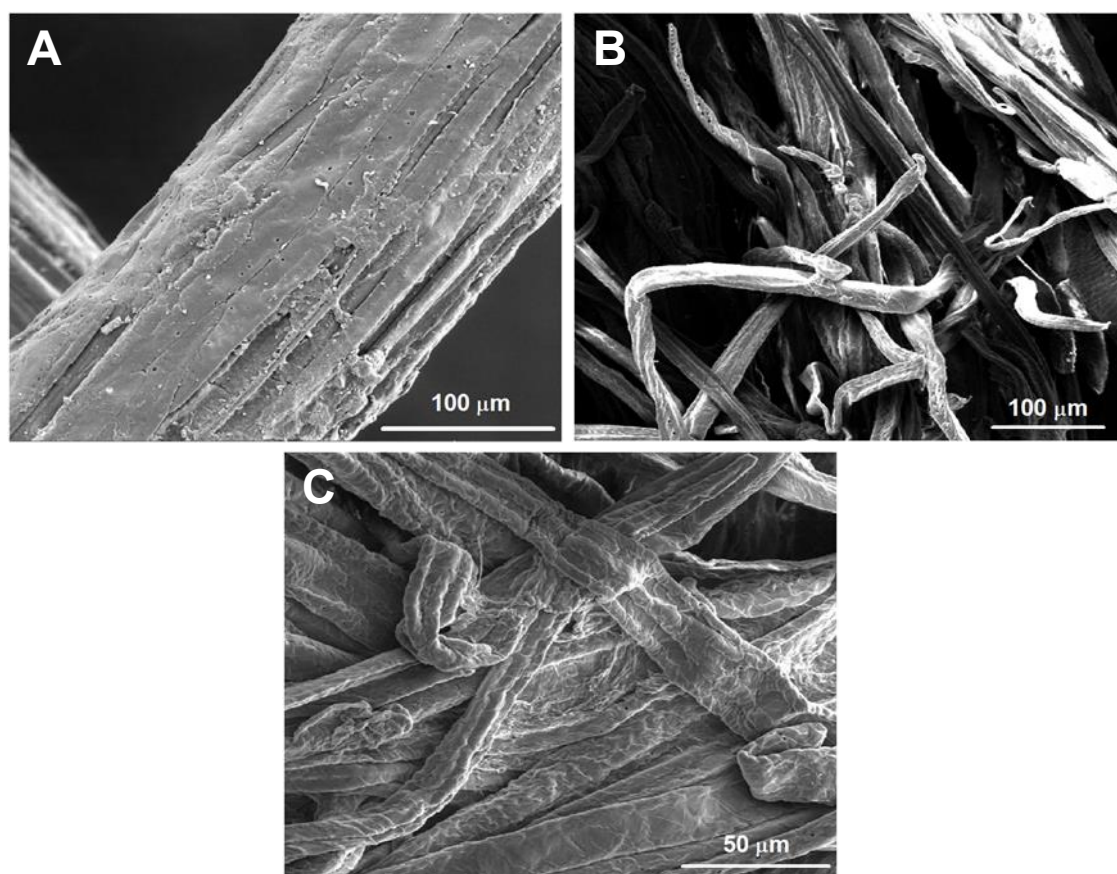

Fig. 2. SEM micrographs of a) agave bagasse, b) pulp after the cooking process, and c) bleached pulp

FTIR

Figure 3 shows the FTIR spectra of the agave bagasse fiber, the pulp obtained from the alkaline cooking, and the pulp obtained after the bleaching process. The agave fiber shows characteristic peaks belonging to cellulose and lignin, where bands of C-H bonds (2918 and 2851 cm^{-1}: asymmetric and symmetric tension vibrations, respectively), C-H bonds (1318 cm^{-1} [crystalline band] (Xu *et al.* 2013; Robles *et al.*

