Obtaining Dissolving Grade Cellulose from the Huizache (*Acacia farnesiana* L. Willd.) Plant

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Considering that many paper mills have modified their pulp manufacturing processes to produce dissolving grade pulps from a wide variety of woods, which can be used for the production of different end products, attempts have also been made to obtain highly purified pulps using several woods and non-timber as raw materials using chemical routes. This paper is an attempt to overcome the problem of the shortage of commercial timber for pulping purposes wherein non-commercial, widely distributed huizache, a woody plant, was evaluated as a raw material for the production of dissolving grade cellulose using an alkaline sulfur anthraquinone-methanol process with a pre-hydrolysis step and optimized conditions of the process. The pulp obtained from the cooking process was subjected to a sequence of elemental chlorine free bleaching. The pulp was analyzed for its performance during the pulping process, Kappa number, ISO brightness, contents of α, β, and γ cellulose, crystallinity index, degree of polymerization, and viscosity. The obtained results revealed high levels of all these parameters for the pulp produced from *Acacia farnesiana*, suggesting this plant could be considered as a raw material alternative for the production of dissolving grade cellulose, which in turn can be used to produce nanocellulose crystals.

Keywords: Acacia farnesiana; Elemental chlorine free bleaching; Alkaline sulfur anthraquinone-methanol process; Soluble grade pulp; α-Cellulose

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INTRODUCTION

In the last decade, a substantial increase in the global consumption of cellulose and paper products, as well as technological challenges in response to economic and ecological demands have been reported (López *et al.* 2003). In response, many paper mills have modified their pulp manufacturing processes to produce dissolving grade pulps from a wide variety of woody raw materials. Dissolving grade pulps are chemically refined pulp products that have high levels of whiteness and α-cellulose contents (> 90%); they can be used for the production of different end products (Durbak 1993; Woodings 2001).

The production of highly purified pulps using several woods as raw materials and non-timber using sulphite and alkaline processes, combined with an acid pre-hydrolysis stage have been reported (Abad *et al*. 2002; Jahan 2008; Chen *et al.* 2016). There is also a mini review presenting the Chinese perspective regarding the market for dissolving pulp and their technologies (Liu *et al.* 2016). These studies have suggested that the quality of the dissolving grade pulp depends on both the properties of the raw material used and the processing method of the pulp. Considering the fact that possible continuous usage of commercial timber for pulping purposes may lead to shortages of such wood, the study of non-commercial wood, *i.e.* wood that currently does not have a commercial application, as in the case of huizache, can be of great interest for the production of dissolving grade pulp. In view of this, there is need to save the commercial timber for other uses while exploring possibilities to use some unused plants for such purposes. The present study is one such study taken up to overcome the possible shortage of commercial timber for pulping purposes and thus leading to finding alternate resources. Mexico has various species of woody plants, of which huizache (*Acacia farnesiana* L. Willd.) (Fig. 1), is widespread and in most cases considered invasive and a soil alteration plant. In fact, the plant used in this study (huizache) to obtain dissolving grade pulp, is considered a pest due to its ability to colonize pastures and other disturbed habitats (Parrota 2000). By using this type of plant, it would be possible to find applications whereby a greater value addition can be achieved for such raw materials.

Fig. 1. Huizache plant from the forest school of the University of Guadalajara

Also, it may be noted that the purpose of this study was not intended to obtain a kraft cellulose for paper production, but to obtain a dissolving grade cellulose for a possible application in the production of cellulose nanocrystals.

This plant is one of the most abundant woody legumes found in Mexico and according to the only statistics available, with a reported area of approximately 1.1 million hectares of coverage as early as 1999 (Ruiz-Luna and Berlanga-Robles 1999). It is reported that the tissue of this wood seems to be medially soft and has medially thick-walled fiber cells that have tissues containing profuse parenchyma (Rodriguez *et al.* 2016). This wood is suitable for paper pulp because of the broad lumen of the fiber cell beside the thin cell wall. Accordingly, the current study was undertaken with the objective of evaluating the huizache plant as a raw material for the production of dissolving grade cellulose.

Dissolving pulp can be defined as having greater than 90% α-cellulose and a degree of polymerization greater than 500. To the best of the authors' knowledge, this is the first study of such being reported. Herein the alkali sulphite-anthraquinone-methanol (ASAM) pulp process was used with modification by adding a pre-hydrolysis step with a diluted sulfuric acid solution of three different concentrations. The hydrolysis conditions are known to affect the properties of the resulting nanocrystals, and these must be sufficiently mild to avoid complete hydrolysis to glucose (Casillas *et al.* 2018).

The reason for the selection of ASAM process are as follows, which are further justified by the results presented later in the manuscript:

According to Kordsachia *et al.* (1992) 'the most meaningful advantage of ASAM pulping in comparison to the kraft process is the easy bleachability of the pulps. The good bleaching response allows the application of an absolutely chlorine free bleaching sequence, without excessively impairing pulp strength. Compared to the strongly alkaline kraft process, sulfite pulping is highly adjustable since it can be applied over a wide pH range and allows the production of various pulp grades. In fact, the ASAM process was developed by the group of one of the authors of this paper. Prof. Prat has regarded ASAM as a promising alternative to the kraft pulping process. Similarly, according to Schubert *et al.* (1998), 'the ASAM process is a technology which meets the challenge of significant improvement in the existing quality grades, pulp performance and favorable economics and therefore declared as a feasible alternative to the leading kraft technology.'

