

ACID- AND BASE-CATALYZED HYDROLYSES OF CORN STALK

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Nowadays agricultural wastes represent an alternative source of renewable raw materials. Different processes can be applied to these alternative materials to separate their components and obtain chemical products with high added value, such as bioethanol, organic acids, monomers, and biopolymers. The main objective of this work is to study the extraction of hemicelluloses from corn stalks using different reagents [H_2SO_4 , HNO_3 , HCl , CH_3COOH , CF_3COOH , $\text{Ca}(\text{OH})_2$, NaOH]. The raw material was characterized and fractionated with autoclave hydrolysis processes (121 °C, 1:20 solid/liquid ratio, 60 min, pH = 4 or 8). Monomeric sugars concentration, TDS, MO, MI, density, and final pH of the hydrolysate were determined. Hemicelluloses were precipitated and analyzed by different techniques (FTIR, TGA and GPC). The highest yield of hemicelluloses extraction was achieved by sulphuric acid (0.98 g/L total sugar content) and the less effective reagent was $\text{Ca}(\text{OH})_2$ (0.52 g/L total sugar content).

Keywords: Corn stalk; Hydrolysis; Catalysts; Hemicelluloses

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INTRODUCTION

Recently interest in the use of lignocellulosic waste materials has been increased due to their overproduction and the need to find new alternatives for the global energy crisis (Kamm and Kamm 2004). These materials represent an important source of polymeric materials with industrial interest due to their renewable origin and biodegradability of their derivatives (Claasen et al. 1999). Due to the wide variety of available lignocellulosic sources, wood is the most used material in the world for cellulose pulp production, for the construction industry, for the biofuels production, and other applications (Lynd et al. 1999). From the technical point of view, non-wood plants (consisting mainly in cellulose, hemicellulose, and lignin) have a variety of qualities in their fibers which, if they are properly exploited, can be used to produce energy, chemical products with high value added, or to produce polymeric materials, revolutionizing new fields of industrial chemistry and biomaterials.

In the field of materials applications cellulose and lignin have received the most attention among the biomass biopolymers. The hemicelluloses are important natural resources having a high potential. In principle they could be used in many applications, but generally they are not being isolated for industrial use yet (Willför et al. 2008).

At a laboratory scale, the xylo-oligosaccharides are being investigated to use them as raw material for biodegradable films with barrier properties. The monomers can be transformed into biopolymers (lactic acid, alditols, aldonic acids, lactones, and polyols)

to produce polyurethanes, polyamides, or polyesters (Grondahl et al. 2004; Hartman et al. 2006; Mikkonen et al. 2010; Glasser et al. 1995). In addition, hemicelluloses can be used to produce films soluble in water and coatings that can be used in numerous applications in the food and pharmaceutical industries (Lin and Zhao 2007; Malafaya et al. 2007), or to produce chemical products as xylitol (Rivas et al. 2002), furfural, or tensoactives (Hass et al. 1990; Parker et al. 1973).

Hemicellulose is a branched structure polysaccharide that comprises between 20 and 35% of the lignocellulosic materials. A main function of this class of compounds is to link the lignin and cellulose. In comparison to the cellulose, taking into account that the hemicellulose is amorphous, hemicelluloses have a higher rate of hydrolysis in acid media and more solubility in alkaline media. In comparison to the lignin, the hemicelluloses are distinguished by resistance to oxidation.

The hemicellulose fraction is composed of short and branched chains with five and six carbon monomers. The main pentoses are xylose and arabinose, and the main hexoses are glucose, mannose, and galactose. At the same time they have different substituents, such as uronic acids, phenolic acids, and acetyl groups. The main functional groups according to the hemicelluloses structure consist of a carbonyl group in the first carbon and hydroxyl groups in other carbons. The carbonyl group of hemicellulose monomers reacts with the hydroxyl group of the fifth carbon of the same monomer, giving a more favourable cyclic structure in aqueous solutions. The carbonyl functional group can undergo oxidation reactions (oxidation of carboxyl group), whereas the hydroxyl groups can undergo esterification reactions (acetylation).

