Journal of Chemical, Biological and Physical Sciences

An International Peer Review E-3 Journal of Sciences

*Available online at*www.jcbsc.org

Section D: Development of Biotechnological Process

CODEN (USA): JCBPAT Research Article

Characterization of Lignocellulosic Biomass Using Five Simple Steps

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Abstract: The pretreatment of the lignocellulosic biomass is the most important step in the biorefinery processes, because it has a high influence on the yield and efficiency of the subsequent treatments. In order to choose the most suitable pretreatment is necessary to characterize the cellulosic feedstock adequately. TAPPI and NREL methods have been used widely in recent years. The first one is useful to characterize the pulp and paper feedstock, and the second one is used in the biofuels production. However these methods are not fully accurate for determining lignocellulosic materials composition, such as corncob. Therefore in this work, we improved the characterization method modifying some steps. The stages of extraction and quantification of lignin and hemicellulose were enhanced by implementing separate procedures for each component. This methodology has been used successfully for different types of corncob, municipal solid waste and water hyacinth.

Keywords: Characterization, hemicellulose, lignin, cellulose, corncob.

INTRODUCTION

There is currently a great interest on the use of lignocellulosic biomass for obtaining ethanol, lactic acid, xylitol, probiotics, resins and other compounds[1-5]. In order to do so, biomass needs to be subject of diverse proceedings to obtain either fermentable sugars or simpler compounds than the polymers that constitute the lignocellulosic biomass. The first step consists on determining its composition as to decide the process to follow and measure the performance in each stage. Otherwise only approximated results would be obtained and scaling up to larger stages can be more difficult due to errors in mass balances.

Lignocellulosic biomass comprises agricultural and agro industrial residues such as straw, stubble, sugar cane bagasse, corncob, fruit rinds and leftover seeds. There are also forestall and municipal residues, as well as those coming from paper and wood[6]. This biomass has a common vegetal origin and is constituted by the polymers: cellulose, hemicellulose, lignin and pectin[7]. The proportion of these polymers varies depending upon the characteristics of the material, which can be herbaceous or woody, homogenous or heterogonous[8].

There are different methodologies as to determine the composition of the lignocellulosic material, some come from the paper and wood industries[9], while other methodologies have been developed in recent years as a consequence of the need for renewable energies' production[10].

Due to the complexity of the plant cell wall (**Figure 1**), the quantification of its components cannot be carried out directly. In general, the methodologies comprises -in first place- the reduction of the particle size and its homogenization so that the reagents used in further stages can easily interact with the plant cell wall. The soluble compounds on water as well as organic solvents are extracted in two steps; these comprise soluble sugars, waxes, pigments, etc.[11]. Subsequently, the biomass is fractioned in its structural components (cellulose, lignin and hemicellulose) for their degradation. The products from this degradation are monomers of polysaccharides and fractions of lignin which can be quantified through a variety of methods[12].

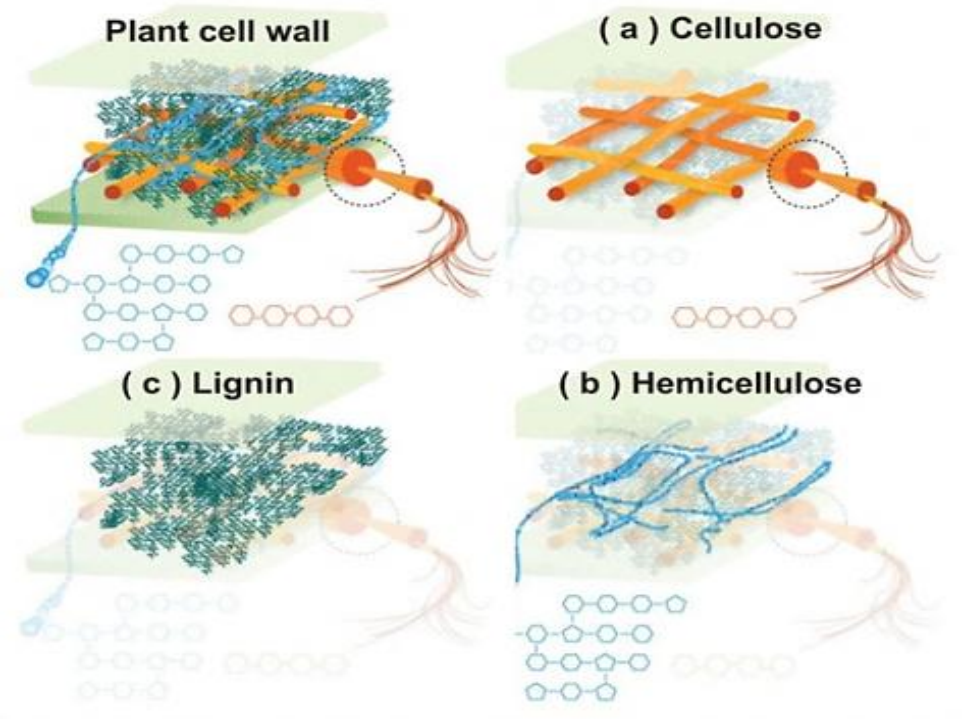

Figure 1: Parts of the plant cell wall.

The accuracy of the analysis largely depends upon the ease with which the structural polymers are fractioned and hydrolysed, which at the same time depends on the complexity of the biomass in terms of its molecular organization[13].

The method proposed on the present work is partially based on the NREL methodology for determining humidity, extractives and particle size[14-16]. This methodology however has been modified as to determine hemicellulose, acid lignin and alkaline lignin concentrations in a more accurate way. This methodology led to the characterization of different lignocellulosic materials: corncob, water hyacinth, sugar cane bagasse and municipal solid waste.

METHODS

Lignocellulosic Materials: The lignocellulosic materials characterized with the methodology proposed in this work were the white and blue corncob, water hyacinth, bagasse and municipal organic waste from the Central de Abasto of Mexico City (Mexico)

The white corncob came from San Andrés Cholula, Puebla, Mexico (latitude, 19° 03′ 00″ North and longitude, 98°18′00″ West). The blue corncob was collected in Acambay, Estado de Mexico, Mexico (latitude, 19° 57' 15'' North and longitude, 99° 50' 39'' West). The water hyacinth was obtained in the Lake of Xochimilco, Mexico City, Mexico (latitude, 19°16' 52'' North and longitude, 99° 4' 43'' West). The sugar cane bagasse is from the sugar mill of Zacatepec, Estado de Morelos, Mexico (latitude, 18° 39' 32'' North and longitude, 99° 11' 42'' West). The municipal solid waste was collected from the Central de Abasto o Mexico City, Mexico (latitude, 19° 20' 4'' North and longitude, 99° 4' 23" West).

