



Extraction and Characterization of Cellulose and Lignin from Sawdust

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Resumen

Se realizó la extracción de componentes celulósicos a partir de residuo de madera obtenido de la fabricación de muebles, el cual previamente fue tratado con extracción Soxhlet para obtener los aceites y otros compuestos solubles en tolueno. El residuo obtenido después de la extracción con tolueno se trató de acuerdo al método Kurschner-Höffer modificado, mediante reflujo con mezcla metanol-ácido nítrico, hidróxido e hipoclorito de sodio. Los residuos obtenidos en cada una de las extracciones fueron analizados mediante Espectroscopía Infrarroja, Calorimetría Diferencial de Barrido. Además se utilizó Difracción de Rayos X con el fin de determinar el grado de cristalinidad de la celulosa.

Palabras clave: aserrín, celulosa, extracción, cristalinidad, difracción de rayos X

Abstract

Cellulosic components were extracted from wood residues obtained from furniture fabrication. The residues were previously treated with Soxhlet extraction to obtain oils and toluene-soluble compounds. The residue obtained after toluene extraction was treated using a modified Kurschner-Höffer method, refluxing with a mixture containing methanol, nitric acid, sodium hydroxide and hypochlorite. The residues obtained from each extraction were analyzed with infrared spectroscopy, differential scanning calorimetry. While X-ray diffraction was used in order to determine the cellulose degree of crystallinity.

Keywords: sawdust, cellulose, extraction, crystallinity, X-ray diffraction.

1. Introduction

Wood has been used for centuries to satisfy people's needs, like tool and furniture fabrication, and house construction. Sawdust is often wasted when working with wood, although it has been used to fabricate agglomerates by mixing it with phenolic resins. The agglomerates have lower commercial value than wood. One alternative to get rid of the sawdust is to burn it, but dioxin emission creates a pollution issue. A less environmentally aggressive alternative is to separate the principal components of sawdust and use them as raw materials in fabrication of resins with potential industrial applications [1,2].

Wood components are divided into three different groups: cell wall compounds, extractable substances and

mineral substances. Cell wall compounds are mainly cellulose, hemicellulose and lignin. Cellulose makes up about 40 to 50% of the total compounds; it is a long chain biopolymer consisting of glucose units. The configuration of its glucoside units differentiates it from starch. Hemicellulose is a high molecular weight heteropolysaccharide, constituted by different monosaccharides like pentose, hexose and uronic acid, forming branched and amorphous structures. It acts as an agglutinant between cellulose and lignin; hemicellulose makes up about 27 to 29% of the cell wall. Lignin is found in a 19 – 35% proportion, only below cellulose [3-7]. Phenolic hydroxyl, aliphatic hydroxyl, methoxyl, carbonyl, carboxyl and sulphonate are its main functional groups. The structures of cellulose and lignin, the main constituents of the cell wall, are shown in figure 1.



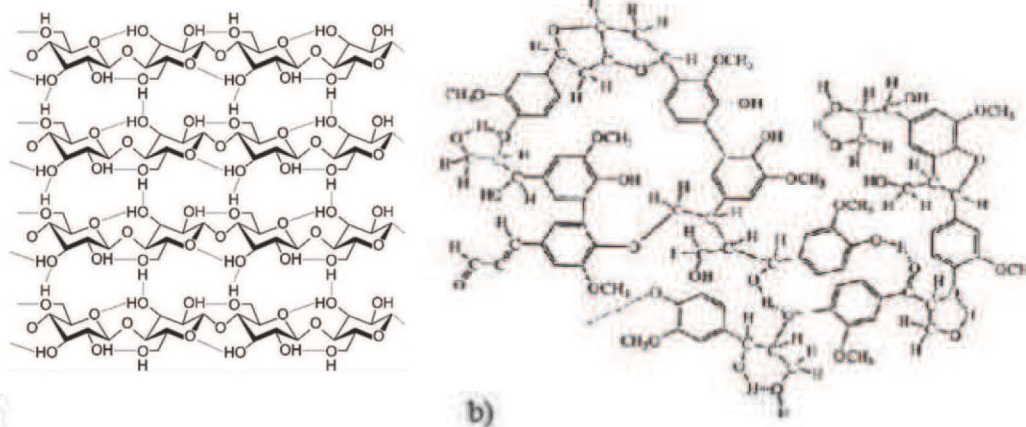


Figure 1. Structures of a) cellulose and b) lignin.