2018]), C-O bonds (1054 and 1030 cm^{-1}), C-O-C bond (1160 cm^{-1}), and a broad O-H maximum between 3600 and 3200 cm^{-1}, as well as bands at 1335 and 1205 cm^{-1} were observed. A small peak at 1734 cm^{-1} corresponding to carbonyl groups (C=O) was attributed to the presence of acetyl ester and carbonyl aldehyde groups in hemicelluloses and lignins (Bessadok *et al.* 2008; Singha and Rana 2010). A band observed at 1610 cm^{-1} corresponds to the vibration of the aromatic ring (C=C stretching). Another vibration in the aromatic ring at 1500 cm^{-1} and the C=C deformation at 1450 cm^{-1} corresponds to lignin (Garside and Wyeth 2006; Xu *et al.* 2013). The signal at 1625 cm^{-1} apparently did not belong to the fiber. However, its presence has been associated with absorbed water and is commonly observed in lignocellulosic spectra (Tronc *et al.* 2007). At 898 cm^{-1}, there is the vibration of the anomeric carbon group of the carbohydrate, C1-H, and at 1635 cm^{-1} the band corresponds to adsorbed water (Bessadok *et al.* 2008; Contreras *et al.* 2010; Yu *et al.* 2013; Anwar *et al.* 2015).
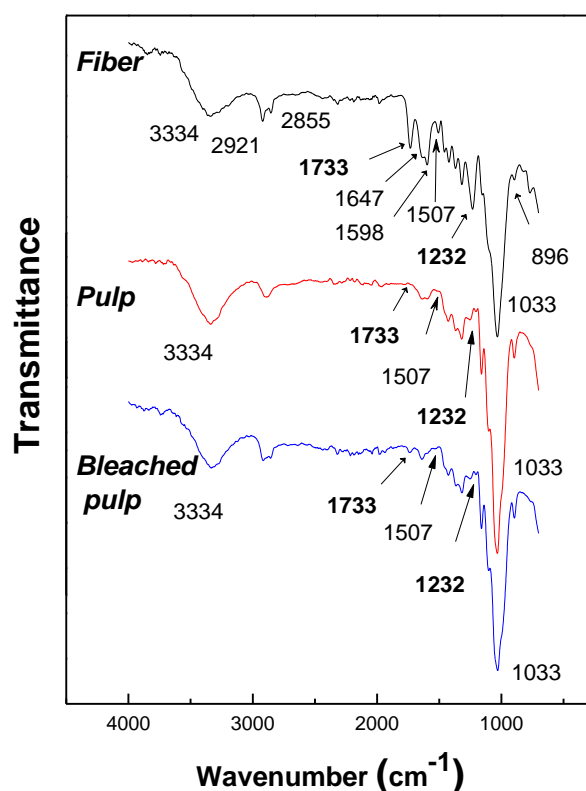
Fig. 3. FTIR spectra of agave fiber, pulp, and bleached pulp

The signals recorded for the bleached pulp and pulp were similar to the signals observed in the fiber spectrum. However, a decrease of the peaks referring to hemicelluloses and lignin was clearly seen in the pulp spectrum, while the peaks were no longer observed in the bleached pulp at 1733, 1507, and 1232 cm^{-1}, which were attributed to $\upsilon_{C=O}$ and $\upsilon_{C=C}$ aromatic ring, and δ_{C-H} from aromatics substituted, respectively. This indicated that during alkaline cooking large proportions of the lignin and hemicelluloses were eliminated, and after bleaching they were totally eliminated. Another important point was the so-called crystalline band (1318 cm^{-1}), which is the peak that shows the preferential directional arrangement of α-celluloses. It was observed that this band was more defined in the bleached pulp spectrum, which was a possible indication of obtaining soluble-grade pulp. Another indication was the signal observed at 3334 cm^{-1}, which was bigger in the spectrum of bleached pulp, and

this can be a symptom of crystallinity, because the hydrogen bond is less flexible in a crystalline structure (Dong *et al.* 1998; Montanari *et al.* 2005).