Materials conditioning: The residues from Mexico City's Central de Abasto (CA), as well as the water hyacinth were chopped and dried outdoors for 10 days due to their high moisture content. The corncob was used once it was dehydrated. After the drying process, both the residues from the CA, the corncob and the water hyacinth were milled in a hammer mill of 5 CP (Veyco). After finishing with the drying process, the material was sifted in a mesh #10 (ASTME 11-87) with a size of 2 mm before being used in subsequent stages. Regarding the bagasse, this was used as it is obtained after the milling process in the sugar mill of Zacatepec, Mexico.

Cellulose, A and B hemicellulose, and lignin identification through infrared spectroscopy by Fourier transformer (FT-IR)

The FT-IR spectrum were carried out in an spectrometer FT-IR (Nicolet Impact 400, USA) which has a resolution of 2 cm^{-1}, using KBr tablets containing 10% of finely ground sample. The region used for the analysis was of 500-4000 cm^{-1}.

Methods for determining the chemical composition

Determination of Moisture: Moisture determination consisted in drying a gram of lignocellulosic material at 110 °C for 4 hours in a Blue M electric oven, model OV-18A. Subsequently, the humidity percentage was determined by the weight difference between the humid material (1 gram in every case) and the final dry sample.

Determination of ash: For the determination of ashes, 1 g of lignocellulosic material was incinerated in a Lindberg/Blue M Moldatherm muffle at a 520 °C temperature for 4 hours. The incinerated material was weight and the ash percentage was calculated by dividing the ash weight by the dried lignocellulosic material weight. The incineration temperature was of 520 °C due to the fact that the carbohydrates (250–350 °C) and lignin (300–500 °C) oxidise at said temperature, thus obtaining CO_2 and evaporating water[17].

Determination of extractives: The extractives were determined in two consecutive stages, during the first one 190 mL of grade HPLC water were used as dissolvent in order to separate the inorganic materials, non-structural sugars, starch and proteins[17]; the temperature of the operation was 93 °C and the reflux time of 5 h.

On the other hand, during the second extraction anhydride ethanol (190 mL) was used as dissolvent to separate the compounds such as terpenoids, waxes, fat acids, phenolic substances and chlorophyll[15, 17]; the extraction temperature was 72 °C and the reflux time of 7 hours. For both stages 2 to 5 g of dried material were fed inside a cellulose extraction thimble (Thimble Filters, ADVANTEC, No. 84, ID 22 x 80 mm) in Soxhlet equipment (extraction camera of 34 mL, Allin condenser and a round-bottomed flask of 250 mL). The extractives percentage was determined by dividing the difference between the initial material weight and the weight after extracting the soluble components in water and ethanol.

Determination of hemicellulose: The hemicellulose was determined using the Du Toit *et al.*[18] method but making some changes during the A and B hemicellulose recovery. For the recovery of hemicellulose A the precipitation pH was reduced from 5 to 4, which enhanced product recovery. With regards of hemicellulose B, the precipitation methodology was modified by augmenting a step in order to avoid the excessive use of solvents and enhance the recovery of hemicellulose B (**Figure 2**).

The material used for the extraction of hemicellulose must be a free sample of extractives since the soluble compounds interfere with the analysis[17]. In order to separate the extractives, 20 g of lignocellulosic material, which was washed 8-10 times in a 250 mL beaker were with approximately 100 mL of boiling water (93°C in Mexico City), were used. Vacuum filtration equipment (GAV PL, model 4CFD3) was used during the washing at a pressure 40 kPa to increase the speed of the washing water extraction. After separating the water soluble extractives, the material was washed with 80 mL of boiling anhydride ethanol (72 °C). During such process, vacuum filtration was used to extract the ethanol of every wash. The material was left to dry at 50 °C in an electric oven (Blue M, model OV-18A) for 8 hours as to remove the remnant ethanol of the sample.

Once the material was dried, an alkaline extraction was performed as to solubilize the fractions A and B that comprise the hemicellulose. The alkaline extraction consisted on putting 2 g of free-extractives material in a 50 mL Erlenmer flask, and then adding 30 mL of a solution 1 *M* of NaOH. The system was stirred at 130 rpm (New Brunswick Scientific Gyrotory Shaker stirrer, model G2) at room temperature (~24 °C) for 24 hours. The insoluble material was separated through vacuum filtration at a pressure of 40 kPa. Subsequently, the insoluble fraction was washed 3 times with 20 mL of deionized water (17 MΩ·cm). To obtain the hemicellulose, the filtrate which pH was 9 was acidified to a pH of 4 by using acetic acid at 50% (w/w). The resultant suspension was stirred for 10-15 minutes at room temperature and subsequently centrifuged (BHG HERMLE Z320 centrifuge, National LabNet Company) at 3300 rpm for 20 minutes. Hemicellulose A was recovered by decantation, the solid was dried to 85°C for 8 hours and then the weight of the product was determined.

The supernatant obtained from the first part was concentrated in a rotary evaporator (Hahnshin Scientific Co, model HS-2001NS of 1 L) to a tenth of its original volume (~8 mL). The concentrated of the supernatant was added drop by drop in methanol anhydrous with a ratio of 1.3 in volume (concentrated-methanol) to precipitate the hemicellulose B. The mixture was centrifuged at 3300 rpm for 20 minutes. Hemicellulose B was recovered by decanting the methanol supernatant and drying the tablet at 85 °C for 8 hours. The weight of hemicellulose B was determined afterwards. The amount of hemicellulose present in the lignocellulosic material is the sum of fractions A and B.