Cellulose molecules have a strong tendency to form hydrogen bonds by inter and intra molecular links. The existence of these links has an important effect on the reactivity of cellulose. Intermolecular hydrogen bonds contribute to the formation of crystalline structures, which are difficult to penetrate by solvents [8]. Evans et al [9] consider that even though there exist a large number of methods to analyze crystallinity, few are useful in determining this parameter in wood celluloses. According to the literature, only X-ray diffraction (XRD), IR spectroscopy and solid state NMR spectroscopy have been used to determine crystallinity in wood cellulose. These three methods are sensitive to different aspects of order and disorder; this is why it's not surprising to find different values for ordered and disordered cellulose using the different techniques [10].

Three different organization types are found in cellulose structures: amorphous and two ordered molecular conformations. The two different crystalline forms are labeled Type I and Type II cellulose. Wood cellulose is mainly present in Type I form.

One method to determine the crystallinity percentage consists in taking an appropriate maximum and minimum intensity from XRD diffractogram to calculate a crystallinity index I_c , given by: [11,12].

$$I_c = \left[\frac{I_{002} - I_{am}}{I_{002}} \right] \times 100$$

Where:

I_{002} : maximum crystalline intensity at 2θ between 22° and 23° for cellulose I (between 18° and 22° for cellulose II)

I_{am} : minimum crystalline intensity at 2θ between 18° and 19° for cellulose I (between 13° and 15° for cellulose II)

Sawdust degradation was performed in the present work using a modified Kurschner – Höffer method [13-15] to extract the main wood compounds; the most important was the cellulose since we propose to use it in industrial materials formulation. Because of our interest in cellulose, we focused mainly on this compound when performing characterization with several analytical techniques.

2. Experimental section

2.1 Materials

Sawdust was obtained from a local logging company, comes from a residue of pine, toluene (Fisher Scientific USA, 99.9%), methanol (Aldrich USA, 99.8%), sodium hydroxide (Aldrich USA, 99%), nitric acid (Fisher Scientific USA, 99.8%). All reagents were used without further purification. Cellulose standard was obtained from Alfa Aesar, USA and Lignin standard from Aldrich, USA.

2.2 Methodology

In a modification of the Kurschner – Höffer method, in order to extract the soluble compounds in toluene and ethanol, 4.0 grams of sawdust were placed in a Soxhlet extraction system, using 100 mL of a toluene:ethanol

(1:1) mixture for a four hours reflux. At the end of this time, toluene and ethanol were separated from the mixture by filtration, the compounds soluble in toluene:ethanol were obtained by evaporation of these solvents by a rotary evaporator. The remnant, consisting of sawdust free of oils, was dried in an oven for three hours and weighed; after this, a 4:1 ethanol:nitric acid mixture (100 mL) was added to the remnant and refluxed for 1.5 hours. When the reflux ended, the product was filtered and washed with distilled water; the liquid obtained was evaporated and the residue obtained was weighed, this residue (residue 1) consists of acid-soluble lignin, the solid obtained from filtering consisting of cellulose and hemicellulose (residue 2), was dried in an oven for three hours and weighed. Finally, the remnant was again refluxed in 100 mL distilled water for one hour, 70 mL NaOH 0.4 N was added, and the reflux continued for an additional hour. The remnant, consisting of cellulose pure, was then filtered, washed and NaClO 3 % w/v was added for bleaching the cellulose, the final product (residue 3) was filtered, washed with distilled water and dried at 105 °C for three hours. The remnants obtained after each treatment were weighed and characterized using a Thermo Scientific

USA IR200 ATR (SeZn crystal) FTIR, 32 scans per analysis, from 650 to 4000 cm^{-1} . The differential scanning calorimetry (DSC) used was TA Instrument MDSC 2920, the conditions used in the analysis were: temperature program 25 to 300 °C, 20°C/min ramp, 50 mL of N_2 per minute, the equipment was a TA instrument MDSC 2920. To determine the degree of crystallinity of the extracted cellulose, an X-ray powder diffractometer (Cu K α radiation, Siemens D500, Germany) measuring 2 θ angles from 5 to 90 degrees, at 1 degree per minute was used.