For the biomass fractionation, different methods can be used, such as hydrolysis (Lavarack et al. 2002; Qiabi et al. 1994; Chamy et al. 1994), physical treatments such as steam explosion (Teng et al. 2010; Montane et al. 1998), or a combination of both (Zimbardi et al. 2007). The autohydrolysis process has attracted much interest during recent years, because it is an environmental and sustainable technology, whose hemicellulosic sugars can be extracted effectively (Carvalho et al. 2004; Garrote et al. 2002). In this work, corn stalks were used as raw material due to the fact that they are an agricultural waste that is usually burned without any value. This waste has been used in a many studies, principally for the production of ethanol, due to its high content in hemicelluloses (Kazi et al. 2010). In other studies, these raw materials also have been used to produce chemical products such as furfural or for the elaboration of composites (Kadam and McMillan 2003).

Different hydrolyses in an autoclave were analyzed for the development of this study, using various acids and bases as catalysts. The main objective was to determine the best catalyst for maximum solubilization of hemicelluloses, minimum degradation of sugars, and minimum solubilization of undesirable compounds. Using the same reaction conditions, different solutions were prepared using different acids (H_2SO_4 , HNO_3 , TFA, and HCl as inorganic acids and acetic acid as organic acid) and bases; in addition to water. Then, except for the sample where just H_2O was used, the pH of the rest of samples was adjusted using different acids and bases. The solution pH was adjusted approximately to 4 and 8 for the acid and base solution, respectively. The liquors obtained from each autoclave hydrolysis were characterized in terms of parameters such as inorganic matter (IM), organic matter (OM), concentration and weight determination

of monomers, and acetic acid content. Finally, all the obtained hemicelluloses were characterized by FT-IR and TGA, in order to determine the purity and yield.

EXPERIMENTAL

Raw Material Conditioning and Characterization

The corn wastes used as raw material in the processes were supplied kindly by the company Straw Pulping Engineering (SPE), S.L. (Zaragoza, Spain). For the conditioning, the corn wastes, with constant moisture, were ground in a mill and then sieved to obtain 4 to 6 mm as the size fraction. For the raw material chemical characterization the contents in ashes (TAPPI T211 om-93), ethanol-toluene extractives (TAPPI T204 cm-97), lignin (TAPPI T222 om-98), α -holocellulose (Wise et al. 1946), α -cellulose, and finally hemicelluloses (Rowell 1983) were determined. All analyses were carried out following standard procedures described in the literature.

Fractionation Process

For raw material fractionation, the corn stalks underwent an autoclave hydrolysis processes. Experimentally 8 different experiments were completed using different catalysts, which were performed under the same conditions (temperature, time, and solid/liquid ratio) and a given pH.

The hydrolysis treatments were carried out in a vertical autoclave "TIMO" with 23 L of capacity, and which supports a maximum temperature of 121 °C and a maximum pressure of 1 atm. Operating conditions were kept constant for all experiments, with a temperature of 121 °C, time of 1 h, and a solid/liquid ratio of 1:20. Preliminary experiments were carried out to select the appropriate solid/liquid ratio. Due to the low density of the corn stalks a maximum value of 1:20 was required to carry out the hydrolysis.

For each experiment different catalysts were used. As inorganic acid: H₂SO₄, HNO₃, TFA, and HCl were used. Acetic acid was used as a representative organic acid, and Ca(OH)₂ and NaOH were used as bases. Finally, pure water was just used as an extractive agent. 5 g of raw material and with the solution of the used reagents were placed in a closed bottle for autoclaving of 250 mL volume. The pH of all solutions, except water, were adjusted to a pH of around 4 for acids and 8 for bases.

Table 1 shows the different experiments that were realized:

Liquors Characterization

Hydrolysis liquors were characterized in terms of density, final pH, total dissolved solids (TDS), inorganic matter content (IM), and organic matter content (OM). In addition, the concentration and weight of monomeric sugars and acetic acid content were determined. In order to determinate the density, each liquor's specific weight was measured in a previously weighed known volume and without moisture. TDS were determined after keeping a weighed sample at 105 °C until constant weight in a furnace (NREL LAP-012). The IM was obtained by weighing the final ashes samples after combustion of the TDS at 525 °C for 3 h (TAPPI T211 om-93), and OM was calculated as the difference between TDS and IM.