The areas of the peaks from the FTIR spectra were obtained by deconvolution and divided by the peak area located at 896 cm^{-1} that was constant for all spectra, the values are shown in Table 2. The results corroborate the disappearance of some peaks (1733, 1507, and 1232 cm^{-1}), where hemicelluloses and lignin exhibit signals, as well as the decrease of other peaks that overlap with those observed in soluble-grade cellulose (1318, 1598, and 1033 cm^{-1}).

Table 2. Area Ratio from FTIR Spectra ($A_\lambda/A_{\lambda = 896}$)

λ (cm^{-1})	$A_\lambda/A_{\lambda = 896}$		
	Fiber	**Pulp**	**Bleached Pulp**
3408	1.07	1.64	1.46
1733	1.17	0.14	0.03
1598	1.48	0.72	0.78
1507	0.52	0.28	0.03
1318	0.93	1.57	1.57
1232	1.86	0.09	0.08
1033	3.81	3.78	3.51

XRD

The crystallinity in lignocellulosic materials is a characteristic attributed to the cellulose structure, which consists of polymeric glucopyranose chains arranged helically and strongly attached by hydrogen bonds (Tronc *et al.* 2007). Figure 4 shows the comparison of the diffractograms of the agave bagasse fiber, the pulp obtained from the alkaline cooking, and the pulp after the bleaching process. It was observed that the signals associated with cellulose were present in all cases, but with different intensity and broadening due to the amount of crystalline cellulose present in each sample and its different components. The widened signals were associated with the presence of non-crystalline particles. This can be seen in the agave fiber and in the pulp after cooking, in which the signals at 2θ = 14.63º, 16.85º, and 22.27º were wider and with lower intensity, showing the planes (1-10), (110), and (200). This was related to hemicelluloses or amorphous cellulose (Park *et al.* 2010; Poletto *et al.* 2013). In contrast, the bleached pulp had sharper signals and peaks at 2θ = 14.4º (101), 16.45º (10-1), 22.43º (002), and 34.92º (040).

It was observed that the planes were not the same and their angles changed, showing a clearer and weaker signal than the other samples. This indicates a higher crystallinity of the pulp and that α-cellulose was obtained (Tronc *et al.* 2007; Robles *et al.* 2015). The diffractograms also illustrate the elimination of impurities and increase in crystallinity as the cooking and bleaching processes were completed, which was corroborated by the increase in the peak intensity.

Using the Rietveld method, a crystallinity value of 79.2% was determined for the bleached pulp (Fig. 5). This value was relatively greater than the values found in literature, which were in the range of 51 and 78.5% (Pires de Figueiredo and Furlan Ferreira 2014; Lomelí-Ramírez *et al.* 2018). This, together with the other characterization techniques, proves that soluble-grade cellulose was obtained.