3. Results and discussion

Table 1 summarizes the amount of soluble substances obtained in the toluene:ethanol mixture, the extractions was carried out in triplicate, according to what is reported in some references, these substances are oils, tannins and low molecular weight resins [14]. These substances were not analyzed qualitatively because the main objective in this work was to quantify and identify cellulose and lignin extracted from sawdust.

Table 1. Quantitative analysis of compounds soluble in toluene:ethanol.

Determination	Experiment 1	Experiment 2	Experiment 3
Compounds soluble in toluene – ethanol	4.45%	4.52%	5.15%

After extracting and purifying the residues 1 and 3, cellulose and lignin were weighed; Table 2 shows the results obtained in triplicate experiments. The variation in the result of the lignin is due to the method itself which involves a series of steps: reflux, filtering and washing with water. On the other hand, the cellulose results in the three experiments did not vary considerably, being obtained in the final residue. However, we consider them acceptable; these values are similar to those reported in TAPPI (Technical Association for the Pulp and Paper Industries) norms for timber species [12]. TAPPI norms reports 38 – 51 % for cellulose and 16 – 30% for lignin. We obtained an average of 46% and 34% for cellulose and lignin, respectively. The higher lignin content is mainly due to the sawdust repose time. When storing wood during long periods of time, chemical changes are observed in its composition, due to microorganisms, which causes lower cellulose content. The cellulose degradation by these microorganisms would explain why

the lignin content observed was higher than the reported values [11].

Table 2. Cellulose and lignin extracted from sawdust.

Experiment	Cellulose (%)	Lignin (%)
1	46.36	30.15
2	46.96	33.11
3	46.95	38.91
Average	46.59	34.06

An FTIR spectrum (figure 2) was obtained from the compound obtained from the sawdust extraction with ethanol/nitric acid (4:1). Bands at 3300 cm^{-1} can be observed corresponding to stretching vibrations of the OH groups, 2929 cm^{-1} from stretching vibrations of aromatic C-H groups, 1426 cm^{-1} from bending vibrations of methylenes, stretching vibrations of



aromatic C=C groups at 1600 cm^{-1} , the band near 1260 cm^{-1} and 1100 cm^{-1} may referred to the and C-O stretching frequency. All these functional groups correspond to lignin. Figure 3 corresponds to an FTIR

spectrum obtained from a lignin standard. It can be observed that figure 2 and figure 3 shows a FTIR spectrum nearly identical.