Table 1. Experiments Carried Out by Autoclave Hydrolysis with Corn Wastes at 121 °C, 60 min and 1:20 as Solid/Liquid Ratio

Experiment	Catalyst	Initial pH
1	H ₂ O	7.42 ± 0.24
2	H ₂ SO ₄	3.46 ± 0.61
3	HNO ₃	3.29 ± 0.50
4	TFA	3.75 ± 0.05
5	HCl	3.93 ± 0.16
6	CH ₃ COOH	3.82 ± 0.24
7	Ca(OH) ₂	8.03 ± 0.09
8	NaOH	8.44 ± 0.33

Quantification of monosaccharide sugars and acetic acid

The hydrolysate sugars composition were determined with a High Performance Liquid Chromatography (HPLC) Jasco LC-Net II /ADC equipped with a photodiode array detector, refractive index detector, and Rezex ROA_Organic Acid H+ (8 %) column. As mobile phase, dissolution of 0.005 N H₂SO₄ prepared with 100 % deionised and degassed water was used (0.35 ml/min flow, 40 °C, and injection volume 20 µL). For the calibration curve, high purity glucose, xylose, arabinose, and acetic acid were used.

For quantification of monomeric sugars, the hydrolysis liquors were subjected to a post-hydrolysis process. The selection of the operating conditions is based on the maximum depolymerisation of hemicelluloses with minimum loss of sugars, being the optimum parameters obtained for this study with the utilization of sulphuric acid (5% w/w) at 100 °C for 15 to 60 min and 4:1 (v/v) as ratio of liquor:acid.

Determination of molecular weight

To determine the molecular weight of liquors, Gel Permeation Chromatography (GPC) was used. A GPC Jasco LC-Net II /ADC equipped with a photodiode array detector, refractive index detector, and column PL aquagel-OH MIXED-H 8 µm was used. As the mobile phase an acid solution of 0.005 N H₂SO₄ and deionised and degassed water was used (0.6 mL/min flow, 40 °C and injection volume 20 µL, using as concentration 2 % in weight). Pullulan Polysaccharide with different molecular weights (between 180 and 805,000 Daltons) were used for the calibration curve.

Precipitation of Auto-Hydrolysis Hemicelluloses

Due to the small volume of liquors, only the direct precipitation method was used to separate the hemicelluloses, by adding directly 3 volumes of ethanol, so hemicelluloses were precipitated in the presence of lignin.

Characterization of Precipitated Hemicelluloses

Fourier Transform Infrared Spectroscopy (FTIR)

Analyzes were performed with a Perkin-Elmer 16PC instrument by direct transmittance. Each spectrum was recorded over 20 scans, in the range from 4000 cm⁻¹ to 600 cm⁻¹ with a 4 cm⁻¹ resolution. A Golden Gate accessory made it possible to perform the analysis without the formation of pills.

Thermogravimetric Analysis (TGA)

Thermal degradation of the samples was studied by Thermogravimetric Analysis (TGA), which was carried out in a TGA/SDTA RSI analyzer from Mettler Toledo that can be worked up to 1600 °C as the maximum temperature. Samples between 5 and 10 mg were heated from 25 °C up to 800 °C with a rate of 10 °C/min, using a constant nitrogen flow as inert atmosphere during the experiment.

RESULTS AND DISCUSSION**Composition of Corn Wastes**

The results for the raw material characterization (% on an oven-dry weight basis) were: ash content: 9.27 ± 0.20 ; ethanol-toluene extractives: 9.92 ± 1.60 ; Klason lignin: 15.87 ± 0.50 ; holocellulose: 55.77 ± 0.90 ; α -cellulose: 33.07 ± 0.30 ; and hemicelluloses: 22.7 ± 1.2 .

Compared to the percentages of hemicelluloses present in different agricultural wastes such as bagasse (19-24 %), barley straw (27-38 %), wheat straw (26-32 %), rice straw (23-28 %), sorghum stalks (25 %), and sorn stalks (28 %) (Reddy and Yang 2005), it was found that corn stover is an appropriate feedstock for the extraction of sugars.

Final pH and Density of the Liquors of Autoclave Hydrolysis

Table 2 presents the results for pH of the hydrolysis liquors.

Table 2. pH of the Autoclave Hydrolysis Liquors

Experiment	Catalyst	Final pH
1	H ₂ O	5.47 ± 0.05
2	H ₂ SO ₄	5.41 ± 0.04
3	HNO ₃	5.45 ± 0.15
4	TFA	5.49 ± 0.06
5	HCl	5.56 ± 0.11
6	CH ₃ COOH	5.16 ± 0.09
7	Ca(OH) ₂	5.62 ± 0.18
8	NaOH	5.61 ± 0.24

As can be seen, the final pH values were similar, although the used catalysts were different. The fact that a similar value of pH was obtained in all processes (although different acids and bases had been used) may be due to the equilibrium reached within the bottles.