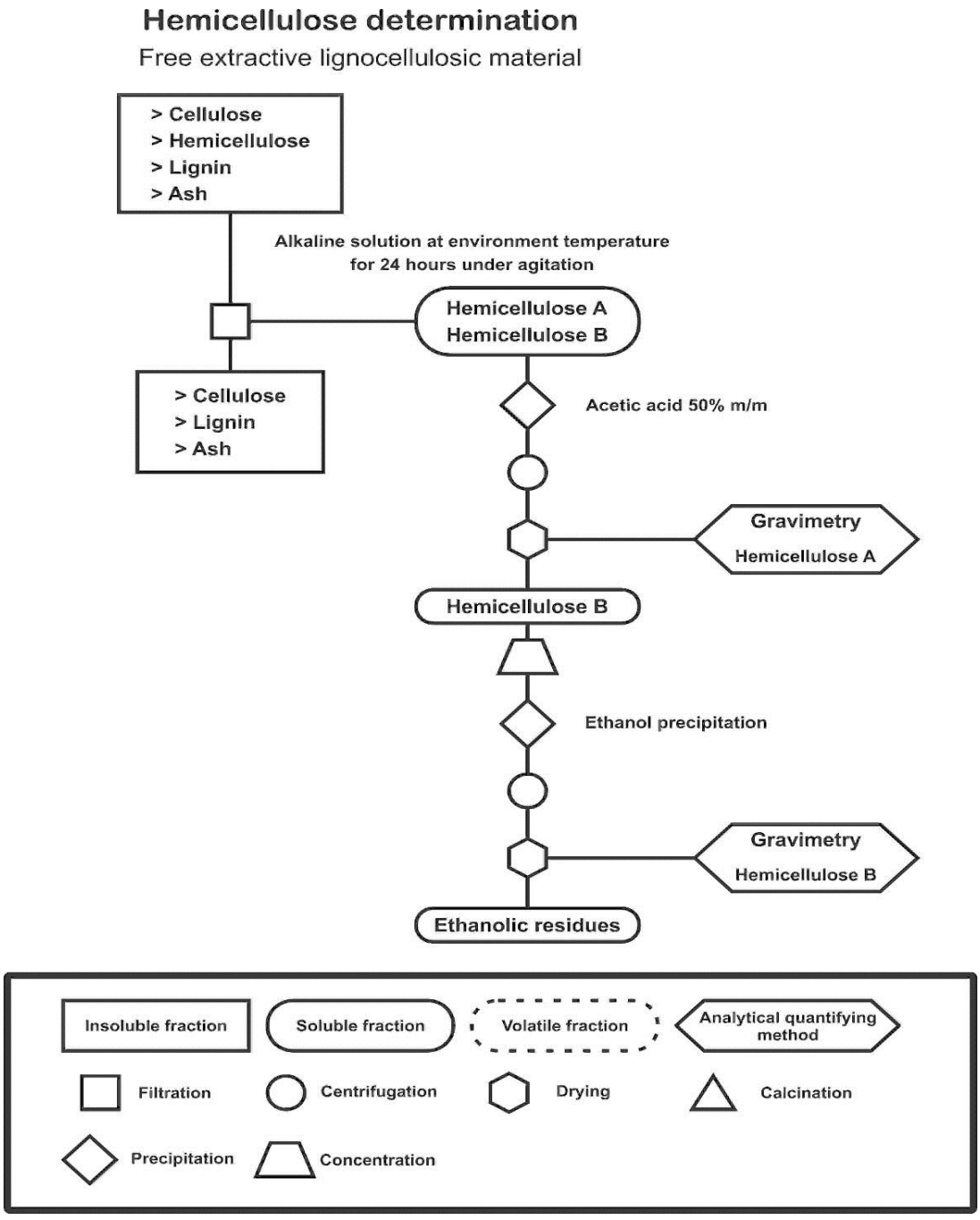

Figure 2: Flowchart for hemicellulose determination on lignocellulosic materials.

Determination of lignin and cellulose: Lignin and cellulose determination comprised 2 stages (**Figure 3**). During the first stage most of the hemicellulose (> 70%) and al the lignin are hydrolysed in an acid media. During the second stage, alkaline lignin and the rest of hemicellulose are extracted thus completely freeing the cellulose.

The first stage is the thermochemical treatment, which consisted of adding 5 g of lignocellulosic dry material in 5 Erlenmeyer flasks (250 mL) and adding 100 mL of a 0.275 *M* of H_2SO_4 solution. The suspension was stirred (New Brunswick Scientific Gyrotory Shaker stirrer, model G2) at 130 rpm during 24 hours at room temperature. Subsequently the flasks with the mix were heated to a temperature of 118 °C. In order to achieve this, the flasks were covered with Bakelite and perfectly sealed with Teflon tape. 2 L of water were then added to a stainless steel steam autoclave (with a gauge) of 21 L (scale of 0-30 psi and 100-133.6 °C). Once the flasks were put inside the steam autoclave the reactor was closed.

The reactor was heated with direct fire until the water vapour reached a manometric pressure of 12 psi. Once such pressure was reached, the flasks were left in the reactor for 30 minutes. Given that the water vapour is saturated and that the thermal equilibrium between vapour and mix of the flasks is reached, temperature was of 118°C. Subsequently the reactor was cooled in a quick way by using water. The manometric pressure was reduced to almost 0 psi in less than 1 minute.

Immediately afterwards the flasks were taken out from the reactor and a vacuum filtration was carried out with a pressure of 40 kPa in order to recover the solid from the flasks. Then, the solid was washed with 60 mL of deionized water (17 MΩ·cm) and the filtrated volume was measured in a 100 mL test tube. The thermochemical treated solid was dried at 40 °C during 8 hours. An aliquot of 5 mL of thermochemical treatment filtrate was taken and centrifuged at 3300 rpm for 15 minutes. The supernatant was vacuum filtered using filtration equipment with sintered glass and a nitrocellulose membrane of 22 μm. The acid lignin concentration was determined by taking 1 mL of sample performing a serial dilution up to 1:1000.

The calibration curve was previously made by using alkaline lignin reagent degree obtained from Sigma-Aldrich. A standard solution (pH=9) was prepared by using deionized water (17 MΩ·cm) and NaOH reagent degree. The concentrations of lignin used were 500, 250, 125, 62.5 y 31.25 ppm. The absorbance of each solution was measured using 3 mL of sample at a wavelength pf 280 nm in Agilent/Varian Cary 50 UV-Vis Spectrophotometer with a cell of quartz of 3.5 mL (Infrasil NIR). The curve of calibration had a correlation coefficient of 0.99927.

The second stage is the delignification process that uses an alkaline media catalysed with hydrogen peroxide. In order to do so a gram of the thermochemical treated solid was taken and put in 5 Erlenmeyer flasks of 50 mL, adding 20 mL of a solution of 0.375 *M* of NaOH and 0.24 mL of a solution 12.8 M of H_2O_2. Subsequently the temperature of the flasks was raised up to 50°C while keeping it in constant stirring (150 rpm) for 3 hours in a New Brunswick incubator model G25. When the reaction time was over, the solid was recovered by vacuum filtration (40 kPa pressure), and then washed with 40 mL of deionized water (17 MΩ·cm) as to remove the surplus of NaOH. The non-degraded solid is the delignified material, which was dried at 80 °C for 8 hours and then weighted.

