SEPARATION AND PURIFICATION OF HEMICELLULOSES BY ULTRAFILTRATION

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Abstract

During hydrolysis treatments, where the main objective is the solubilization of hemicelluloses, several undesirable reactions may occur. As a result, monomeric sugars and nonsaccharide compounds are obtained in the liquor. In the present study, autohydrolysis liquor resulting from the corn waste hydrolysis treatment (180 ºC, 30 min) was filtered successively increasing the membrane cutoff (1, 5, and 10 kDa) to observe the potential of this technology for hemicellulose purification and fractionation by molecular weight. The experimental results showed that the 10 kDa retentate liquor fraction has the highest hemicellulose concentration (6.10 g/L) and it was constituted by defined molecular weight components (Mw = 2880), with low content in smaller compounds and inorganic material. Hemicelluloses have been isolated from each fraction and were analyzed by different analytical techniques (FT-IR, TGA, ^{1}H NMR, and CHNS-O elemental analysis) to determine that it was possible to improve the physicochemical characteristics of the original liquor by ultrafiltration technology.

1. Introduction

Lignocellulosic biomass, mainly agricultural and forestry residues, is becoming a potential renewable energy and product source. Fossil fuel reserves are running out, and global warming is becoming a reality.[1] Therefore, it is necessary to search for an alternative to the oil economy, with renewable resources based on biorefinery being a very promising alternative. Biorefinery technologies include a primary separation of the main constituents of lignocellulosic biomass -cellulose, hemicelluloses, and lignin- as well as further treatment and processing of these compounds for their conversion into value-added products, biofuels and chemicals.[2] The economic competitiveness of these processes is dependent on feedstock collection and transportation costs,[3] but it also depends on the separation and purification technologies used in the process.

Following the biorefinery concept, in addition to cellulose and lignin exploitation, hemicellulose utilization would largely benefit the effectiveness and competitiveness of this process. The hemicelluloses, mainly substituted xylooligosaccharides in lignocellulosic materials, have xylan as the major hemicellulose component. Xylan is a polymer made up of xylopyranose units containing a variety of attached groups (including mainly arabinose, acetyl groups, and uronic acids).[4] In its oligomeric form, xylooligosaccharide can be used to produce functional foods based on their beneficial health effects. Different chemical products (xylitol, lactic acid) or biofuels such as bioethanol,[5] methane, or biohydrogen[6] can be obtained from hemicellulose fermentation processes. Moreover, furfural can be obtained through dehydration of sugars[7] and is useful for producing paints, solvents, plastics, glass fibers, resin, and surfactants.[8] Another future line of investigation is the application of hemicelluloses for the production of composites where the monomers can be transformed into biopolymers (polyols,[9] lactic acid, alditols, aldonic acids, and lactones) for the formation of

polyurethanes, polyesters, and polyamides. Sugar based polymer films for the production of biodegradable packaging films[10] are being studied. Another potential application of hemicelluloses would be for paper making additives, which could substitute for starch or other petrochemical-based cationic polymers.[11]

The autohydrolysis treatment, an environmentally friendly process which uses only water as reagent, is an effective process for hemicellulose extraction. Unfortunately, many undesirable reactions such as solubilization of extracts, solubilization of hemicellulosic monomers, dissolution of acid phenolic components, formation of degradation products, and neutralization of the ashes can occur.[12] For that reason, it is necessary to carry out pretreatment of the raw material, or further process liquor purification, or both[13] for subsequent utilization of hemicellulose. According to its use and required purity, different physicochemical purification sequences may be used.

The physical purification methods of hemicellulose hydrolysate including evaporation, precipitation, nanofiltration and ultrafiltration,[14] liquid-liquid extraction,[15] ion exchange resins,[16] and adsorption techniques[17],[18] are mainly used to remove inorganic salts, sugar decomposition products, and phenolic compounds which inhibit the fermentation by microorganisms. Ultrafiltration technology, a well-established separation process in industry, was used in several studies to separate polysaccharides from other molecules, to concentrate the solution, and to reduce the alcohol volume used for its precipitation.[19] Vegas et al.[20] studied the water treatment of rice husks (containing soluble xylan-derived products) with nanofiltration and ultrafiltration membranes for concentrating and removing both monosaccharides and nonsaccharide compounds. The utilization of ceramic membranes for refining xylooligosaccharides containing autohydrolysis liquors from eucalyptus wood was also studied by Gullón et al.,[21] with conclusions about the

potential of membrane processing for these purposes. The performance of various polymeric nanofiltration and ultrafiltration membranes was investigated during separation of hemicellulose from alkali process liquors by Schlesinger et al.[22] They showed that hemicellulose was almost quantitatively retained at molar masses above 1000 g/mol by most of the studied membranes.