Further, it is reported that the process can be used to produce excellent dissolving pulp grades (Patt *et al.* 1997). The technical feasibility of this process has been established in extensive pilot plant trials, including various steps, which include continuous total chlorine free (TCF) bleaching, methanol recovery, liquor evaporation, and combustion of black liquor. It is thus concluded that the above-mentioned results clearly indicate possibility of the commercial scale operation of the process without major risks.

Since, the ASAM cooking liquor would contain NaOH, Na_2SO_3, metanol, and anthraquinone besides addition of H_2SO_4 during the pretreatment and chlorine dioxide to be used in ECF bleaching, one has to consider the issue of chemical recovery because even a published report as late as 2013 has indicated that the 'ASAM process has the unfavourable chemical recovery system needed for sulfite processes whereby the industrial implementation of the ASAM process failed because of the methanol demanding explosion proof equipment' (Klingberg 2013). However, it may be noted that the experiments have been done at laboratory scale in this study, and accordingly the reagents used in the cooking process are at this level and no reagent recovery was attempted. At this juncture it may be difficult to say about the reagent recovery at the pilot level although the reagent recovery may be possible. For example, alcohol can be recovered by distillation.

Other points to consider are the steps for dealing with the dissolved lignosulfonate during the ASAM cooking process because ASAM cooking liquor would be used to remove lignin. In fact, it is reported that although lignosulphonate has a potential application regarding sustainable development in geotechnical engineering, it is disposed of as a waste product, which leads to very high disposal cost (Alazigha 2015). It may also be possible to use the lignosulfonates dissolved during the ASAM cooking process for other applications, such as a fuel briquette binder, as an adhesive in wood fiber boards and drilling fluids (to reduce the viscosity and resistance in sludge drilling muds), as an internal fuel for the recovery of energy and reagents in the production of paper, as a binder in the construction and treatment of roads, *etc.* (Alonso Rubio 2004; Astuy 2016).

The unbleached pulp obtained from the cooking process was bleached using an elemental bleaching sequence without chlorine gas (Elemental Chlorine Free-ECF). Considering the possible uses of the wood pulp, particularly in paper industry, the pulp was analyzed for several parameters of interest, such as pulp yield, Kappa number, ISO whiteness, α, β, γ and cellulose content, viscosity, *etc*.

EXPERIMENTAL

Materials

Samples of huizache wood were collected from the spring forest region, located in the municipality of Tala, Jalisco, Mexico. The huizache wood was peeled off in the Department of Wood, Pulp, and Paper of the University of Guadalahara, Guadalahara, Mexico. Next, previously debarked huizache wood was cut into chips using a Bruks brand chipper (Mekaniska AB, type: 980 AH (Manufacturer:Bruks, Arbra, Sweden) with four blades. Subsequently, the chips were classified using a vibrating screen (Manufacturer: Lorentzen and Wettre AB, Helsinki, Finland) separated by different sizes. During the classification, the following screen sizes were used: 40-mm holes, grids with separations of 10 mm, 8 mm, and 7 mm, in addition to a tray for fines. The selection of chips was carried out *via* screening with 7-mm grids. The sampling and preparation of wood for analysis used in this study was followed according to the TAPPI T257-cm-02 (1985) standard.

The analysis of the extractable content in the huizache samples was carried out according to the TAPPI standard (T 204 cm-97), performing these in triplicate. The lignin content was carried out according to the TAPPI standard (T 222 om-98). The determination of holocellulose was carried out according to the method described by Wise. The determination of ashes in the wood was carried out according to the TAPPI standard (T 211 om-93). Determination of pentosans was made according to the TAPPI standard (T 223 cm-84).

The results of the chemical composition of the huizache, are presented in Table 1.

Table 1. Chemical Composition of Huizache (all in %)

Removable	Lignin	Holocelluloses	Ashes	Pentosans
4.17	17.40	62.88	3.55	11.40

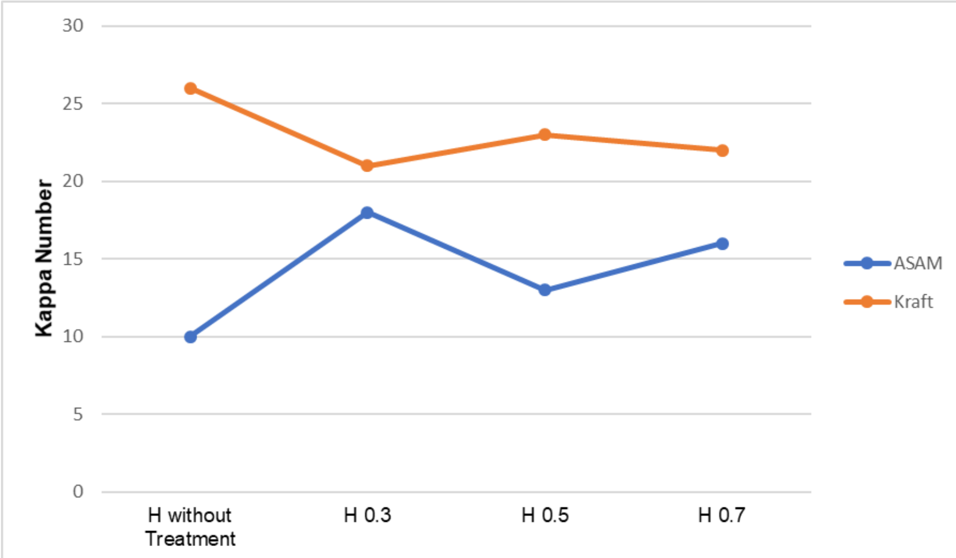

Fig. 2. Comparison of Kappa number of the kraft and ASAM processes with pre-hydrolysis and without pre-hydrolysis for huizache

Tests of Kappa number and yield were carried out in triplicate in pulping processes kraft and ASAM for huizache with treatment and without pre-hydrolysis treatment.