In order to precipitate the alkaline lignin, the filtered liquor was acidified with acetic acid to 50% (m/m) up to pH 3 stirring constantly for 30 minutes. The mix was centrifuged at 3300 rpm for 20 minutes. The supernatant was decanted and the precipitate was dried at 80 °C for 8 hours. The weight of the alkaline lignin was determined afterwards and the supernatant was discarded. Finally, 0.3 g of delignified material were taken and incinerated at 520 °C for 4 hours as to determine the amount of cellulose (initial material mass minus mass of ashes).

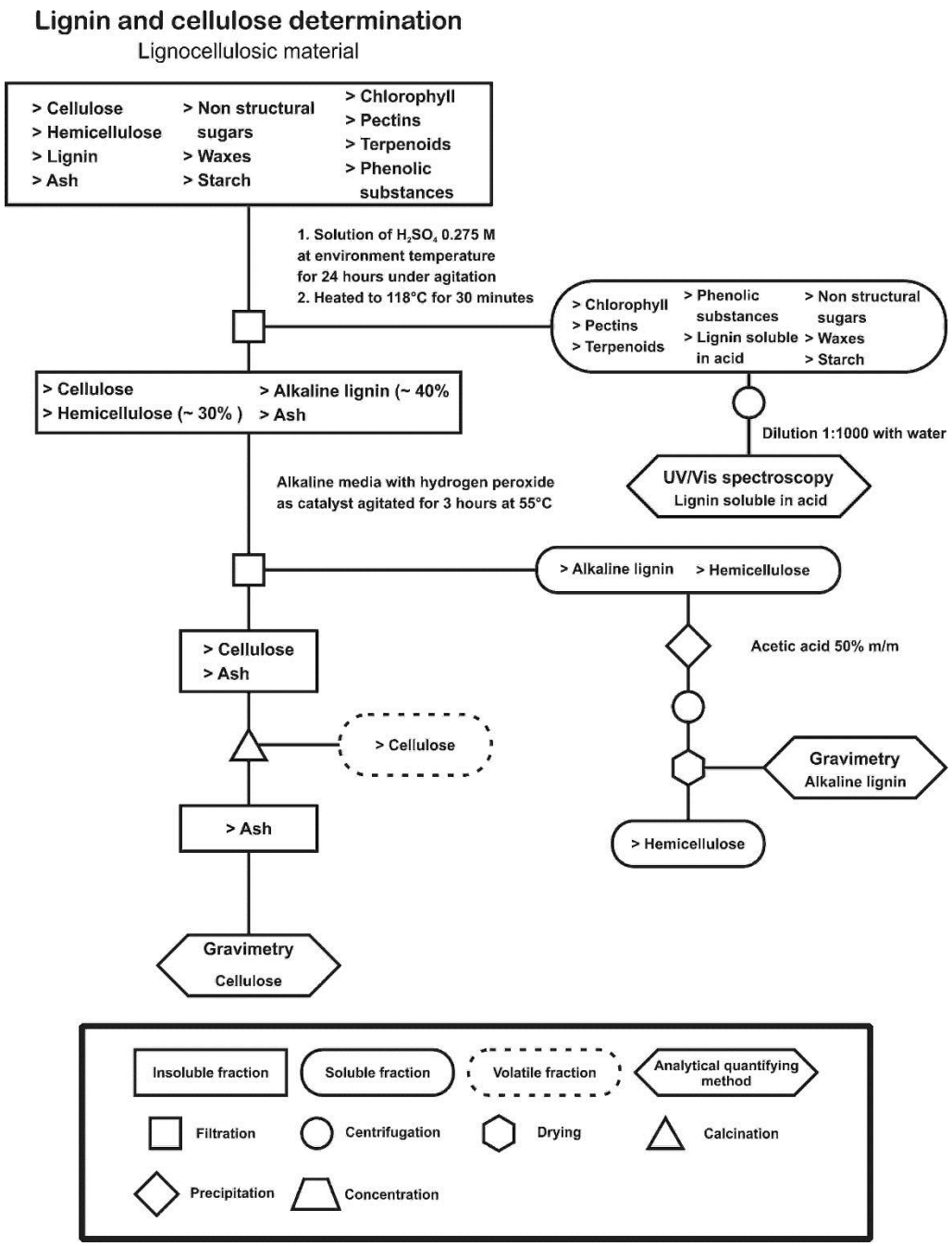

Figure 3: Flowchart for lignin determination on lignocellulosic materials.

Determination of pectin: The pectin determination was carried out solely in the municipal solid waste since there is a large quantity of pectin to be recovered from such waste.

The pectin was determined using the Mexican Rule (*Norma Mexicana*: NMX-F-347-S-1980[19]. The methodology consists in putting 50 g of lignocellulosic material in a 600 mL beaker and adding 400 mL of distilled water. The suspension was let to boil for one hour keeping the added volume of water constant. Afterwards, the water was decanted to a 500mL volumetric flask and diluted to the mark. The filtration was

carried out with extra fine paper Whatman #4 taking 5 aliquots of 100 mL for this solution. 100 mL of water and 10 mL of NaOH *1N* were added. The flask was let to rest for 8 hours. Subsequently 50 mL of water were added in a solution of acetic acid 1 *N* to each aliquot and let that each solution to rest for 5 minutes. Later 25 mL of a $CaCl_2$ 1 *N* solution were slowly added while maintaining the stirring constant, and then were let to rest for 1 hour. The solutions were heated to boiling point and filtrated while still warm through dry filter paper. The filter paper was perfectly washed with hot water until all the traces of $CaCl_2$ were removed. Finally, the filter paper and residues were transferred to the low form weighing bottle and dried at 105 °C until constant weight was achieved and the masses were determined.

RESULTS

Chemical composition of the materials: Table 1 shows the results of the chemical composition of the lignocellulosic materials studied. **Tables 2, 3, 4** and **5** show the chemical composition of the corncob, water hyacinth, sugar cane, and municipal solid waste obtained by other authors. It can be observed in **Table 1** that the sum of the cellulose fractions, hemicellulose, acid lignin, alkaline lignin and ashes ranges between 92-98%. The extractive fraction is between 3-5% (not included in Table 1). Regarding the pectin fraction (municipal waste) a value of 6% was obtained.

Table 1: Chemical composition of lignocellulosic materials.