This cellulose presents unique applications and high value, as it can serve as the raw material for the production of cellulose nanocrystals, a nanomaterial that is being used in various areas of research such as medicine, chemistry, biology, and engineering, among others.
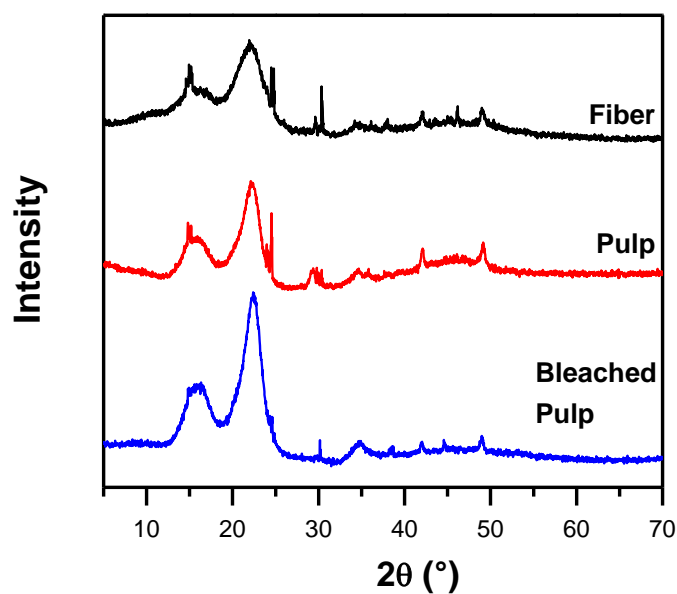
Fig. 4. XRD diffractograms of agave fiber, pulp, and bleached pulp
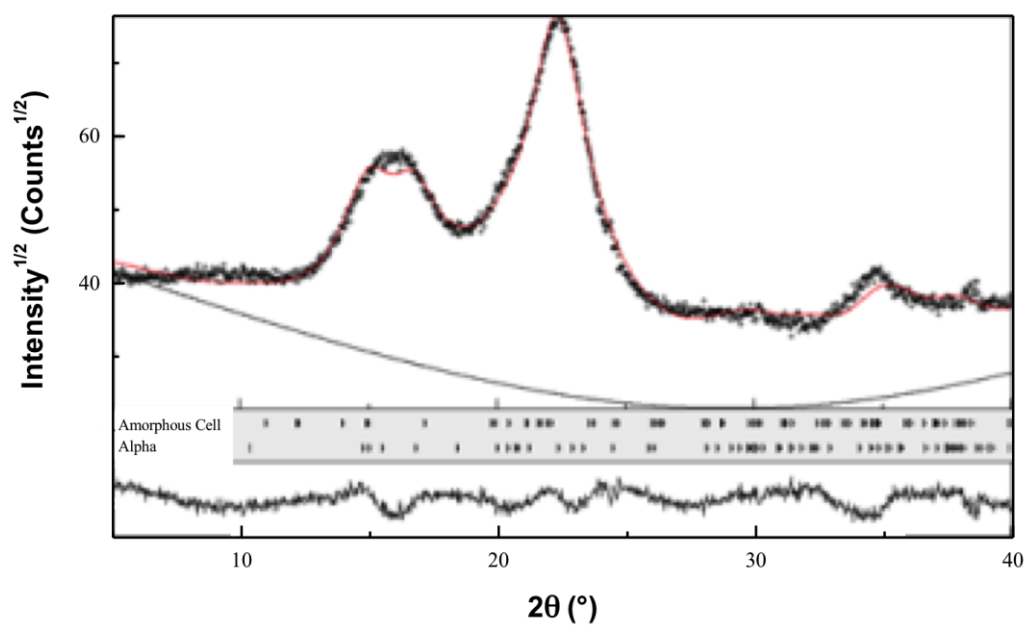

Fig. 5. XRD of the bleached pulp analyzed *via* the Rietveld method

CONCLUSIONS

1. Cellulose pulp was successfully obtained with a Kappa number (KN) of 23 ± 3. The yield of alkaline cooking was 40%, the α-cellulose was 83 ± 3%, viscosity was 10.18 cp, and the degree of polymerization (DP) was 830. In the bleaching process, approximately 10% of the total pulp was lost.

2. Soluble-grade cellulose had an α-cellulose value of 94 ± 3%, a brightness of 87.5%, a viscosity of 11.53 cp, and a DP value of 750. With the bleaching process, the value of α-cellulose increased, while viscosity and DP were not considerably affected.

3. The SEM micrographs showed that the agave fibers were gradually separated until they reached the soluble grade of cellulose pulp. In FTIR spectrograms, the disappearance of peaks attributed to lignin and extractives were observed, thereby contributing to the fact that the bleaching process eliminated these pulp components.

4. The high crystallinity was due to the fact that the -OH peak area of the pulp increased. The XRD analysis indicated the elimination of impurities and the increase in crystallinity as the cooking and bleaching processes were performed. Using the Rietveld method, a crystallinity of 79.2% was determined for the bleached pulp. These results indicate that soluble-grade cellulose pulp was successfully obtained.