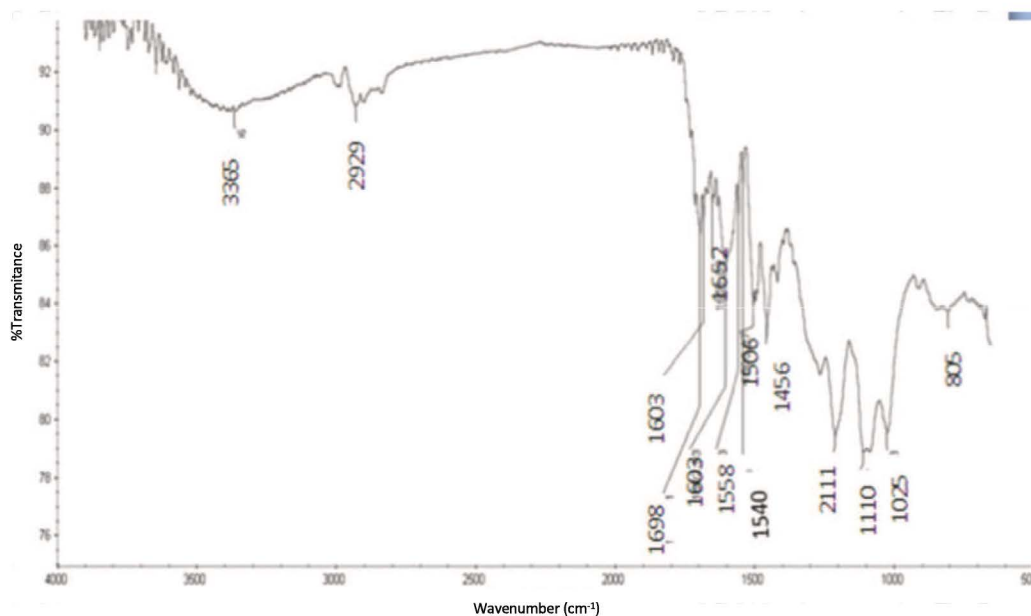


Figure 2. FTIR spectrum for lignin obtained from sawdust extraction.

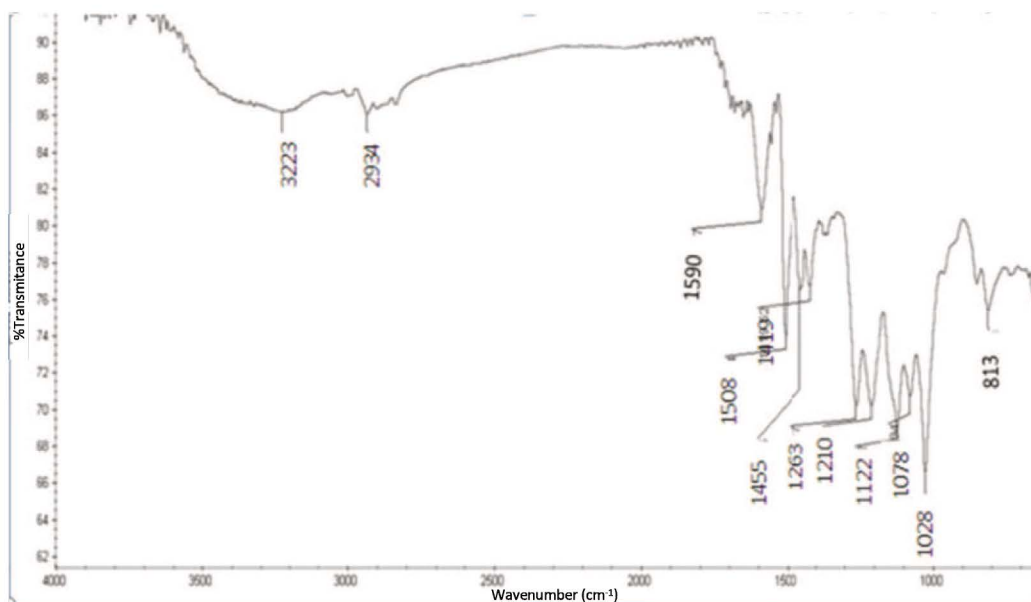


Figure 3. FTIR spectrum obtained from a lignin standard.

Figure 4 shows a FTIR spectrum taken from the final compound (residue 3) obtained when performing the

modified Kurschner – Höffer method. It also contains a typical O-H stretching vibration band at $3,330\text{ cm}^{-1}$, the

bands near to 1600 cm^{-1} may referred to C=C stretching and the C-O stretching band is presented at $1,023\text{ cm}^{-1}$. These bands show the presence of cellulose related

functional groups. We can then suppose the fraction obtained from this third sawdust extraction was cellulose.