Figure 2 shows the obtained Kappa number for the kraft and ASAM pulping processes, for the sample of huizache without prehydrolysis and with prehydrolysis at 0.3, 0.5 and 0.7% of H_2SO_4. These results indicate that the lower lignin content for the ASAM process compared to that of kraft process.

Figure 3 shows the performance between the kraft and ASAM cooking processes for huizache, without prehydrolysis and with prehydrolysis at 0.3, 0.5 and 0.7% of H_2SO_4, indicating that the best performance is for the ASAM process.

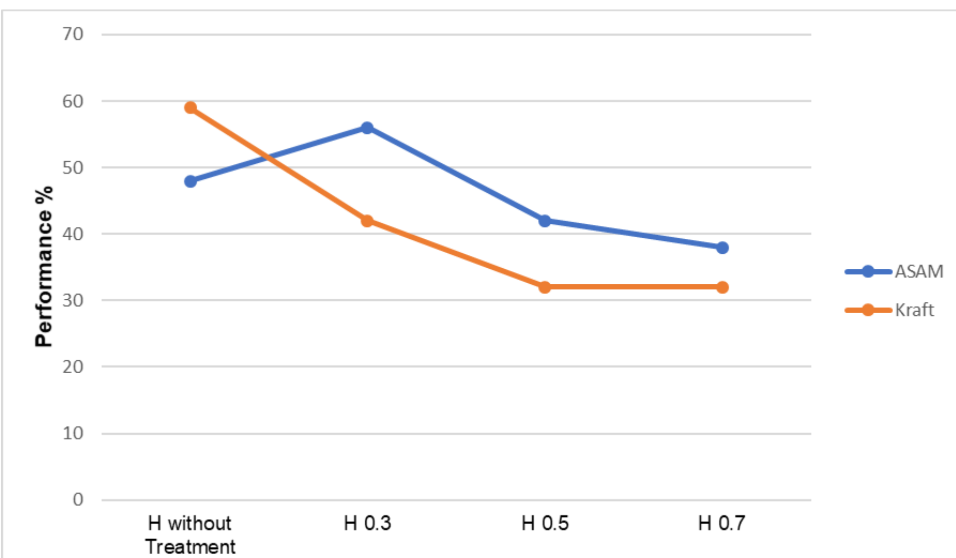

Fig. 3. Comparison of the performance of the kraft and ASAM processes with pre-hydrolysis and without pre-hydrolysis for huizache

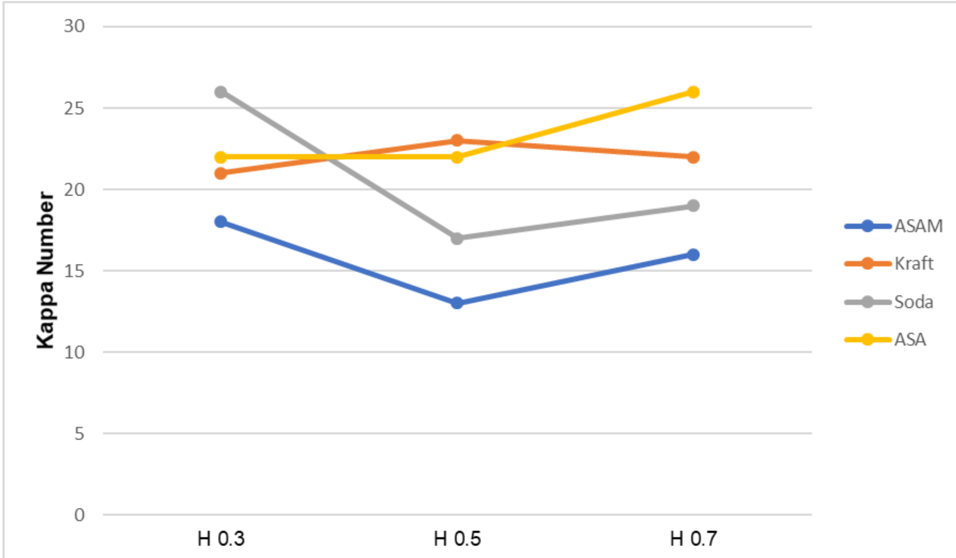

Fig. 4. Kappa number of huizache pulp obtained with the ASAM, kraft, soda, and ASA processes

To understand which process is the best for the treatment of the huizache, cooking was carried out with four processes, *viz.*, the kraft process, the anthraquinone soda process, the ASA process, and the ASAM process.

Figure 4 shows the performance of each pulping process based on Kappa number. The lower the value of this number, the higher was the amount of lignin eliminated. Once again from Fig. 4 it can be seen that the ASAM process is the best process in view of highest elimination of lignin amongst the four processes attempted.