ACKNOWLEDGMENTS

REFERENCES CITED

Andrade, M. F., and Colodette, J. L. (2014). "Dissolving pulp production from sugar cane bagasse," *Industrial Crops and Products* 52, 58-64. DOI: 10.1016/j.indcrop.2013.09.041

Anwar, B., Bundjali, B., and Arcana, I. M. (2015). "Isolation of cellulose nanocrystals from bacterial cellulose produced from pineapple peel waste juice as culture medium," *Procedia Chemistry* 16, 279-284. DOI: 10.1016/j.proche.2015.12.051

Balam-Cocom, R. J., Duarte-Aaranda, S., and Canché-Escamilla, G. (2006). "Obtention and characterization of composites of henequen 'pineapple' fibers and polypropylene," *Revista Mexicana de Ingeniería Química* 5(1), 39-44.

Bessadok, A., Marais, S., Roudesli, S., Lixon, C., and Métayer, M. (2008). "Influence of chemical modifications on water-sorption and mechanical properties of Agave fibres," *Composites Part A: Applied Science and Manufacturing* 39(1), 29-45. DOI: 10.1016/j.compositesa.2007.09.007

Bolio-López, G. I., Valadez-González, A., Veleva, A., and Andreeva, A. (2011). "Cellulose whiskers from agro-industrial banana wastes: Isolation and characterization," *Revista Mexicana de Ingeniería Química* 10(2), 291-299.

Carchi, D. (2014). *Aprovechamiento de los Residuos Agrícolas provenientes del cultivo de Banano para obtener Nanocelulosa* [*Use of Agricultural Wastes from*

Banana Harvest to Obtain Nanocellulose], Master's Thesis, Universidad de Cuenca, Cuenca, Ecuador.

Carvalho, K. C. C., Mulinari, D. R., Voorwald, H. J. C., and Cioffi, M. O. H. (2010). "Chemical modification effect on the mechanical properties of hips/ coconut fiber composites," *BioResources* 5(2), 1143-1155. DOI: 10.15376/biores.5.2.1143-1155

Casillas, R. R., López López, M. del C., Becerra Aguilar, B., Dávalos Olivares, F., and Gundappa Satyanarayana, K. (2019). "Obtaining dissolving grade cellulose from the huizache (*Acacia farnesiana* L. Willd.) Plant," *BioResources* 14(2), 3301-3318.

Chávez-Guerrero, L., Sepúlveda-Guzmán, S., Rodríguez-Liñan, C., Silva-Mendoza, J., García-Gómez, N., and Pérez-Camacho, O. (2017). "Isolation and characterization of cellulose nanoplatelets from the parenchyma cells of *Agave salmiana*," *Cellulose* 24(9), 3741-3752. DOI: 10.1007/s10570-017-1376-9

Colunga García-Marín, P., Larqué Saavedra, A., Eguiarte, L. E., and Zizumbo-Villareal, D. (2007). "Una mirada al horizonte [A look to the horizon]" in: *En lo Ancestral hay Futuro: Del Tequila, los Mezcales y Otros Agaves [In the Ancestral There is Future: From Tequila, Mezcal and Other Agaves]*, P. Colunga-García Marín, A. Larqué Saavedra, L. E. Eguiarte, and D. Zizumbo-Villareal (eds.), CICY, CONACYT, CONABIO, SEMARNAT, INE, Ciudad de México, México.

Contreras, H. J., Trujillo, H. A., Arias, G., Pérez, J., and Delgado, E. (2010). "Espectroscopia ATR-FTIR de celulosa: Aspecto instrumental y tratamiento matemático de espectros [ATR-FTIR cellulose spectroscopy: Instrumental aspect and mathematical treatment of spectra]," *e-Gnosis* 8(9), 1-13.