Sample	Corncob of blue corn		Corncob of white corn		Water hyacinth		Sugarcane bagasse		Municipal solid waste	
Component	Composition									
	%	± □	%	± □	%	± □	%	± □	%	± □
Cellulose	28.00	± 0.73	29.06	± 0.76	22.38	± 1.37	43.89	± 0.49	19.38	± 0.15
Hemicellulose	39.89	± 1.21	35.52	± 0.85	23.44	± 0.18	33.38	± 1.74	35.29	± 0.53
Acid lignin	16.02	± 0.97	14.57	± 0.38	19.41	± 1.79	8.80	± 0.81	20.63	± 0.34
Alkaline lignin	12.81	± 0.33	11.08	± 0.29	7.62	± 2.11	8.86	± 0.07	7.36	± 0.38
Ash	1.65	± 0.06	1.92	± 0.08	19.65	± 0.32	4.51	± 0.13	12.62	± 0.18
Moisture	6.33	± 0.26	6.32	± 0.21	10.00	± 0.08	49.34	± 2.14	9.40	± 0.33

Results for the corncob: The determination of cellulose in the blue and white corncob rendered a percentage of 28.00% and 29.06%. These values are within the composition range of **Table 2**. Kumar *et al.* reported that the corncob obtains an approximated percentage of 34.45% of α-cellulose[22,23], which is very similar to the one obtained here. In some works larger amounts of cellulose have been reported, which can be a consequence of the fraction still containing lignin. In the present study, this faction is composed by α-cellulose. This (α-cellulose) is defined as the portion of the insoluble material in a solution of sodium hydroxide at 17.5% in mass, due to the fact that they have a high degree of polymerization. Furthermore, β-cellulose is the portion that is dissolved and that is precipitated when the solution is neutralized, while γ-cellulose is the dissolved part that remains soluble in the neutral or slightly acid solution. Fractions β and γ have a lower degree of polymerization and are known as hemicelluloses.

The cellulose can also be identified as the amount of glucans present in the lignocellulosic materials. Lee *et al.* and Makishima *et al.*[21] report that the amount of glucans present in the corncob is of 29.70% and 37.00%, respectively[21, 25]. The values determined in this stud fall within this range, hence it's possible that the extracted fraction is high purity cellulose.

Table 2: Review of chemical composition of corncob.

Component	Hallocellulose	Glucan	Pentosan	Cellulose	Hemicellulose	Lignin	Klason lignin	Alkaline lignin	Acid lignin	Ash	Reference
Corncob	-	-	-	31.40	29.90	22.00	-	-	-	-	Varga *et al.*(2005)[20]
	-	29.70	33.30	-	-	-	3.40	-	12.70	2.70	Makishima *et al.* (2009)[21]
	73.04 α-cellulose: 34.45 β-cellulose: 18.73 γ-cellulose: 19.84	-	28.23	-	-	16.03	14.01	-	2.02	-	Kumar *et al.*(2010)[22]
	73.04 α-cellulose: 34.45 β-cellulose: 18.73 γ-cellulose: 19.84	-	28.23	-	-	-	14.01	-	-	2.21	Kumar *et al.*(2010)[23]
	-	-	-	32.00	35.00	20.00	-	-	-	4.00	Jeevan *et al.*(2011)[24]
	-	37.00	29.99	-	-	-	13.90	-	-	-	Lee *et al.*(2011)[25]
	-	-	-	27.48	36.37	28.60	-	19.95	8.05	-	Zhang *et al.*(2011)[26]
	-	-	-	37.44	39.81	12.57	-	-	-	-	Sunarti *et al.*(2011)[27]
	-	-	-	32.30-45.60	39.80	6.70-13.90	-	-	-	-	Zych *et al.*(2008)[28]
	-	-	-	59.40	6.50	22.20	-	-	-	-	Tessa-Marie *et al.*(2012)[29]

The percentages of hemicellulose in the blue and white corncob were of 39.89 and 35.52%, respectively. According with the information provided in **Table 2**, the range of hemicellulose composition is of 6.50-39.81%, while for the pentosans is of 28.23-33.30%. When the hemicellulose is determined by alkaline concentrated extraction the fractions obtained are β and γ-cellulose, which reported percentage, is of 38.57% [22, 23]. Therefore similar results to those of other authors were obtained in this work.

Lignin has been reported in four different forms: Klason lignin (KL) which is obtained from the hydrolysis with sulphuric concentrated acid at 72% in weight; soluble lignin in acid media (ASL); soluble lignin in alkaline media (BSL); total lignin (TL) that is the sum of KL and ASL or else the sum of ASL and BSL. With our methodology the ASL fraction was of 16.02% (blue corncob) and 14.57% (white corncob). The compositions of BSL were of 12.81% (blue corn cob) and 11.08% (white corncob). Therefore the compositions obtained where similar to the reported values (**Table 2**). The ashes fraction obtained was of 1.65% (blue corncob) and 1.92% (white corncob). These values are similar to the ones reported in **Table 2**.

Results for the water hyacinth: Fort the water hyacinth a cellulose fraction of 22.38% was obtained, this means that this value falls within the value range shown by literature (**Table 3**). Since the water hyacinth used was composed mainly by leaves, the percentage of cellulose is similar to those reported for this part of the plant. With regards to the hemicellulose fraction, the determined value was of 23.44% which is within the range of **Table 3**. Lignin composition was of 27.03%, similar in this case to the values reported for the whole plant. The ashes amount, which depends on the concentrations of water diluted metals, was of 19.65% value, thus found in the rage of **Table 3.**

Table 3: Review of chemical composition of water hyacinth.

Component	Cellulose	Hemicellulose	Lignin	Ash	Reference
Water hyacinth	18.20	48.70	3.50	—	Nigam (2002)[30]
	19.50 31.00 18.00 17.80 25.61	33.40 22.00 33.97 43.40 18.42	9.27 7.00 26.36 7.8 9.93	25.70 15.00 — 20.2 16.39	Gunnarsson and Mattsson (2007)[31]
	46.70		27.70	18.20	Girisuta *et al.* (2008)[32]
Leaves Whole plant	19.70 35.00	27.10 18.30	—	—	Mishima *et al.* (2008)[33]
	18.40	49.20	3.55	—	Kumar *et al.* (2009)[34]
Leaves Stems Roots	28.91 28.23 17.07	30.80 26.35 15.25	4.59 17.44 14.63	12.95 20.26 49.97	Cheng *et al.* (2010)[35]
	18.20	29.30	2.80	1.20	Ma *et al.* (2010)[36]
	27.00	20.30	10.00	20.80	Su *et al.* (2010)[37]
	25.00	35.00	10.00	20.00	Bhattacharya *et al.* (2010)[38]
	40.20		6.50	—	Harun *et al.* (2011)[39]

Results for the sugar cane bagasse: The cellulose obtained was of 43.89%, similar to the values reported by other authors both for cellulose and glucans. For the hemicellulose the percentage obtained was of 33.38%, a value slightly higher than those reported (**Table 4**). This can be a consequence of having traces of lignin in the polysaccharide structure during the hemicellulose extraction Those traces are around 11.21% with respect to the total composition[46]. It is worth mentioning that our methodology presents as an advantage the fact that the amount of polysaccharide is determined, unlike other methods that add up the generated monosaccharides during the hydrolysis. Sluiter *et al* report that for sugar generation from hemicellulose, one should multiply the polysaccharide mass by 0.88 [47]. TL and ashes compositions' measures (**Table 1**) were similar the ones shown in **Table 4**.