This work has been focused on the purification and separation of hemicelluloses from autohydrolysis liquor of corn waste using the ultrafiltration process. Although many studies have been published about this technology, the purification of corn waste hydrolysate using ceramic membranes has not been studied yet. Ceramic membranes have been hailed for their advantageous properties when compared to polymeric membranes. Although ceramic membranes are more expensive than organic polymeric membranes, they possess advantages of temperature stability, resistance toward solvents, a well-defined stable pore structure,[23] and the possibility for sterilization. In this work, corn waste, categorized as one of the lignocellulosic biomass sources,[24] was subjected to the autohydrolysis process and the hydrolysate liquor was filtered successively increasing the ceramic membrane cutoff (1, 5, and 10 kDa) for hemicellulose purification and fractionation. The original liquor and different fractions obtained by ultrafiltration were characterized in terms of pH, total dissolved solids (TDS), inorganic matter content (IM), and organic matter content (OM). Then, all fractions were submitted to posthydrolysis process to quantify and characterize monomeric sugar units by high performance liquid chromatography (HPLC) and their molecular weights were determined by gel permeation chromatography (GPC). Moreover, different analytical techniques such as Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), nuclear magnetic resonance

(^{1}H NMR), and CHNS-O elemental analysis were used in the precipitated hemicelluloses for further physicochemical characterization.

2. Material and Methods

2.1 Raw Material Conditioning and Characterization

The cornstalks used in the experiment were kindly supplied by the company Straw Pulping Engineering (SPE), S.L. (Zaragoza, Spain). The residue was dried to constant moisture, and it was ground in a mill and sieved to obtain the 4-6 mm size homogeneous fraction.

The chemical compositions of the initial raw material and solid fraction obtained after autohydrolysis process were analysed following standard methods and procedures found in the literature: ash (TAPPI T211 om-93); ethanol-toluene extractives (TAPPI T204 cm-97); Klason lignin (TAPPI T222 om-98); α-holocellulose,[25] α-cellulose,[26] and hemicellulose content.

2.2 Fractionation Process

The corn wastes were treated by the autohydrolysis process for maximum hemicellulose solubilisation under optimized conditions previously determined: temperature of 180 ºC, time of 30 min, and a solid:liquid ratio of 1:20 (w/w). For that purpose, a 4 L batch reactor (Autoclave Engineers EL0723 Iberfluid) equipped with an electronic control unit for pressure and temperature control was used. The process time was taken into account after the desired temperature was reached. When the reaction time was ended, the reactor was cooled and then the hydrolysis liquor was separated from the solid phase by filtration.

2.3 Ultrafiltration Process and Permeates Characterization

The filtration module (Figure 1) used in the present study, Membralox XLAB 5, was supplied by PALL Corporation. It is equipped with a 3 L double jacket feed tank (1), volumetric recirculation pump (2), Membralox T1-70 membrane module (3), BF3 back pulse (4), relief valve (5), back pressure membrane valve (6), permeate valve (7), feed tank drain valve (8), pump drain valve (9), and manometers (10-11).

The ultrafiltration process temperature was controlled using a constant cooling water flux around the tank to avoid hydrolysate degradation by temperature. The process temperature was kept constant at 22.8 ºC. The flow rate was adjusted to its maximum level corresponding to the maximum pressure allowed by the system (4 bar) to improve permeate flow. The used ceramic membranes (with cutoffs of 1, 5, and 10 kDa) were supplied by TAMI Industries. They were a multichannel type of membrane, consisting of seven channels with 2 mm internal diameter, external diameter of 10 mm, and a surface of 110 cm^2. The length of the membranes was 250 mm, while the breaking pressure was about 80 bar.