Dong, X. M., Revol, J.-F., and Gray, D. G. (1998). "Effect of microcrystallite preparation conditions on the formation of colloid crystals of cellulose," *Cellulose* 5(1), 19-32. DOI: 10.1023/A:1009260511939

Esmeraldo, M. A., Barreto, A. C. H., Freitas, J. E. B., Fechine, P. B. A., Sombra, A. S. B., Corradini, E., Mele, G., Maffezzoli, A., and Mazzetto, S. E. (2010). "Dwarf-green coconut fibers: A versatile natural renewable raw bioresource. Treatment, morphology, and physicochemical properties," *BioResources* 5(4), 2478-2501. DOI: 10.15376/biores.5.4.2478-2501

Espino, E., Cakir, M., Domenek, S., Román-Gutiérrez, A. D., Belgacem, N., and Bras, J. (2014). "Isolation and characterization of cellulose nanocrystals from industrial by-products of *Agave tequilana* and barley," *Industrial Crops and Products* 62, 552-559. DOI: 10.1016/j.indcrop.2014.09.017

Ferraz, J. M., Del Menezzi, C. H. S., Teixeira, D. E., and Martins, S. A. (2011). "Effects of treatment of coir fiber and cement/fiber ratio on properties of cement-bonded composites," *BioResources* 6(3), 3481-3492. DOI: 10.15376/biores.6.3.3481-3492

Garside, P., and Wyeth, P. (2006). "Identification of cellulosic fibres by FTIR spectroscopy differentiation of flax and hemp by polarized ATR FTIR," *Studies in Conservation* 51(3), 205-211. DOI: 10.1179/sic.2006.51.3.205

Granados Sánchez, D. (1993). *Los Agaves en México*, Universidad Autónoma Chapingo, (ed.), Universidad Autónoma Chapingo, Ciudad de México, México

Hubbe, M. A., Rojas, O. J., Lucia, L. A., and Sain, M. (2008). "Cellulosic nanocomposites: A review," *BioResources* 3(3), 929-980. DOI: 10.15376/biores.3.3.929-980

Iakovlev, M., You, X., Van Heiningen, A., and Sixta, H. (2014). "SO_2 – ethanol – water (SEW) fractionation process: Production of dissolving pulp from spruce," *Cellulose* 21(3), 1419–1429. DOI: 10.1007/s10570-014-0202-x

Iñiguez-Covarrubias, G., Díaz-Teres, R., Sanjuan-Duenas, R., Anzaldo-Hernández, J., and Rowell, R. M. (2001). "Utilization of by-products from the tequila industry. Part 2: Potential value of *Agave tequilana* Weber *azul* leaves," *Bioresource Technology* 77(2), 101-108. DOI: 10.1016/S0960-8524(00)00167-X

Jaouadi, M., M'sahli, S., and Sakli, F. (2015). "Optimization and characterization of pulp extracted from the *Agave Americana* L. fibers," *Textile Research Journal* 79(2), 110-120. DOI: 10.1177/0040517508090781

Jiménez Muñoz, E., Prieto García, F., Prieto Méndez, J., Acevedo Sandoval, O. A., Rodríguez Laguna, R., and Otazo Sánchez, E. M. (2014). "Utilization of waste agaves: Potential for obtaining cellulose pulp," *Ciência e Técnica Vitivinícola* 29(11), 138-152.

Kalia, S., Dufresne, A., Cherian, B. M., Kaith, B. S., Avérous, L., Njuguna, J., and Nassiopoulos, E. (2011). "Cellulose-based bio- and nanocomposites: A review," *International Journal of Polymer Science* 2011(1), Article ID 837875. DOI: 10.1155/2011/837875

Libby, C. E. (1968). *Ciencia y Tecnología Sobre Pulpa y Papel*, C. E. Libby (ed.), CECSA, Ciudad de México, México.

Lomelí-Ramírez, M. G., Valdez-Fausto, E. M., Rentería-Urquiza, M., Jiménez-Amezcua, R. M., Anzaldo, J., Torres-Rendón, J. G., and García-Enriquez, S. (2018). "Study of green nanocomposites based on corn starch and cellulose nanofibrils from *Agave tequilana* Weber," *Carbohydrate Polymers* 201, 9-19. DOI: 10.1016/j.carbpol.2018.08.045

Mariano, M., El Kissi, N., and Dufresne, A. (2014). "Cellulose nanocrystals and related nanocomposites: Review of some properties and challenges," *Journal of Polymer Science Part B: Polymer Physics* 52(12), 791-806. DOI: 10.1002/polb.23490

May, R. (1980). "Pulp yields for various processes and wood species," U. S For. Serv. Res. Note FPL-031, (https://www.fpl.fs.fed.us/documnts/fplrn/fplrn031.pdf).