By carrying out the hydrolysis in closed containers, the escape of gases or volatile compounds formed during the hydrolytic treatment was avoided, resulting in an equilibration between liquors and condensed gases.

With respect to the density, the values were almost the same, between 0.97 and 0.98 g/cm³, so the use of different catalysts did not significantly affect this property of the liquors.

Liquors Characterization

The liquors characterization was aimed at determining the most optimum catalyst to maximize the solubilisation of organic matter (OM) and minimize the solubilisation of inorganic matter (IM). According this objective, it was found that the catalyst that gave the maximum composition in OM was HNO_3 with 0.54 % of OM, followed the H_2O with 0.53 % (Fig. 1). The minimum composition of OM was obtained using the $\text{Ca}(\text{OH})_2$ catalyst with 0.43 %. With respect to the IM, the maximum value was reached using H_2O with 0.27 %, and the minimum value was obtained using HNO_3 with 0.17 %.

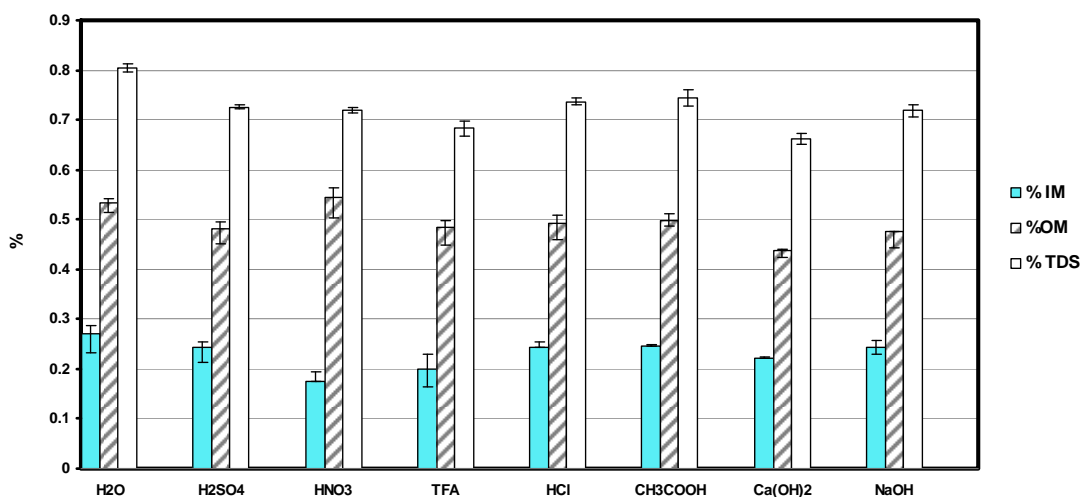


Fig. 1. Content in IM (%), OM (%) and TDS (%) of the hydrolysates

In summary, the best liquor was obtained using HNO_3 as catalyst, because it was the liquor with maximum content in OM and minimum content in IM, with a value of 0.54 % of OM, 0.17 % of IM, and 0.72 % of TDS.

With the purpose of calculating each hydrolytic process' yield, the weight of raw materials after hydrolysis was considered. The loss weight of raw material between before and after cooking, along with the amount of dry matter that liquors recovered after hydrolysis, added up in almost all experiments to approximately 100% of yield. The lowest yields were obtained using HCl and $\text{Ca}(\text{OH})_2$ with 95 and 96%, respectively.

Quantification of Monosaccharide Sugars and Acetic Acid

In Fig. 2 it can be observed that liquor with H_2SO_4 achieved the maximum concentration of total sugars, with 0.98 g/L (0.0867 g total sugars/g hemicelluloses in raw material, 0.0145 g glucose/g hemicelluloses in raw material, 0.0383 g xylose/g hemicelluloses in raw material, and 0.0338 g glucose/g hemicelluloses in raw material). In general, the liquors obtained using acids and water, except the obtained liquor using HCl, yielded more sugars than those catalyzed by bases. The lowest total sugars were in liquors obtained using $\text{Ca}(\text{OH})_2$, with 0.52 g/L (0.0455 g total sugars/g hemicelluloses in raw material, 0.0013 g glucose/g hemicelluloses in raw material, 0.0126 g xylose/g hemicelluloses in raw material, and 0.0315 g glucose/g hemicelluloses in raw material).