Figure 5 presents the performance behavior of the four processes studied, *viz.*, ASAM, kraft, soda, and ASA processes. The best performance once again was with the ASAM process considering a prehydrolysis with 0.5% H_2SO_4.

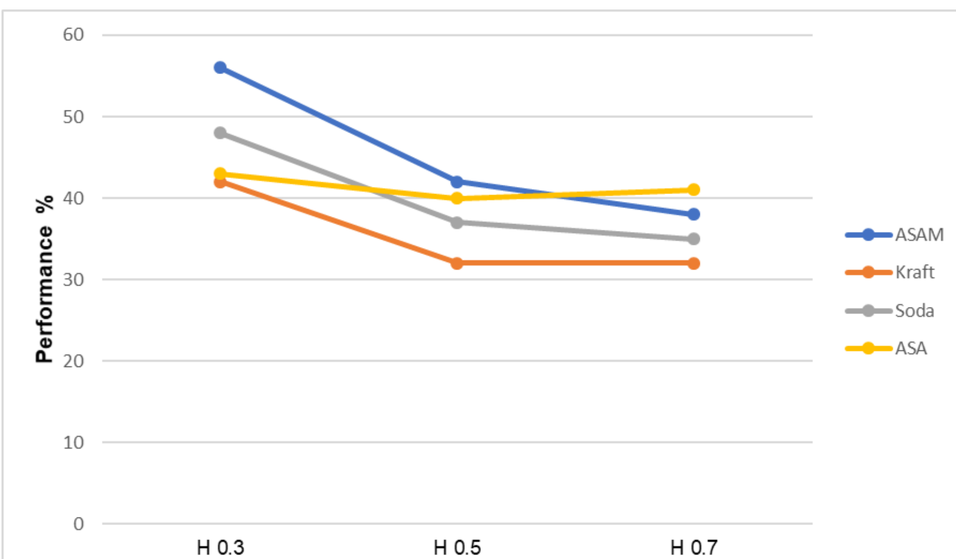

Fig. 5. Performance of the huizache pulps obtained with the cooking processes ASAM, kraft, soda, and ASA

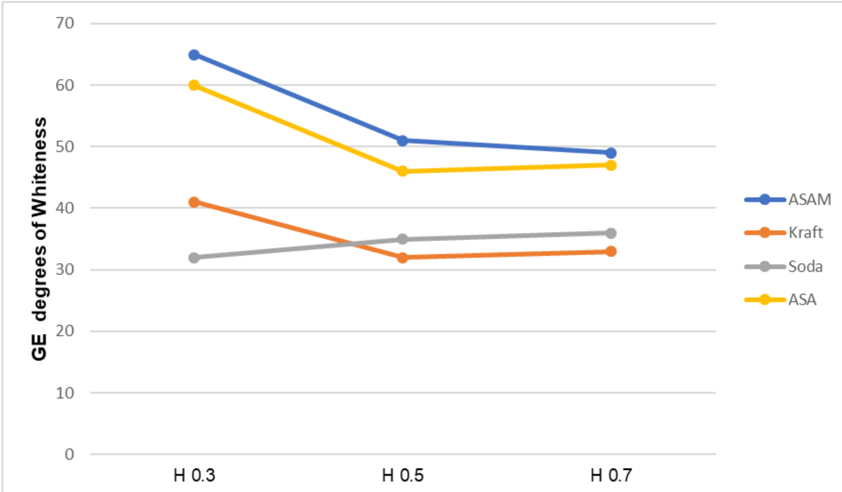

Fig. 6. Whiteness of the huizache pulp for the ASAM, kraft, soda, and ASA cooking processes, by the ASTM D985 method

Figure 6 presents the values of whiteness obtained from the pulp of the different cooking processes used in this study. It can be seen that the highest whiteness corresponded to the ASAM cooking process.

Thus, from the results presented in Figs. 2, 3, 4, 5, and 6 for the four cooking processes studied, the best results are observed for the ASAM process, and therefore it was decided to use the ASAM cooking process for the treatment of the huizache in the present study.

Methods

The objective of this study was to produce dissolving grade cellulose from huizache plant, but not to produce paper grade cellulose. Contents of *α*, *β*, and *γ* cellulose, % whiteness along with % opacity, viscosity, degree of polymerization, identification of functional groups (using FT-IR), and analysis of crystallinity by means of X-ray diffraction have been determined. These are the necessary parameters required for the dissolving grade cellulose, which is further used to prepare cellulose nano crystals. Although it is well known that water retention value for the pulp is an important quality for many other characteristics such as accessibility, web-forming capabilities, and eventual dewatering of the fibers, the test for this was not carried out, since it was not intended to produce dissolving grade cellulose.

Acidic acid hydrolysis treatment

The pretreatment with sulfuric acid refers to the treatment of the chips before the cooking with acid. The pretreatment with sulfuric acid is the treatment of dissolving grade cellulose with acid for the production of cellulose nanocrystals as was done in the present study. This pretreatment is to eliminate the hemicelluloses. It may be noted that this is different from the autohydrolysis, which 'is a process that heats lignocellulosic materials in aqueous media at temperatures in the range 130 to 230 °C. During treatments, hemicelluloses are depolymerized and converted into soluble oligomers (the major reaction products), and mono-sugars'.