The autohydrolysis liquor was filtered successively increasing the membrane cutoff. The different fractions obtained (permeates of 1, 5, and 10 kDa and retentate of greater than 10 kDa) in addition to the brute liquor were characterized by the determination of their inorganic matter (IM), organic matter (OM), and total dissolved solids (TDS) contents, sugar monomeric concentrations, and molecular weights. TDS were measured after a weighed sample was kept at 100 ºC until constant weight (NREL

LAP-012). IM was determined after combustion of the liquor at 525 ºC (TAPPI T211 om-93), and OM was calculated as the difference between TDS and IM.

The characterization and quantification of sugar monomers of all fractions were carried out in a Jasco LC Net II/ADC high performance liquid chromatograph (HPLC) equipped with a refractive index detector and a photodiode array detector. A Phenomenex Rezex ROA HPLC column (300 mm x 7.8 mm) with a precolumn (Phenomenex Security Guard holder with carbo-H+ cartridges) was used for the experiments. The mobile phase was constituted by 0.005 N H_2SO_4 prepared with 100% deionized and degassed water. The injection conditions were 0.35 mL/min flow rate, 40 ºC, and injection volume of 20 µL. High purity D-(+)-glucose, D-(+)-xylose, D-(-)-arabinose, and acetic acid were used for the calibration curve.

For the quantification of monomeric sugars, the hydrolysis liquors were subjected to a posthydrolysis process, using sulphuric acid (5% w/w) at 100 ºC with a ratio of liquid:acid of 4:1 (v/v).[27] The selection of operating conditions of the posthydrolysis process was based on the maximum depolymerization of hemicelluloses with minimum loss of sugars. For this purpose, every 30 min a small aliquot of posthydrolysis liquor was analyzed to determine the optimal time for the hemicellulose depolymerization.

Moreover, the weight-average (Mw) and number-average (Mn) molecular weights and polydispersities (IP = Mw/Mn) of the different liquors fraction were determined by gel permeation chromatography (GPC). A Jasco LC-Net II/ADC GPC equipped with a photodiode array detector and refractive index detector was used. The column was PL aquagel-OH MIXED-H 8 µm. As the mobile phase, the same solution used for HPLC techniques at conditions of 0.6 mL/min flow rate, 40 ºC, and injection volume of 20 µL

were employed. The calibration curve was made using pullulan polysaccharides with different molecular weights (between 180 and 805 000 Da).

2.4 Precipitation of Autohydrolysis Hemicelluloses and Characterization

The precipitation of hemicelluloses was achieved by adding 3 volumes of ethanol to each fraction. Various analytical techniques such as Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), nuclear magnetic resonance (^{1}H NMR), and CHNS-O elemental analysis were used to determine the precipitated hemicellulose physicochemical properties.

FT-IR measurements were performed in a Perkin-Elmer 16PC instrument by direct transmittance. Each spectrum was recorded over 20 scans, in the range from 4000 to 600 cm^{-1} with a resolution of 4 cm^{-1}.

Thermal degradation of the samples was studied by a Mettler Toledo TGA/SDTA RSI analyzer. The samples of ~5 mg were heated from 25 to 800 ºC at a rate of 10 ºC/min, using a constant nitrogen flow as inert atmosphere during the experiments.

The chemical structure of hemicellulose was also studied through ^{1}H NMR spectrometry using a Bruker 500 MHz spectrometer at a frequency of 250 MHz with an acquisition time of 0.011 s at 25 ºC. The spectrum was recorded over 32 scans, and deuterated water (D_2O) was used as solvent and as internal.

The elemental analysis of carbon, hydrogen, nitrogen, sulfur, and oxygen contents of the precipitated fractions was performed to determine the purity of obtained hemicelluloses. Elemental analysis was done in an EA Euro 3000 series elemental analyzer from EuroVector SpA, Milano, Italy. Total oxidation of the samples (10 mg) was conducted at 1020 ºC for CHNS configuration and at 1090 ºC for oxygen. The combustion products were separated in a chromatographic column (GC 2 m 6 x 5 mm).