According to Fig. 2, the main monomers in all liquors were xylose and arabinose. In liquors obtained with bases and with HCl, the predominant monomer was arabinose (63 to 71 % of total sugars), while in liquors obtained with water and with acids, except HCl, the predominant monomer was xylose (42 to 45 % of total sugars). In conclusion, we can deduce that corn stalks hemicelluloses were composed mainly by xylan and arabinoxylan polysaccharides.

On the other hand, by using acids (except for HCl) it was possible to achieve more solubilisation of xylose and arabinose, while using bases and HCl only promoted the solubilisation of arabinose monomeric sugar. Finally, the liquors that resulted from the use of acids and water had more solubilisation of glucose, so these catalysists (except for HCl) allow more solubilisation of hemicelluloses monomeric sugars.

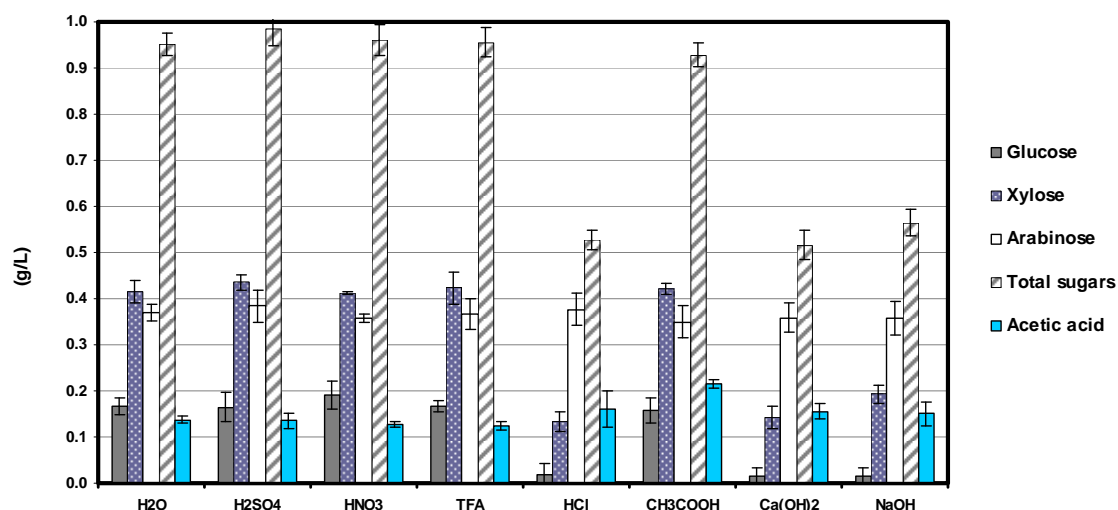


Fig. 2. Quantification of monomeric sugars

Figure 3 represent the results of post-hydrolysis. Each liquor was subjected to post-hydrolysis to achieve more concentration of monomeric sugars. As result, it was observed that only in liquors obtained with water and H₂SO₄ a higher quantity of total sugars at 15 min (1.06 g/L or 0.093 g of total sugars/g of hemicelluloses in raw material, and 1.1 g/L or 0.097 g of total sugars/g of hemicelluloses in raw material respectively) was achieved. The rest of the liquors presented lower quantities of total sugars, so the post-hydrolysis produced more degraded compounds.

Determination of Molecular Weights

Table 3 presents the results the molecular weights and their percentages obtained by GPC analysis. For all samples the higher molecular weight ranged between 2700 and 3450, and the lower molecular weight between 300 and 390. The percentage of these fractions was different for each liquor. It can be seen that for the liquors in which more solubilized monomeric sugars were present there was a higher proportion of lower molecular weights. In contrast, the liquors with lower solubilized monomeric sugars exhibited a higher proportion of higher molecular weights.