Prior to the firing process, the chips were treated with a 0.5% sulfuric acid solution for 30 min. Steam was applied at a pressure of 90 psi in a cooker-defibrator, designed and fabricated in the authors' department. This equipment is closed system for pressure and temperature, which can be fixed as per requirement. Steam is fed until reaching the desired pressure and temperature values. Once the process of pre-hydrolysis was complete, the equipment was cooled, the valves were opened to vent the pressure, and then the pre-hydrolysis liquor was removed. Then, the material was washed repeatedly until the remnants of acid liquor were removed. The chips were dried to the temperature and humidity conditions of the environment.

ASAM cooking process

After the pre-hydrolysis process with sulfuric acid, the chips were subjected to an ASAM pulping (cooking) process, according to the parameters reported earlier (Morales 2013). This process was performed in a Jayme digester (Manufacturer: Scientific and Technical Services at the UPC, Barcelona, Spain), pressurized equipment designed with temperature control by means of electrical resistances, with the purpose of applying the temperature and pressure necessary to obtain cellulose pulp. The cooking conditions that were used are summarized in Table 2.

Table 2. Parameters and Conditions of Pulping Used in the Cooking Process of the Chips of Huizache

Conditions Used During ASAM Pulping	
Loading of Reactive (%)	24
Relationship Na_2SO_3/NaOH	70/30
Methanol Concentration (% Volume)	20
Concentration of Anthraquinone (%)	0.1
Hidromodule (mL / gms)	5:1
Maximum Temperature (ºC)	170
Maximum Time to Reach Temp (min)	45
Maximum Reaction Time at Temp. (min)	150

Purification of the huizache pulp

The pulp of huizache was treated in a disc refiner (Sprout, Waldron & Co., PA, USA) for the purpose of defibrating the material, which was then passed through a diaphragm scrubber with a slotted plate with 0.15 mm opening to remove impurities. The accepted pulp was centrifuged to eliminate the water and subsequently homogenized. Finally, the fibrous material and the amount of moisture present were determined, stored in plastic bags, and closed. Then, the plastic bags were stored under refrigeration for until its use in subsequent bleaching tests.

Evaluation parameters of ASAM cellulose pulp or evaluation of the pulp after the ASAM process

The pulp of huizache was subjected to various tests, to determine some quality parameters, which include the performance of the pulping process, Kappa number, whiteness, bleaching process, and high purity pulp. Methods of determination of these are explained below:

a. Performance of the pulping process:

The yield is the sum of the accepted weight of pulp and the rejects (on a dry basis) calculated using the formula given below:

$$\% \text{ Performance} = \left[\frac{\text{Final dry weight}}{\text{Initial dry weight}}\right] * 100 \qquad (1)$$

b. Kappa number:

The analysis of the lignin content (called 'Kappa' number) was conducted according to the TAPPI T236-cm-85 standard (1985). The degree of delignification of the pulp is an evaluation criterion in pulp prior to the bleaching process and during bleaching.

c. Whiteness:

The level of whiteness was measured before, during, and at the end of the bleaching process according to the TAPPI T452-om-98 standard (year), in addition to the color of the bleached pulps and the raw pulps, using the measurement system of color CIE $L*$, $a*$, and $b*$. A Data Color International Spectrophotometer (Elrepho 3000; Manufacturer: Data Color, New Jersey, USA) was used for the measurement of these properties.

d. ECF bleaching process:

Following the conditions suggested earlier by other researchers (Lopez *et al.* 2003; Muñoz 2013), the raw huizache pulps were subjected to an ECF bleaching process. The parameters studied the sequences and conditions applied, which are summarized in Table 3.

Table 3. Conditions Used During Bleaching of the Pulp of Huizache by ECF Bleaching Process

ECF Bleaching Sequences						
Control Parameters	1st stage chlorine dioxide (ClO_2)	2nd stage alkaline extraction (NaOH)	3rd stage chlorine dioxide (ClO_2)	4th stage peroxide (H_2O_2)	5th stage alkaline extraction (NaOH)	6th stage peroxide (H_2O_2)
Temperature (° C)	70	70	80	70	30	70
Time (Min.)	60	60	180	180	60	180
Consistency	10	10	10	10	10	10
ClO_2	Kappa number X 0.24	-	2.5	-	-	-
NaOH	-	$\%C_1 = ClO_2/2 + 0.2$		1	10	1
H_2O_2	-	-		2	-	2
DTPA*	-	-		0.1	-	0.1
$MgSO_4$	-	-		0.1	-	0.1
Na_2SiO_3		-		0.2	-	0.2
Initial pH	3.0 – 3.5	12 – 12.5	5.0 – 5.5	11.5		11.5
Final pH	7.0	-	-	-	7.0 – 7.5	10.5

*- DTPA: diethylenetriamine penta acetic acid

Evaluation of high purity pulp (ECF)

The bleached huizache pulp was analyzed by various control tests (mostly standardized TAPPI methods). These include determination of the following: (i)- whiteness (%) measured using Elrepho 3000 spectrophotometer (Datacolor, NJ, USA); (ii) CIE (International Commission on illumination)- L^* representing the lightness of different colors, starting from zero for black to 100 for perfect white; a^* representing red color when the number is positive, green when it is negative and zero when it is grey; and finally, b^* represents yellow color when positive, blue color when it is negative, and is zero for grey as per TAPPI T 527 om-94 (1994), (iii)- α, β, and γ-cellulose contents using the TAPPI T203-om-93 (1993) standard; (iv)- lignin content by the determination of the Kappa number according to the TAPPI T236-cm-85 (1985) standard; and (v)- the degree of polymerization through viscosity tests. All of the tests were conducted to verify whether the α-cellulose of the chosen raw material could meet the desirable parameters for dissolving grade cellulose.