Table 4: Review of chemical composition of sugar cane bagasse.

Component		Glucan	Pentosan	Cellulose	Hemicellulose	Lignin	Ash	Reference
Sugar cane bagasse		–	–	45.40	28.70	23.04	2.07	Fernandes Pereira *et al.* (2011) [40]
		–	–	45.00	25.80	19.10	1.00	Canilha *et al.* (2011[41]
		–	–	35.20	24.50	22.20	20.90	Alves Rezende *et al.*(2011)[42]
		42.90	22.80	–	–	–	–	Zhang *et al.*(2012)[43]
		–	–	45.50	27.00	21.10	2.20	Rocha *et al.*(2012)[44]
Variety	Harvest year							
55	2009	35.10	27.10			19.60	1.60	
70	2009	36.10	26.50			20.40	1.80	
74	2009	36.90	25.50			19.70	2.00	
101	2009	40.70	28.50			14.40	0.80	
104	2009	34.10	28.20	–	–	16.40	0.90	Benjamin *et al.* (2014)[45]
114	2009	38.30	29.70			16.10	0.90	
55	2011	38.30	25.30			20.30	1.50	
70	2011	37.40	24.20			20.10	1.90	
74	2011	38.10	23.00			22.30	1.20	
101	2011	39.10	26.70			15.50	2.70	
104	2011	36.80	25.60			16.40	2.80	
114	2011	37.30	28.00			16.80	2.50	

Results for the municipal solid waste: The municipal solid waste is a heterogeneous mixture of different compounds that have mainly an organic origin. Due to the heterogeneity of the municipal solid residue, the cellulose composition, hemicellulose and lignin can be found in a very wide range (**Table 5a and 5b**).

The material used during the research was comprised mainly by leaves and stems of herbs and flowers, peels of fruits and vegetables and ripe fruit. The composition of the cellulose was of 19.38% (**Table 1**). In this sense, Li *et al* report a fraction of cellulose of 18.76% for the potato peel, and Komilis and Ham report a percentage of 14.71% for a mixture of leaves, twigs and tree seeds. Therefore it can be considered that by using our methodology several values similar to those obtained by other authors are obtained. Furthermore, the hemicellulose composition was of 35.29%, which falls in the superior range reported in **Table 5.a**. The lignin composition of the material was of 27.99%. Finally, the ash percentage obtained (12.6%) is under the ranges of **Table 5.a.**

Table 5a: Review of chemical composition of Municipal solid waste.

Component	Cellulose	Hemicellulose	Lignin	Ash	Reference
	35.00-50.00	20.00-35.00	15.00-25.00	–	Van Wyk (2001)[48]
Municipal solid waste	45.00 - 60.00		–	–	Kjeldsen *et al.* (2002)[49]
Seeds	25.51	4.20	25.21		
Grass	39.67	16.89	17.63		
Leaves	9.48	3.24	33.80		
Branches + leaves + seeds	14.71	12.87	42.89		
Office paper + leaves + seeds	68.13	6.71	6.50		
Yard wastes	27.20	11.25	24.34		
Yard wastes + seeds	26.82	10.23	24.54		Komilis and Ham (2003)[50]
Food wastes	46.90	0.00	12.03	–	
Food wastes + seeds	42.51	0.73	14.33		
Mixed paper	69.66	7.79	15.90		
Mixed paper + seeds	65.41	7.45	16.80		
Mixed paper + yard wastes	57.97	8.49	18.57		
Mixed paper + food wastes	64.62	7.16	16.71		
Yard wastes + food wastes	31.65	8.75	21.53		
Mixed paper + food and yard wastes	47.39	6.89	17.66		

Table 5b: Review of chemical composition of Municipal solid waste.

Component	Cellulose	Hemicellulose	Lignin	Ash	Reference
Landfill (L)	42.40	–	10.90		
L	25.60	6.60	7.20		
L	63.40	–	15.70		
Residencial refuse (R)	51.20	11.90	15.20		
R	28.80	9.00	23.10		
R	38.50	8.70	28.00		
R	48.20	10.60	14.50		
R	36.70	6.70	13.60	–	Barlaz (2006)[51]
R	43.90	10.00	25.10		
R	54.30	10.80	12.10		
L	22.40	5.80	11.00		
Residential food waste (RFW)	55.40	7.20	11.40		
RFW	40.90	6.10	7.40		
RFW	32.20	11.00	15.00		
Carrot peelings	39.49			9.71	
Potato peelings	18.76	–	–	9.04	Li *et al.* (2007)[52]
Grass	21.60			16.57	

Newspaper	46.12	6.78
Scrap paper	67.07	16.32

FT-IR identification of the polysaccharides and lignin:

Cellulose: Spectrums FT-IR of the sugar cane bagasse and white corncob cellulose are provided in **Figure 4**. The spectrums show the characteristic signals for the cellulose and traces of lignin. The functional groups assigned to each signal are presented in **Table 6**. Signals A, M, N corresponds to the hydroxyl group of primary and secondary alcohols present in the cellulose. The methylene group is in the signals B, C, G, H. Evidence of the existence of the glucose units that form the polysaccharide are signals K, L and O. Polysaccharides as the cellulose can absorb water in their structure, which is confirmed by the presence of D and G. Since cellulose is an insoluble product in an alkaline media, and given the complexity of the plant cell wall, it inevitably contains traces of lignin in its structure. Signals in E, F, I, J y P point out the presence of lignin traces in the sample.

Table 6: Functional groups assignation to the FT-IR spectrum for the cellulose extracted from the cane bagasse and the white corncob.