Montanari, S., Roumani, M., Heux, L., and Vignon, M. R. (2005). "Topochemistry of carboxylated cellulose nanocrystals resulting from TEMPO-mediated oxidation," *Macromolecules* 38(5), 1665-1671. DOI: 10.1021/ma048396c

Morán, J., Vazquez, A., and Cyras, V. P. (2008). "Extracción de celulosa y obtención de nanocelulosa a partir de fibra sisal - Caracterización [Cellulose extration and obtaining of nanocellulose from sisal fiber - Characterization]," *Asociación Argentina de Materiales* 1(1), 1-6.

Park, S., Baker, J. O., Himmel, M. E., Parilla, P. A., and Johnson, D. K. (2010). "Cellulose crystallinity index: Measurement techniques and their impact on interpreting cellulase performance," *Biotechnology for Biofuels* 3(10), 1-10.

Peng, B. L., Dhar, N., Liu, H. L., and Tam, K. C. (2011). "Chemistry and applications of nanocrystalline cellulose and its derivatives: A nanotechnology perspective," *Can. J. Chem. Eng.* 89(1), 1191-1206. DOI: 10.1002/cjce.20554

Pires de Figueiredo, L., and Furlan Ferreira, F. (2014). "The Rietveld method as a tool to quantify the amorphous amount of microcrystalline cellulose," *Journal of Pharmaceutical Sciences* 103(5), 1394-1399. DOI: 10.1002/jps.23909

Poletto, M., Pistor, V., and Zattera, A. J. (2013). "Structural characteristics and thermal properties of native cellulose," in: *Cellulose - Fundamental Aspects*, T. van de Ven, and L. Godbout (eds.), Intech Open Limited, London, UK, pp. 45-68. DOI: 10.5772/50452

Ponce-Reyes, C. E., Chanona-Pérez, J. J., Garibay-Febles, V., Palacios-González, E., Karamath, J., Terrés-Rojas, E., and Calderón-Domínguez, G. (2014). "Preparation

of cellulose nanoparticles from agave waste and its morphological and structural characterization," *Revista Mexicana de Ingeniería Química* 13(3), 897-906.

Ramires, E. C., and Dufresne, A. (2011). "A review of cellulose nanocrystals and nanocomposites," *TAPPI Journal* 2011, 7-14.

Robles, E., Fernández-Rodríguez, J., Barbosa, A. M., Gordobil, O., Carreño, N. L. V., and Labidi, J. (2018). "Production of cellulose nanoparticles from blue agave waste treated with environmentally friendly processes," *Carbohydrate Polymers* 183, 294-302. DOI: 10.1016/j.carbpol.2018.01.015

Robles, E., Salaberria, A. M., Herrera, R., Fernandes, S. C. M., and Labidi, J. (2016). "Self-bonded composite films based on cellulose nanofibers and chitin nanocrystals as antifungal materials," *Carbohydrate Polymers* 144, 41-49. DOI: 10.1016/j.carbpol.2016.02.024

Robles, E., Urruzola, I., Labidi, J., and Serrano, L. (2015). "Surface-modified nano-cellulose as reinforcement in poly(lactic acid) to conform new composites," *Industrial Crops and Products* 71, 44-53. DOI: 10.1016/j.indcrop.2015.03.075

Rodríguez Macías, R., Alcantar González, E. G., Iñiguez Covarrubias, G., Zamora Natera, F., García López, P. M., Ruiz López, M. A., and Salcedo Pérez, E. (2010). "Caracterización física y química de sustratos agrícolas a partir de bagazo de agave tequilero [Physical and chemical characterization of agricultural substrates from tequila agave bagasse]," *Interciencia* 35(7), 515-520.