Chemical analysis of bleached pulp

The bleached pulp was evaluated by measuring various parameters of interest, such as the Kappa number as per TAPPI T236-cm-85 (1985), viscosity according to γ-cellulose TAPPI T230-om-94 (1994), whiteness (% ISO) as per TAPPI T452-om-98 (1998), and α, β, and contents as per TAPPI T203-om-93 (1993).

Fourier transform infrared (FTIR) studies of α-cellulose (dissolving grade cellulose)

To carry out a chemical analysis of the pulp, by means of attenuated total reflectance (ATR) FTIR using FTIR equipment (FTIR Spectrum GX, Perkin Elmer, Mexico city, Mexico) test sheets were prepared in the laboratory with an approximate grammage (paper density) of 130 g/m², according to the standard TAPPI T218-sp-97 (1997). The sheets were formed in a 20-cm diameter Porcelain Buchner funnel, using a Whatman No. 6 filter paper base with a pore diameter of 3 μm. Each sheet was placed in wooden frames (as a half tensor) and dried to the conditions of the environment for a period of 24 h. The sheets were obtained from the suspension of bleached pulp and formed in a sheet former according to TAPPI T218-sp-97 (1997). The bleached pulp was analyzed with the FTIR spectrophotometer equipment described below.

This analysis is useful to verify the chemical structure of the material produced by identifying the functional groups present in the high purity pulp obtained from *Acacia farnesiana*. The FTIR analysis was conducted on approximately 10 g of (dry weight basis) huizache cellulose pulp sheets using a FTIR spectrometer (Nicolet Magna Protege 460, Thermo Electron Corporation, WI, USA) in the transmission mode, with a resolution of 4 cm^{-1} and 100 sweeps.

X-ray diffraction (XRD) studies

The crystallinity of the obtained material was determined by the powder X-ray diffraction method (PXRD), using a Siemens D 5000 Diffractometer equipment (Fischer Technology Inc, CA, USA) with CuKα radiation (α = 1.5418 Å and energy 8.047 eV). The voltage and applied current were 40 kV and 30 mA and the spectra were obtained in the 2θ range of 10º to 40º.

The percentage of crystallinity of the samples was calculated in the X-ray analysis by the method developed by Segal *et al.* (1959) Eq. 2,

$$X_c\,(\%) = 100[1 - (I_1/I_2)] \quad (2)$$

where, I_1 is the intensity of the minimum peak and I_2 is the maximum intensity of the crystalline peak. The size of the crystal was calculated using the equation of Cullity (1978) as shown in Eq. 3,

$$t = 0{:}9\lambda \,/\, B \cos\Theta \quad (3)$$

where, t is the crystal size (µm), λ is the wavelength of the radiation used (λ_{Cu}), B is the width (µm) at the average height of the diffraction peak of the sample, Θ is the position of the diffraction peak (degrees), and 0.9 is the shape factor of the crystal.

RESULTS AND DISCUSSION

Evaluation of the ASAM Process

Figure 3 compares the performance between the kraft and ASAM cooking processes for huizache, without prehydrolysis and with prehydrolysis at 0.3, 0.5 and 0.7% of H_2SO_4, which indicates that the best performance was from the ASAM process.

To define which process is the best for the treatment of the huizache, cooking was carried out with the kraft process, the anthraquinone soda process, the ASA process, and the ASAM process. Figure 4 shows performance of each pulping process, according to the number of kappa, which indicates that at a lower value, a greater amount of lignin was eliminated. This implies that the ASAM process was the best process, since more lignin was eliminated.

Figure 5 shows the behavior of the ASAM, kraft, soda, and ASA processes with respect to performance. Considering a prehydrolysis with H_2SO_4 of 0.5%, the best performance was once again by the ASAM process.

The whiteness obtained from the pulp of the different cooking processes is shown in Fig. 6, which indicates that the highest whiteness corresponds to the ASAM cooking process.

According to the information presented in Figs. 2, 3, 4, 5, and 6, among the four cooking processes studied in the present study, it was decided to use the ASAM cooking process for the treatment of the huizache. In fact, this was the reason why the soda pulping process, which should probably be sufficient for delignification of the huizache plant, was not used in the present study, taking into account the high yield, the kappa number, and the whiteness obtained in the used process.

Evaluation of the Pulp After the ASAM Process

Low hemicelluloses content (1.6 %) was observed in the chips of huizache plant after pre-hydrolysis with an aqueous solution of 0.5 % sulfuric acid, which helped to obtain a yield of 42 % and a Kappa number of 12 in the unbleached cellulose. The reported typical value of hemicelluloses is approximately 20 % to 27 % (Mao 2007; Núñez 2008).

It may also be noted that in the bleaching process, about 5 to 9 % of the pulp was lost after cooking. Thus, when the above-mentioned loss (5 to 9%) is subtracted from the yield of 42% obtained in the ASAM process, a net yield of 33 to 37% of bleached pulp will still be good enough after the bleaching stage.