Signal	Cellulose		Assignation
	Cane bagasse	White corncob	
A	3377.03	3411.68	ν –OH
B	2916.72	2902.51	ν C-H symmetric; in - CH_2 -
C	2854.03		ν C-H asymmetric; in - CH_2 -
D	1637.48	1647.35	δ -OH, adsorbed water
E	1597.02		Lignin traces
F	1507.93	1511	Lignin traces
G	1426.96	1432.21	δ-CH2, δ-OH
H	1372.83	1372.81	Aliphatic C-H
I	1319.83	1327.14	Lignin traces
J		1263	Lignin traces
K	1163.67	1163.24	ν (C-C) ring breathing, asymmetric
L	1112.34	1112.12	ν (C-O-C), ν (C-C) from glycosidic bonds
M	1055.48	1058.5	ν (C-OH) secondary alcohol
N	1036.03		C-OH deformation of primary alcohol
O	897.91	897	δ (CH), ring
P	831.01		Lignin traces

Hemicellulose A and B: During the research 2 fractions of hemicellulose were extracted (A and B). **Figure 5** shows the FT-IR spectrum for the water hyacinth and the white corncob. Bands A and M are assigned to the hydroxyl groups of the polysaccharides, while signals B, C, H and I indicate the presence of the methylene group. Monomeric units of hemicellulose produce K and L signs. Furthermore, signal D indicates the existence of acetyl group found as substituent in the principal structure. Bands E, F and I confirm the hydrophilic of the sample. Finally, for hemicellulose A the presence of lignin traces is registered in G and B, and for the fraction B it is found in J (**Table 7**).

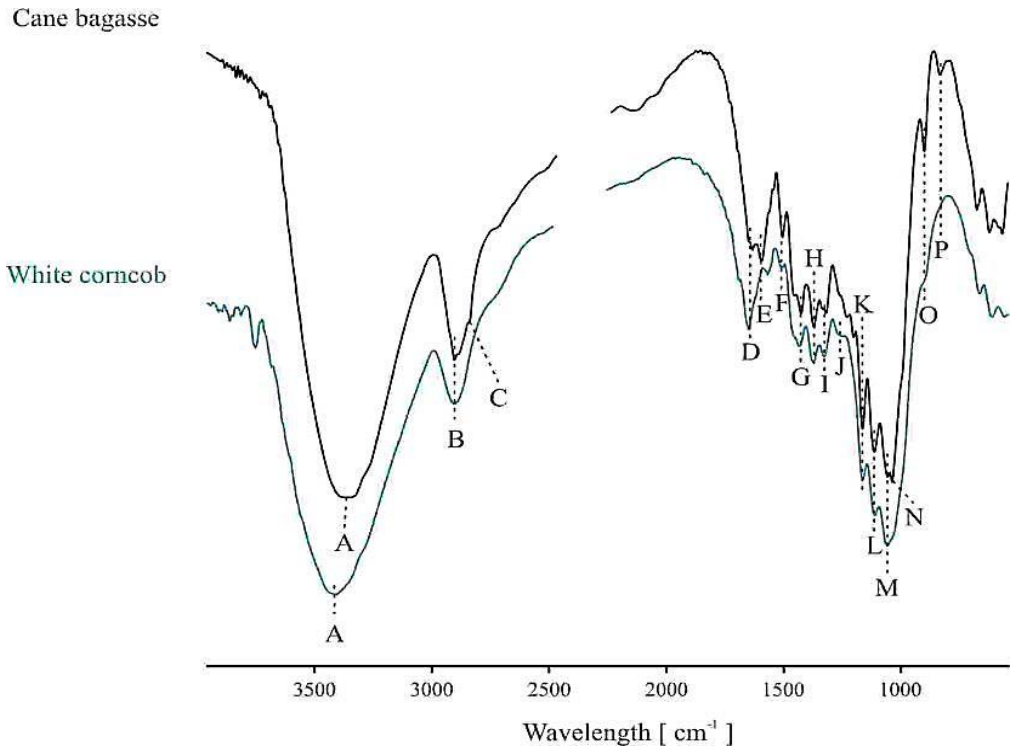

Figure 4: FT-IR spectrum of cellulose isolated form the sugar cane bagasse and white corncob using the lignin and cellulose determination method.

Lignin: Lignin is a polymer formed by phenolic units (coumaryl alcohol, coniferyl and sinapyl) that have a complex arrangement that lacks uniformity, which makes it a rather hard to characterized material when found in its native form. Nevertheless, after being extracted through an oxidation reaction as done in this research, different functional groups related to the monomeric units that allow its identification can be found (**Table 8**). FT-IR spectrums of **Figure 6** contain the spectrums of the lignin extracted from the municipal solid waste, sugar cane bagasse and white corncob.

The distinctive functional groups of the alkaline lignin are the hydroxyl group that is found in the phenolic units and in the aliphatic portions that form the polymer structure. Vibrations A, I and Q represent the hydroxyl group. Furthermore, bands C, D, I y K correspond to the methyl and methylene groups. The aromatic structures have very specific vibrations that can be observed in bands B, G, H, J y R. In addition monomer units (guaiacyl

and syringyl) can also be identified in vibrations L, N, O and T (syringyl) and M, Q and S (guaiacyl). These units are interconnected by ether groups, and this statement is clarified when the P signal is observed. The lignin obtained through an extraction with oxidizing agents produce carbonyl groups. Signal E is characteristic of the carboxylic acid generated when the lignin is recovered. Finally, signal F is for the aryl ketone groups substituted in position 3.

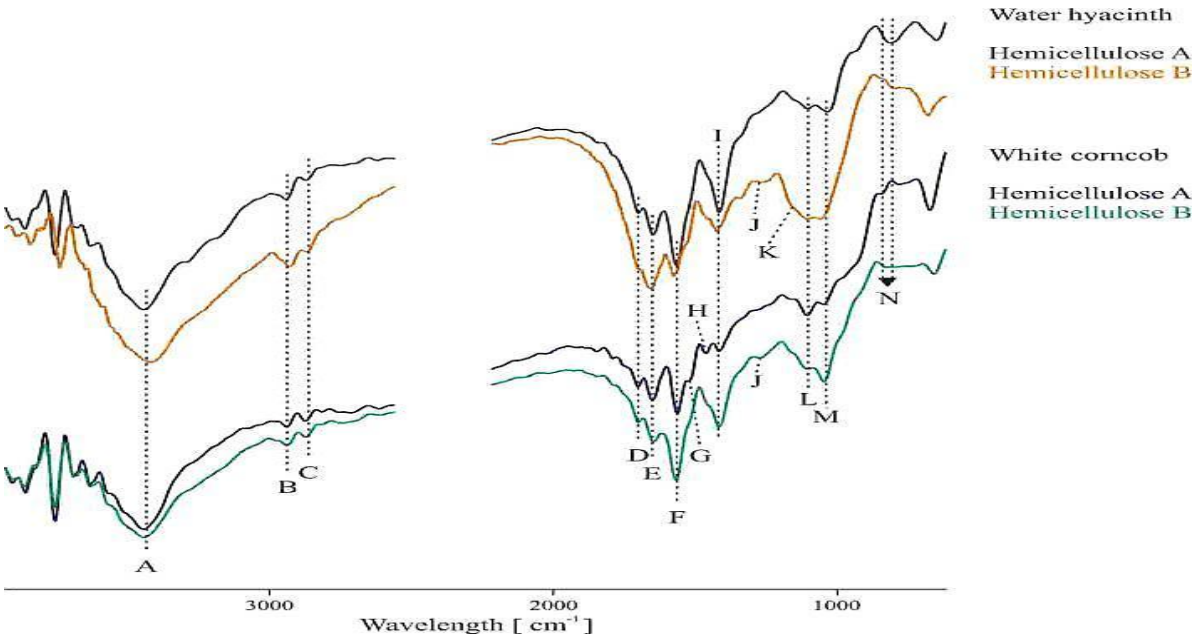

Figure 5: FT-IR hemicellulose spectrum obtained when performing the hemicellulose composition Determination of the water hyacinth and the white corncob.