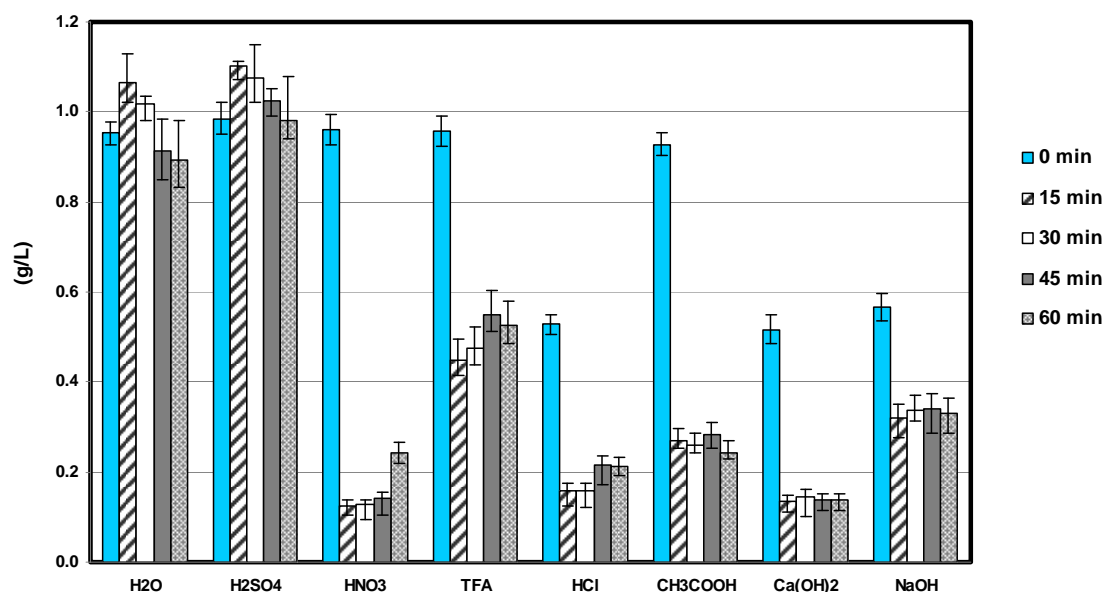


Fig. 3. Quantification of total sugars in liquors after post-hydrolysis

Increasing the solubility means that hemicellulosic sugar's long chains are broken, resulting in shorter monomeric chains; therefore, the molecular weight will be lower. Having a lower solubility of hemicellulosic sugars, the dissolved sugars would be composed of longer chains, and therefore, the determined molecular weight will be higher.

Table 3. Results of GPC Analysis

	Higher M_w	%	M_w/M_n	Lower M_w	%	M_w/M_n
H ₂ O	2709	47.76	1.11	302	52.24	1.05
H ₂ SO ₄	2353	58.30	1.03	301	41.62	1.04
HNO ₃	3100	75.30	1.02	387	24.70	1.04
TFA	3350	70.45	1.02	332	29.55	1.09
HCl	3440	77.90	1.02	375	22.91	1.02
CH ₃ COOH	3427	79.38	1.02	370	20.62	1.02
Ca(OH) ₂	3409	73.62	1.02	368	26.38	1.02
NaOH	3339	90.30	1.03	361	9.70	1.03

Precipitation of Autoclave Hemicelluloses

Due to the small quantity of the remaining liquors left after the characterization of each liquor, the hemicelluloses were precipitated directly by adding three volumes of ethanol. As a result, small quantities of hemicelluloses with brown appearance were obtained, and this was sufficient for characterization (from 50 mL of liquors 10-30 mg of hemicelluloses were precipitated).

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR absorption spectra were reported between 4000 and 600 cm^{-1} for all precipitated hemicelluloses in the presence of lignin.

Figure 4 shows hemicelluloses FTIR spectra obtained using HNO_3 , H_2O (higher sugars solubilization), $\text{Ca}(\text{OH})_2$ and HCl (lower total sugars). Figure 5 shows an enlargement of the part with lower wavenumbers.