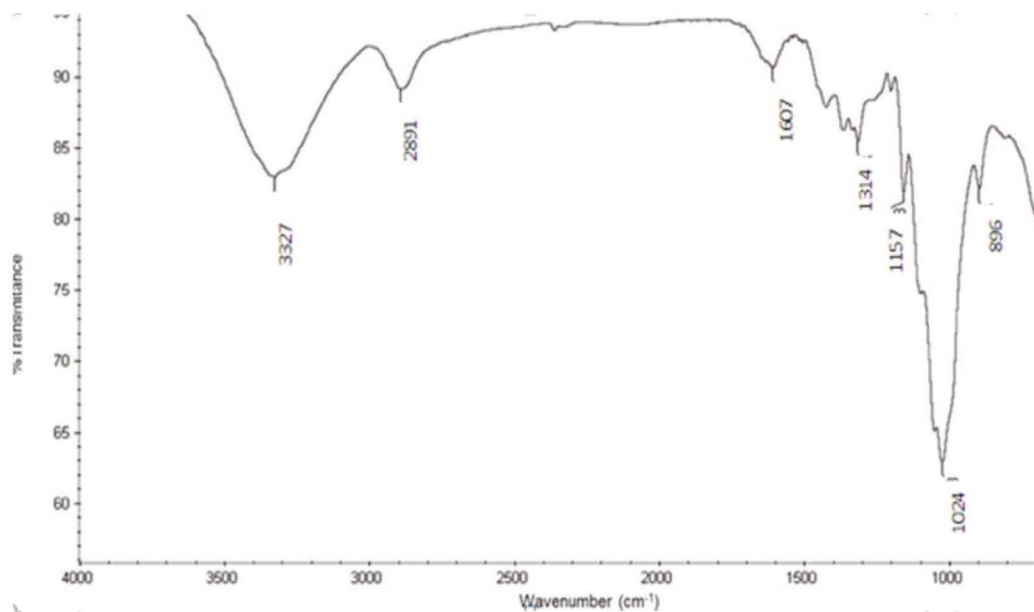


Figure 4. FTIR spectrum from the cellulosic compound obtained after sawdust extraction.

Figure 5 shows a FTIR spectrum obtained from a microcrystalline cellulose standard obtained from Alfa Aesar Co, USA, the standard and the cellulose extracted from pine sawdust show spectra nearly identical, indicating that there was no lignin or hemicellulose in the final extracted compound.

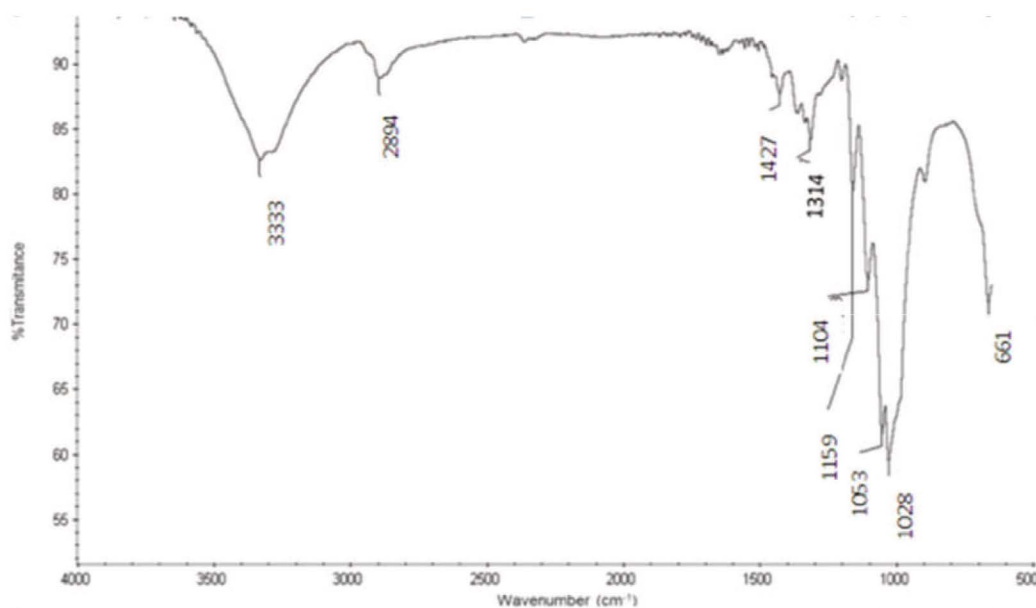


Figure 5. FTIR spectrum obtained from cellulose standard.

The information obtained from DSC indicates that the cellulose extracted from sawdust presents a similar thermic behavior to cellulose standard, figures 6 and 7. In both thermograms no transition can be seen, the baseline increased along temperature indicating that the samples are degraded when both are heated above 50 °C. In addition to the decomposition, the cellulose (standard and extracted) doesn't show fusion below 300 °C, enthalpic transitions due to phase changes or melting were not observed. Cellulose extracted from sawdust, on the other hand, showed a slight change below 100 °C, suggesting a transition was present at this temperature probably due to the presence of small amount of water (figure 7).