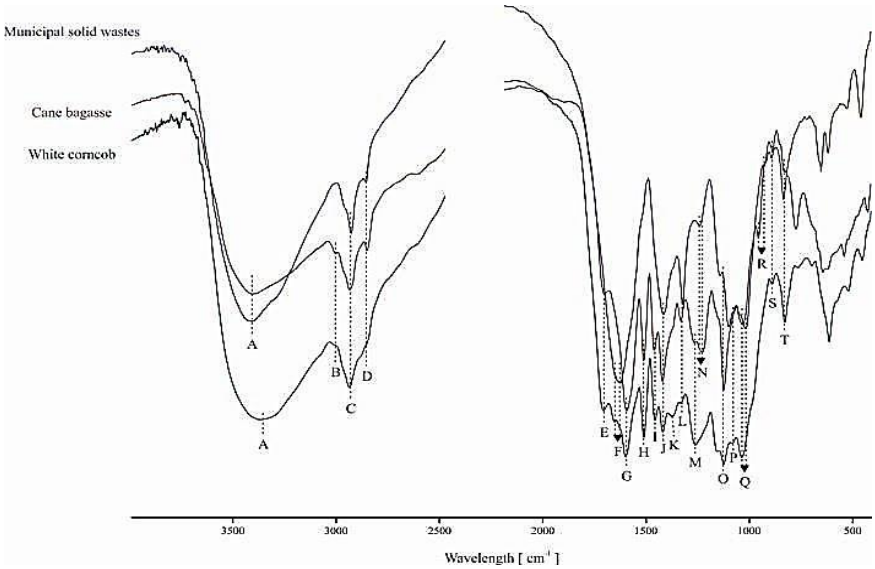

Figure 6: FT-IR spectrum of the lignin obtained while performing the alkaline lignin composition determination for the urban solid residue, sugar cane bagasse and white corncob.

Table 7: Functional groups assignation for the signals on the FT-IR spectrum for hemicellulose A and B extracted from water hyacinth and white corncob.

Signal	Hemicellulose A		Hemicellulose B		Assignation
	White corncob	Water hyacinth	White corncob	Water hyacinth	
A	3444.55	3442.83	3442.62	3436.55	ν -OH
B	2939.54	2941.66	2938.38	2936.71	ν -(CH) symmetric
C	2873.72	2871.52	2872.63	2876.79	ν -(CH) asymmetric
D	1701.41	1700.71	1700.50	1693.96	ν (C=O) acetyl group
E	1651.26	1649.35	1648.46	1646.30	δ -OH, adsorbed water
F	1563.60	1565.91	1566.97	1569.05	δ H-O-H, absorbed water
G	1524.98				Lignin traces
H	1462.72				δ-CH_2-CO-
I	1417.06	1416.53	1416.94	1413.09	δ-CH2, δ-OH
J			1273.09	1254.57	Lignin traces
K	1106.97	1104.63	1106.06		ν (C-O-C), ν (C-C) from glycosidic bonds
L				1093.32	Ring vibrational
M	1049.30	1035.03	1047.09	1044.17	ν (C-OH) secondary alcohol
N	846.52	812.96			Lignin traces

Table 8: Functional groups assignation for the signals on the FT-IR spectrum for the lignin extracted from municipal solid residue, sugar cane bagasse and white corncob.

Signal	Lignin			Assignation
	MSW[a]	Cane bagasse	White corncob	
A	3409.30	3404.44	3360.79	ν -OH
B		3001.12	3080.72	ν-CH in poly-nuclear system
C	2926.33	2934.77	2933.13	ν C-H symmetric; in - CH_3 and - CH_2 -
D	2852.20	2848.67	2879.20	ν C-H asymmetric; in - CH_3 and - CH_2 -
E		1702.98	1706.60	ν - C=O Carboxylic acid
F	1623.77		1644.00	ν -C=O Carbonyl groups in conjugated *p*-substituted aryl ketones
G		1593.21	1599.14	Characteristic of aromatic rings due to the aromatic
H		1511.15	1512.09	skeletal vibrations
I		1460.17	1458.35	δ-CH_2, δ-OH
J	1415.24	1420.04	1420.62	Characteristic of aromatic skeletal vibrations
K			1371.14	Aliphatic C-H in CH_3 not in OMe
L	1323.08	1330.80	1331.61	Syringyl ring (4) breathing with ν - C-O
M		1264.81	1263.49	Guaiacyl ring (5) breathing with ν - C-O

N	1241.75	1228.56		Syringyl ring (4) breathing
O	1141.54	1123.66	1126.61	Aromatic C-H in plane deformation of syringyl type (4)
P	1099.56		1086.69	ν (C-O-C) Ether
Q	1019.14	1032.78	1039.78	Aromatic C-H in plane deformation guaiacyl type (5) and C-O deformation of primary alcohol
R	955.82	929.77		- HC=CH - out of plane deformation
S	892.37	885.89	893.84	δ C-H out of plane vibration at guaiacyl units
T	831.16	834.61	832.60	δ C-H out of plane vibration at position 2 and 6 of the syringyl units

CONCLUSIONS

Comparing the outcomes of the composition percentages of each fraction obtained through the set of methodologies with those reported in literature these result reliable because all of them fall within the ranges published during the last 14 years.

According with the analysis of the infrareds spectrum it can be stated that, both in a qualitative and quantitative way, the extraction, recovery and identification of materials is correct.

The ease of the techniques to isolate each component and their quick application are points in favour of allowing are used during the research of the potential represented by the lignocellulosic materials as raw material. In addition to this, a large majority of these analyses are gravimetric and volumetric analyses, this rendering the methodology available to any research laboratory without having the need of purchasing sophisticated equipment for the quantification.

ACKNOWLEDGEMENTS

We thank FICSAC-UIA (Project: C132020) and CONACYT-Scientific Branch (Mexico) for financial support.

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