3. Results and discussion

3.1 Composition of Raw Material and Autohydrolysis Solid Fraction

The raw material presented the following chemical composition (% on an oven-dry weight basis): ash content, 9.27 ± 0.20; ethanol-toluene extractives, 1.08 ± 0.10; Klason lignin, 17.18 ± 2.40; holocellulose, 62.89 ± 3.50; α-cellulose, 30.96 ± 2.70; hemicelluloses, 31.93 ± 0.79. On the other hand, the solid fraction obtained after autohydrolysis process presented the following composition (%on an oven-dryweight basis): ash content, 5.43 ± 0.12; ethanol-toluene extractives, 7.78 ± 0.30; Klason lignin, 17.62 ± 1.09; holocellulose, 78.20 ± 4.80; α-cellulose, 53.94 ± 5.90; hemicelluloses, 24.26 ± 1.10.

The initial composition in hemicellulose of corn residues is comparable to that of other lignocellulosic materials: rice straw (20.50%), wheat straw (21.70%), corn stover (23.86%),[28] and barley straw (27.00%).[29] It could be concluded that the hemicellulose percentage found in corn wastes suggested the suitability of this material as a source for sugar extraction. However, a high amount of ashes was observed, constituted generally by silicates and mineral components. These components could cause impurities in the autohydrolysis liquor. Taking into account the composition of the solid fraction after the autohydrolysis process, a decrease in ash and hemicellulose content could be observed while the percentage of ethanol-toluene extractives and cellulose increased. The decrease in percentage of hemicellulose (with a corresponding increase of cellulose) can be attributed to the partial solubilization of this fraction in the autohydrolysis liquor, whereas the high amount of extractives observed could be due to the higher solubility of waxes, resins, tannins, etc. after raw material treatment. The solid residue recovered

after the autohydrolysis process (including material losses caused by washing of the pulp) was 52.56% of initial raw material.

3.2 Autohydrolysis Liquors Characterization

Table 1 represents the pH and IM, OM, and TDS contents for studied autohydrolysis liquors and for different fractions obtained by ultrafiltration. As can be observed in Table 1, the percentage of TDS increases from the 5 kDa (0.90%) to the >10 kDa fraction (2.21%), leading to the conclusion that the most of the material has been retained in the higher cutoff membranes. However, this observation is not adequate for 1 kDa permeate because it contains one of the highest TDS values (1.36%). This percentage is influenced by the high amounts of OM (0.92%) and IM (0.44%) found in this fraction, which can be attributed to low molecular weight molecules produced by process conditions and separated through this membrane. Therefore, comparing with the other fractions, the percentage of IM was the highest in the 1 kDa permeate, and the OM was higher in the 1 kDa permeate than in the 5 kDa permeate but it was lower than in the 10 and >10 kDa fractions.

The characterization and quantification of sugar monomers of all fractions are represented in Table 2. It can be seen that the raw liquor contains 3.11 g/L sugar concentration after 60 min of posthydrolysis time (P60). It can be noticed that the optimal posthydrolysis time was 60 min for all fractions, with a noticeable decrease in the concentration of sugars observed over 90 min. The concentration of sugars recovered in brute liquor constituted about 19.24% of the hemicelluloses present in the raw material. Taking into account the material balance, 56% of hemicelluloses present in the raw material could be recovered in autohydrolysis liquor; 43% of hemicelluloses remain in the pulp. This difference between the obtained yield and the expected results

could be attributed to the material losses during the pulp washing and the unavoidable degradation of hemicelluloses during the autohydrolysis process.

On the other hand, the monomeric sugar concentration at 60 min (P60) increased for the 5 kDa permeate (1.59 g/L) to the value of 6.08 g/L for the >10 kDa retentate. Moreover, the 1 kDa permeate contains a considerably high amount of monomeric sugars, reaching a concentration of 2.86 g/L at optimal posthydrolysis time. It was observed that the best fraction in hemicellulose content was the >10 kDa retentate fraction, concluding that most of the hemicelluloses were retained by higher cutoff membrane. These results are in agreement with the obtained OM results.

For hemicellulose monomeric characterization, it can be observed that 80% of the total dissolved sugar was constituted by xylose, widely used in industrial applications, whereas the arabinose and glucose monomers were present in relatively small quantities. The concentration of these sugars indicated that the hemicelluloses in corn residues were mainly composed of xylan and arabinoxylan-type polysaccharide, which is in agreement with the results obtained by other authors.[30] The acetic acid content reached a maximum value of 0.68 g/L, remaining approximately constant with posthydrolysis time and the membrane cutoff.