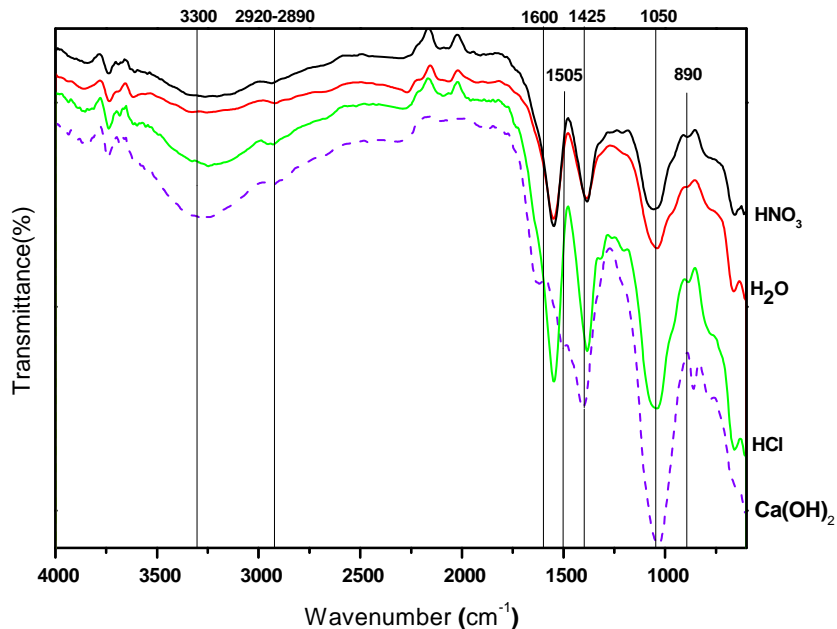


Fig. 4. IR spectra of obtained hemicelluloses with different catalyst

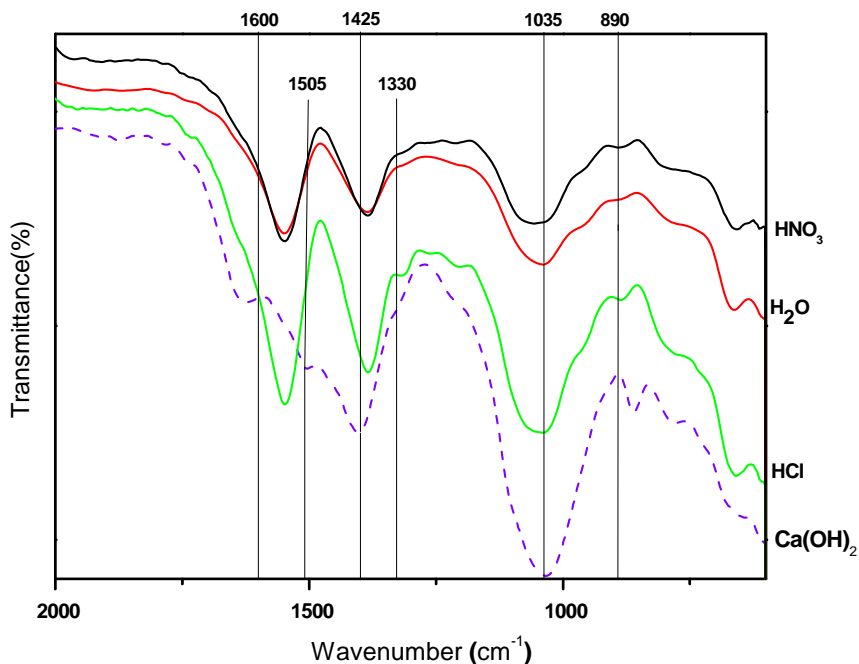


Fig. 5. IR spectra of hemicelluloses with enlarged scale

The first absorption band recorded in the spectra at 3300 cm^{-1} and was due to aromatic and aliphatic OH groups. The next bands (between 2920 and 2850 cm^{-1}), are associated with the CH vibration of CH_2 and CH_3 groups. The bands at 1600 , 1505 and 1425 cm^{-1} correspond to aromatic skeletal vibrations of lignin (García et al. 2010). The presence of lignin contamination in all samples was due to the used precipitation method. At 1035 cm^{-1} appears the aromatic C-H deformation as a complex vibration associated with the C-O, C-C stretching and C-OH bending in polysaccharides. Finally, the 890 cm^{-1} band was referred to the domain of β -glycosidic bonds between sugars.

On the other hand, it can be observed how the intensities changed in each band, which corresponds to the amount of that group in precipitated hemicelluloses. In the case of lignin, the bands (1600 , 1505 and 1425 cm^{-1}) had more intensity in hemicelluloses samples obtained with $\text{Ca}(\text{OH})_2$ and HCl , so these hemicelluloses samples could contain more lignin.

Thermogravimetric Analysis (TGA)

The hemicelluloses obtained from each liquor were subjected to thermogravimetric analysis (TGA) from 25 to $800\text{ }^\circ\text{C}$. Three significant stages of weight loss were obtained in the derivate of each analysis (TDG). The first weight loss at $100\text{ }^\circ\text{C}$ can be attributed to the loss of moisture. The second loss of weight in the range 250 to $300\text{ }^\circ\text{C}$ is due to the decarboxylation of hemicellulose (liberation of CO_2 , CO , and some hydrocarbon). Finally, the last loss of weight at $450\text{ }^\circ\text{C}$ may be related to the links between lignin and hemicelluloses. The thermogram with more concentration of hemicelluloses is represented in Fig. 6. This thermogram showed 3% of total weight of moisture and 25% of total weight of hemicelluloses.