Evaluation of Whiteness of the Prepared Pulp

It was mentioned earlier that to prepare dissolving-grade cellulose from fibrous material, cellulose pulp should have specific properties such as high level of whiteness and a high degree of purity. Table 4 lists the results in respect of the degree of whiteness and opacity in the cooked and bleached pulp of the raw material (*A. farnesiana)* chosen in this study. Table 3 shows that the degree of whiteness of the pulp after cooking was 37.3%, while it was 91% after bleaching. Similarly, the opacity of the pulp after cooking was 88.3%, and it was 79.0% after bleaching.

The whiteness obtained by bleaching is due to the elimination of chromophoric compounds and hexenuronic acids present in hard woods by the action of chlorine dioxide due to its specificity for bleaching (Pinto *et al.* 2005). It should be noted that the percentage of whiteness required for cellulose for derivatives (also called 'soluble grade cellulose') is the equivalent to that of cellulose to obtain rayon textiles (the cellulose to obtain rayon textile, is the same dissolving grade cellulose) (Klemm *et al.* 2005).

Table 4. Percentage of Whiteness and Opacity in Cooked and Bleached pulp of *Acacia farnesiana*

% Whiteness and opacity (Elrepho 3000)	
Whiteness of cooked pulp (%)	37.3
Opacity of cooked pulp (%)	88.3
Amount of white bleached pulp (%)	91.0
Amount of bleached pulp opacity (%)	79.0

Chemical Analysis of Bleached Pulp

Table 5 shows the chemical composition of bleached cellulose, viscosity, and degree of polymerization obtained in the present study. It is interesting to note that these results are similar or even superior to the previously reported values. For example, Roman and Winter (2004) have reported an α-cellulose content varying between 90 to 92% in sulphite pulps, which could be used depending on the application; Klemm *et al*. (2005) and Durbak (1993) worked with *A. farnesiana* and obtained the amount of bleached pulp that exceeded the minimum value obtained in the sulphite treatment of the raw material.

Table 5. Cellulose Fractions, Viscosity, and Degree of Polymerization in Pulp to Dissolve *Acacia farnesiana*

Properties of Bleached Pulp (High Purity)	
α-Cellulose (%)	94.6
β-Cellulose (%)	0.5
γ-Cellulose (%)	2.7
Viscosity (cp)	8.25
Degree of polymerization (DP)	699.0

For the values of α-cellulose, it has been reported that high values of this constituent indicate a lower degradation of the polymer chain, which in turn is reflected in several of its properties such as the crystallinity index or viscosity (Macdonald 2011;

Schild and Sixta 2011). Peng *et al.* (2011) has defined the purity of the cellulose obtained as 'technical grade cellulose' with values in the range of 200 < n < 1000. The above results indicate that with ECF bleaching on huizache cellulose it is feasible to obtain high purity cellulose.

It should be noted that the DP can vary depending on the species selected for the study or the method used to isolate it. For example, in the present study, a DP value of 699 was obtained, which was within the acceptable range as a dissolving grade pulp. In contrast, Macdonald (2011) worked with *Eucalyptus globulus* wood pulp and obtained DP values between 300 and 1700, while the pulp of annual plants, such as sugarcane bagasse, reported a minimum DP value of 500. In the case of *E. globulus*, the values are typically between 300 and 1700 (Schild and Sixta 2011). In contrast, for microcrystalline cellulose from sugarcane bagasse, the DP values have been reported to be between 1250 and 1545 (García-García *et al.* 2013).

FTIR Studies of α-Cellulose (Dissolving Grade Cellulose)

Figure 7 shows the FTIR spectrum of pulp prepared in the present study. From the FTIR-ATR analysis one can see a characteristic spectrum of cellulose, with bands of vibration of various groups or characteristic bonds, which are explained below:

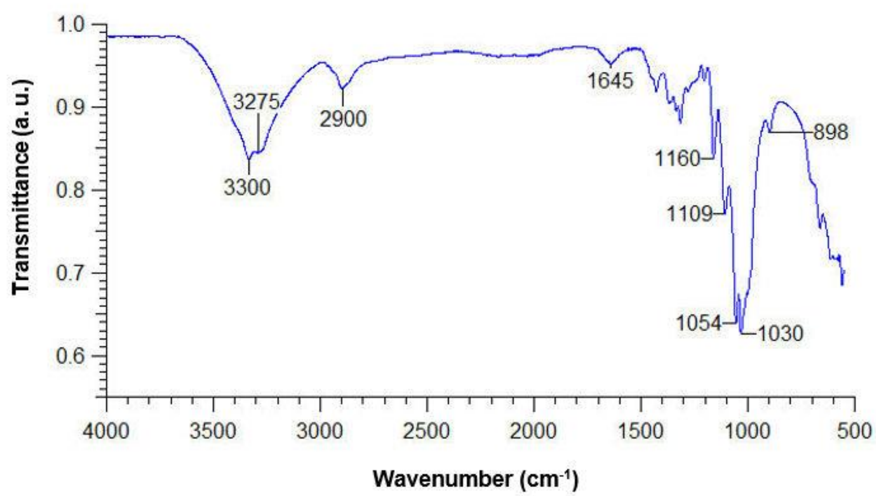

Fig. 7. Characterization by FTIR chemical analysis, dissolving grade cellulose extract obtained from huizache

The band at 2900 cm^{-1} is attributed to stretching vibrations of the CH links; the bands at 1054 and 1030 cm^{-1} are characteristic of the C-O bond; signals at 1160 cm^{-1} of the C-O-C bond are also apparent; at 898 cm^{-1} there is the vibration of the anomeric carbohydrate carbon group C1-H (Viloria *et al.* 2014); the wide band between 3600 and 3200 cm^{-1} is due to the O-H stretch (Contreras *et al.* 2010).