On the other hand, in the 10 kDa retentate fraction a higher monomeric concentration (6.10 g/L) was observed than in raw liquor (3.11 g/L). This fact could be explain by the better conditions to fractionate the oligomeric sugars in refining liquor (10 kDa retentate) than in the original autohydrolysis liquor. The presence of different type of solubilized molecules in the original autohydrolysis liquor (which has been

partially purified by ultrafiltrated membranes) could interfere in the consumption of the posthydrolysis catalyst and therefore affects the depolymerization of hemicelluloses.

Finally, the GPC technique was carried out to obtain the molecular weight distribution of all liquor fractions. This study aimed to observe the effectiveness of membranes for compound separation in relation to their molecular weights. Results of GPC analysis- number-average molecular weight (Mn), weight average molecular weight (Mw), polydispersity (IP = Mw/Mn), and percentage of the molecule in the liquor- are shown in Table 3.

The GPC chromatograms obtained showed two main peaks corresponding to two different molecular weight components in the liquors (except in the >10 kDa retentate). It could be observed that 85% of the molecules present in the 1 kDa liquor permeate have a molecular weight of Mw = 1839, whereas the molecular weight of the 5 kDa permeate reached Mw = 2772. The molecular weight of the main fractions of liquor of 5, 10, and >10 kDa presented similar values. On the other hand, the percentage of the second fraction, corresponding to low molecular weight molecules in these liquors (varying from 341 to 404), disappears for the >10 kDa fraction as demonstrated by Figure 2. It could be concluded that with the smallest cutoff membranes was achieved in the >10 kDa fraction a defined molecular weight molecule which was constituted by Mw = 2880 molecular weight components and by monodisperse polymers, IP = 1.02. On the other hand, the fractions obtained by 5 and 10 kDa membranes have higher molecular weights than that of raw liquor. This molecular weight difference is influenced by the separation effect.

3.3 Physicochemical Characterization of Precipitated Hemicelluloses

3.3.1 Chemical Structure by FT-IR Analysis

The FT-IR spectra of hemicelluloses precipitated by different fractions are shown in Figure 3. As can be observed in IR analysis, the bands found at 3300 and 2920-2850 cm^{-1} indicated the OH stretching and CH bond deformation of CH_2-CH_3 groups. These bands appeared more intense in hemicellulose precipitate from the 10 kDa retentate fraction. The peak found at 1598 cm^{-1} might be due to the presence of water[31] or to the stretching of carboxylic acids forming intermolecular hydrogen bonds[32] in the precipitated samples. The peak found at 1408 cm^{-1} is characterized by CH and OH bending, whereas the small band observed at 1320 cm^{-1} (stretching of C=O group of syringyl ring) indicates the existence of some phenolic compounds in the precipitated hemicelluloses. The band found at 1248 cm^{-1}, whose intensity is greater in the 10 kDa retained fraction, is referred to C-O stretching of ether bonds. Finally, the hemicellulosic presence is observed mainly at 1040 cm^{-1}, the origin typical of xylans (indicating the predominance of this monomer, which is in agreement with sugar analysis), and at 898 cm^{-1}referred to the domain of β-glycosidic bonds between sugars. The hemicellulose precipitate from the original liquor (not shown) had a similar 10 kDa retentate infrared spectrum; its spectrum it was considered to be a mixture of the different precipitated hemicellulose fractions.

3.3.2 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of the different fractions is presented in Figure 4. The behavior of precipitated hemicelluloses from ultrafiltrated fractions with temperature can be observed.