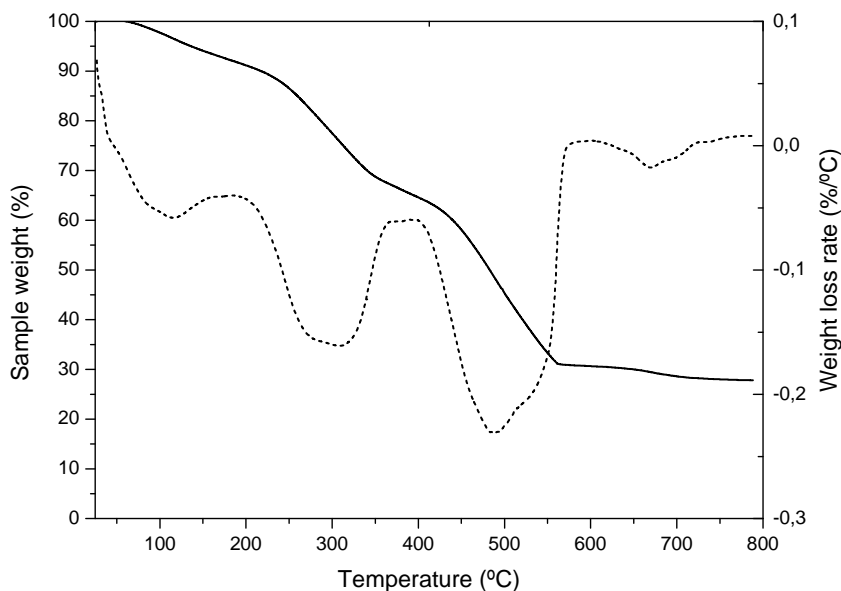


Fig. 6. TGA (solid line) and TDG (dashed line) of hemicelluloses obtained with H_2O only (residue: 27.83 %)

All graphs that were obtained from each set of hemicelluloses presented similar results. The amount of residue was the main difference. The hemicelluloses with the least residue, i.e. with a value of residue of 27.83% (Fig. 6), were obtained with the liquor in which just water was used. Hemicelluloses with the highest residue, i.e. with 38.78% of residue, were obtained when using HCl in the autoclave hydrolysis. The remaining set of results with more residue were with NaOH and H₂SO₄ (37.05 and 35.68 % respectively), while the results with less residue were with TFA and HNO₃ (32.12 and 32.38 % respectively).

CONCLUSIONS

1. Due to the amount of hemicelluloses of corn stalks and the abundance of these agricultural wastes, corn stalks were chosen as raw material for extraction of hemicelluloses. After using different catalysts under the same conditions, we obtained the following results: the best catalysts that maximize the organic matter (OM) and minimize the inorganic matter (IM) are HNO₃ and water by itself. Otherwise, acids such as HCl or bases such as Ca(OH)₂, solubilized lower amounts of hemicellulosic sugars. The liquor in which H₂SO₄ was used as a catalyst had 0.48 % of OM, 0.24 % of IM, and 0.73 % of total dissolved solids (TDS), solubilizing approximately 15.6 % of the hemicellulosic sugars. In turn, this liquor presented a substantially higher residue (35.7 %).
2. Another good option would be to use water as a single agent. This liquor had 0.53% of OM, 0.27% of IM, and 0.8 % of TDS, solubilizing 17% of the hemicellulosic sugars. The precipitate from liquor in which H₂O had been used was purer in hemicelluloses, with 27.83% of residue.
3. The use of a catalyst for the extraction of hemicelluloses is more useful in hemicellulosic monomers solubilization, but it has the disadvantage that the use of catalysts produces more impure hemicelluloses with more residues.
4. The experiment in autoclave hydrolysis could be improved by increasing the reaction time, in order to obtain more solubilization of hemicelluloses.
5. With respect to the catalyst, some acids such as H₂SO₄, HNO₃ or H₂O as only extractive agents are the best option for corn stalks hemicelluloses extraction under the used conditions (121 °C, 60 min, and 1:20 as solid/liquid ratio).
6. The obtained hemicelluloses could be used in many applications to produce chemicals with high added value or to produce polymeric materials.

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