Of special interest are the vibrations of the OH groups, since they are fundamental for the characterization of the cellulose crystallinity in which vibrations of intramolecular and intermolecular hydrogen bridges can be found (Zara *et al*. 2017). The vibration at 3305 cm^{-1} is typical of samples with high crystallinity or purity.

The 3275 cm^{-1} band is assigned to an intermolecular hydrogen bridge between the hydrogen of the OH group on carbon 6 in the glucose unit of a cellulose chain and the oxygen of the OH group on C3 of another glucose unit belonging to the adjacent chain (Contreras *et al.* 2010).

The bands of main interest should be 3305 cm^{-1} (samples with greater crystallinity) and 3845 cm^{-1} (samples with less ordered structure). The band between 1630 cm^{-1} and 1650 cm^{-1}, assigned to adsorbed water, should also be checked carefully, since the less crystalline a sample of cellulose, the more easily it can accommodate water molecules in its structure (Fengel and Wegener 1989). Thus, the lower the crystallinity, greater is the expected intensity in this band.

With this analysis, the feasibility of using this ECF bleaching process to eliminate non-cellulosic material and obtain high purity cellulose was verified.

XRD Studies

Figure 8 shows the representative XRD spectra of optimally bleached pulps, isolated by pulp ECF bleaching by the ASAM process.

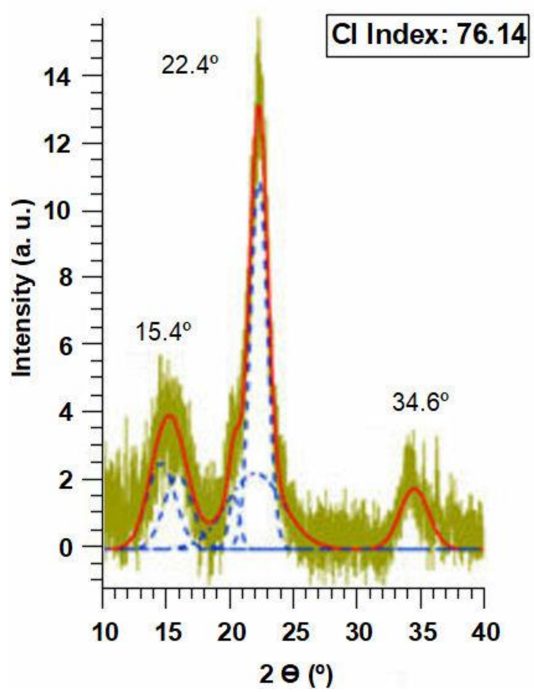

Fig. 8. X-ray spectrum of bleached huizache pulp samples through an ECF bleaching process

As shown, the characteristic peaks of the crystalline regions were located around $2\theta = 15°$ (peak 101), $2\theta = 23°$ (peak 002), and $2\theta = 34°$ (040), while the peaks due to the amorphous regions were located around $2\theta = 18°$ and $2\theta = 20°$. All of these are in agreement with those observed in cellulose samples reported by others (Anderson *et al.* 2003; Park *et al*. 2010). The value of the crystallinity index (CI) calculated according to the XRD de-convolution method (Park *et al*. 2010) is approximately 76.

Finally, based on the above mentioned results of high levels of whiteness, α-cellulose content (94.6 %), DP of 699, and viscosity values were obtained from the huizache pulp, which are higher than the minimum values (> 90% α-cellulose content and DP > 500) and therefore considered adequate to produce cellulose nanocrystals. These results further suggest that this plant (*Acacia farnesiana)* could be considered as an alternative raw material for the production of dissolving grade cellulose, which can be used in the production of nanocrystals of cellulose. In fact, this aspect has been looked into by the authors and is presented as a companion publication (Casillas *et al.* 2019).

CONCLUSIONS

1. The hydrolysis treatment applied before the cooking process contributed to greater elimination of non-cellulosic materials from the huizache wood. The optimal conditions for this process were obtained using a 0.5 wt. % sulfuric acid solution with a temperature of 160 ºC under a pressure of 90 psi for 30 min of treatment time.
2. The huizache wood showed a good degree of delignification. The pulp generated by the ASAM process showed excellent bleaching.
3. The data obtained from the characterization of bleached huizache pulp with an ECF bleaching sequence indicated that it is possible to obtain purified cellulose samples with whiteness levels up to 91% ISO and α-cellulose content greater than 90%. These pulps also show a very good degree of crystallinity (76% to 79%) and degree of polymerization of 699.
4. The high levels of whiteness, α-cellulose content, and viscosity values obtained from the huizache pulp suggest that this plant (*Acacia farnesiana)* could be considered as an alternative raw material for the production of dissolving grade cellulose, which can be used in the production of nanocrystals of cellulose.

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