Rosli, N. A., Ahmad, I., and Abdullah, I. (2013). "Isolation and characterization of cellulose nanocrystals from *Agave angustifolia fibre*," *BioResources* 8(2), 1893-1908. DOI: 10.15376/biores.8.2.1893-1908

Salcedo Luna, J., Castro Montoya, A. J., Rico, J. L., and Campos García, J. (2010). "Optimization of acid hydrolysis of bagasse from *Agave tequilana* Weber," *Revista Mexicana de Ingeniería Química* 9(1), 91-97.

Satyanrayana, K. G., Flores-Sahagun, T. H. S., Dos Santos, L. P., Dos Santos, J., Mazzaro, I., and Mikowski, A. (2013). "Characterization of blue agave bagasse fibers of Mexico," *Composites Part A: Applied Science and Manufacturing* 45, 153-161. DOI: 10.1016/j.compositesa.2012.09.001

Singha, A. S., and Rana, R. K. (2010). "Effect of pressure induced graft copolymerization on the physico-chemical properties of bio-fibers," *BioResources* 5(2), 1055-1073. DOI: 10.15376/biores.5.2.1055-1073

Siqueira, G., Tapin-Lingua, S., Bras, J., Da Silva Perez, D., and Dufresne, A. (2011). "Mechanical properties of natural rubber nanocomposites reinforced with cellulosic nanoparticles obtained from combined mechanical shearing, and enzymatic and acid hydrolysis of sisal fibers," *Cellulose* 18(1), 57-65. DOI: 10.1007/s10570-010-9463-1

Siqueira, G., Tapin-Lingua, S., Bras, J., Da Silva Perez, D., and Dufresne, A. (2010). "Morphological investigation of nanoparticles obtained from combined mechanical shearing, and enzymatic and acid hydrolysis of sisal fibers," *Cellulose* 17(6), 1147-1158. DOI: 10.1007/s10570-010-9449-z

Snyder, R. L. (1993). *The Rietveld Method*. R. A. Young (ed.), Oxford University Press, Oxford. ISBN: 0198555776

TAPPI T203 cm-09 (2009). "Alpha-, beta- and gamma-cellulose in pulp," TAPPI Press, Atlanta, GA, USA.

TAPPI T205 sp-02 (2002). "Forming handsheets for physical tests of pulp," TAPPI Press, Atlanta, GA, USA.

TAPPI T230 om-13 (2013). "Viscosity of pulp (capillary viscometer method)," TAPPI Press, Atlanta, GA, USA.

TAPPI T236 om-06 (2006). *"*Kappa number of pulp," TAPPI Press, Atlanta, GA, USA.

TAPPI T452 om-08 (2008). "Brightness of pulp, paper, and paperboard (directional reflectánce at 457 nm)," TAPPI Press, Atlanta, GA, USA.

Tronc, E., Hernández-Escobar, C. A., Ibarra-Gómez, R., Estrada-Monje, A., Navarrete-Bolaños, J., and Zaragoza-Contreras, E. A. (2007). "Blue agave fiber esterification for the reinforcement of thermoplastic composites," *Carbohydrate Polymers* 67(2), 245-255. DOI: 10.1016/j.carbpol.2006.05.027

Xu, F., Yu, J., Tesso, T., Dowell, F., and Wang, D. (2013). "Qualitative and quantitative analysis of lignocellulosic biomass using infrared techniques: A mini-review," *Applied Energy* 104, 801-809. DOI: 10.1016/j.apenergy.2012.12.019

Yu, H. Y., Qin, Z. Y., Liu, L., Yang, X. G., Zhou, Y., and Yao, J. M. (2013). "Comparison of the reinforcing effects for cellulose nanocrystals obtained by sulfuric and hydrochloric acid hydrolysis on the mechanical and thermal properties of bacterial polyester," *Composites Science and Technology* 87, 22-28. DOI: 10.1016/j.compscitech.2013.07.024