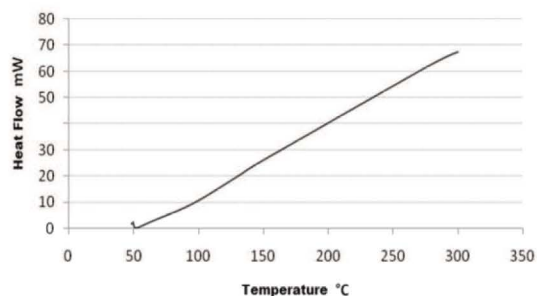


Figure 6. DSC thermogram of cellulose standard.

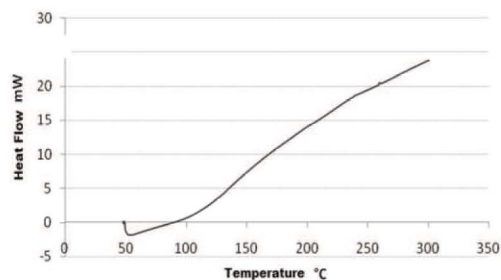


Figure 7. DSC thermogram of sawdust extracted cellulose.

Degree of crystallinity determination

X-Ray diffractograms, shown in figures 8 and 9, reveal there were no significant differences between the cellulose extracted in the third stage of the method and the cellulose standard. According to the literature, the cellulose extracted from sawdust showed a type I crystalline structure [16].

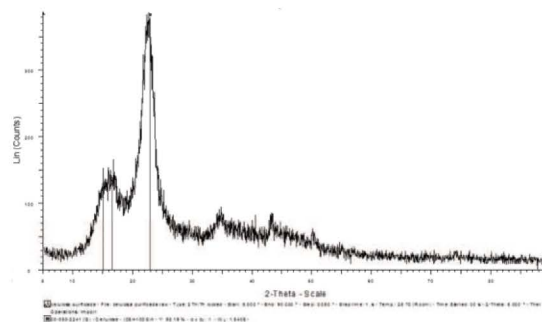


Figure 8. X-ray diffraction spectra of cellulose obtained from sawdust.

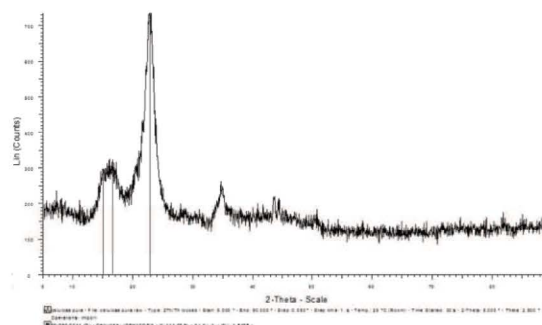


Figure 9. X-ray diffraction spectra of cellulose standard.

The crystallinity index (I_c) was also analyzed for both celluloses, obtaining 70.27% and 73.68% for standard cellulose and sawdust extracted cellulose, respectively. Crystallinity indexes reported in references range from 70 to 85% (10), so we can conclude we obtained similar results; although the I_c of extracted cellulose was slightly higher due to the fact that during heat treatment and extraction the crystallinity tends to increase, however this greater I_c is not significant.

$$I_c \text{ (extracted cellulose)} = \frac{380 - 100}{380} \times 100 = 73.68$$

$$I_c \text{ (standard cellulose)} = \frac{740 - 220}{740} \times 100 = 70.27$$

A high crystallinity index was thus obtained (references report an I_c value between 70 and 80%), but it should be remembered that this index varies depending on the type of tree, wood and treatment.

4. Conclusions

Sawdust extraction was performed to obtain cellulose and lignin, which were identified by FTIR after being isolated and purified. The extraction percentage was 46% and 34% for cellulose and lignin respectively; the hemicellulose was not quantified, only was extracted in order to purify the extract of cellulose. Cellulose was characterized with FT-IR, X-ray diffraction was used in order to determine degree of crystallinity. According to the results obtained by DSC, the extracted cellulose and the standard were degraded warmed from 50 up to 300 °C. After extraction from sawdust, the cellulose can be used in formulating a number of important materials

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6. References

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