The hemicellulose precipitates from the 1 and 5 kDa fractions showed three well-separated maximum weight losses at the same temperatures: at 100 ºC due to the sample moisture, at 300 ºC due to decarboxylation of hemicellulose (releasing CO, CO_2, and some hydrocarbons), and at 450 ºC possibly due to the presence of lignin,[33] which is in agreement with obtained FT-IR results. The hemicellulose decomposition peak corresponds to 11.13 and 8.89% of the weight losses for the 1 and 5 kDa precipitated fractions, respectively. Both precipitates (Figure 4a) showed a high percentage of residue, 62% at 800 ºC, respectively. This residue may be justified by the presence of inorganic material that has filtered through 1-5 kDa cutoff membranes and perhaps by the presence of small lignin molecules. The analysis of the TGA curve of precipitated hemicellulose from 10 kDa retentate liquor showed also three weight loss rates (as original liquor), but the second one (at 275 ºC) which corresponds to 40% of weight losses, is more pronounced due to the predominance of hemicellulose fraction in the precipitate. Although 10 kDa retentate hemicelluloses have relatively higher molecular weight than the others, the hemicellulose thermal degradation temperatures decrease from 300 to 275 ºC. Moreover, the intensity of the third peak (at 450 ºC) was reduced, indicating the predominance of well-defined fraction at 275 ºC which is in agreement with GPC results. The level of residue in 10 kDa retentate hemicelluloses was about 35%, much lower than in the 1-5 kDa precipitated hemicelluloses.

3.3.3 ^{1}H NMR Spectroscopy

^{1}H NMR spectra of hemicellulose obtained from the 10 kDa retentate liquor fraction is shown in Figure 5. The main chemical shifts at 4.43, 4.07, 3.74, 3.51, 3.33, and 3.25 ppm were assigned to the H-1, H-5 equatorial, H-4, H-3, H-5 axial and H-2 protons of the β-D-xylopyranose units of hemicelluloses, respectively.[34] The characteristic resonance from anomeric proton of glucuronic acid residue was detected at 5.27 ppm. Aseries of low intensity signals at 4.5-4.7 ppm were assigned to anomeric protons in partially acetylated xylopyranosyl residues.[35] The solvent (HDO) peak appeared at 4.71 ppm. It could be concluded that the hemicellulose is constituted mainly by xylose with arabinose and glucuronic acid as substituents, as demonstrated by HPLC and ^{1}H NMR results.

3.3.4 CHNS-O Elemental Analysis

Elemental analysis of carbon, hydrogen, nitrogen, sulfur, and oxygen content for the precipitated fractions can reveal the purity of obtained hemicelluloses. In Table 4 are represented the elemental analysis values obtained from precipitated hemicelluloses from each fraction.

It can be seen in Table 4 that high carbon, hydrogen, and oxygen percentages (39.44, 4.74, and 36.12%) were found in 10 kDa retentate precipitated hemicellulose. The elemental analysis obtained for commercial xylose by Cagnon et al.[33] showed similar results, approximately 38% C, 6% H, and 48% O. In the hemicellulose fraction precipitated from 1 kDa, the presence of 4% sulfur has been observed. This fact confirms that hemicellulose precipitate from the 1 kDa fraction is the most contaminated by the presence of sulfur and other salts followed by the 5 kDa hemicellulose fraction, which is in agreement with the high residues found in the TGA analysis reported in section 3.3.2.

It could be concluded that the use of ultrafiltration technology is a good technique as a first step for hemicellulose purification.

4. Conclusions

This study confirms that it was possible to improve the physicochemical characteristics of brute autohydrolysis liquor by ultrafiltration technology. For that purpose, the brute hydrolysate liquor (resulting from the corn waste hydrolysis treatment) was filtered successively increasing the ceramic membrane cutoff (1, 5, and 10 kDa) for hemicellulose purification and fractionation. The results showed that the 10 kDa retentate fraction had the highest content in OM and hemicellulosic sugars (constituted mainly by arabinoxylan-type polysaccharides). In addition, this fraction is characterized by defined molecular weight molecules while other fractions (including the brute liquor) contain a mixture of a wide range of different molecular weight components. On the other hand, according to the TGA and elemental analysis, the precipitated samples of this fraction had higher content in hemicellulose and lower residue and sulfur content than other ultrafiltrated fractions. The lower molecular weight sugars (results shown by the GPC technique) and inorganic matter, such as salts, were retained by smaller cutoff membranes. It could be concluded that the improvement in properties observed in the 10 kDa retentate liquor (more rich in hemicellulose, less polydispersity, and low impurities) is due to the use of ultrafiltration. Therefore, the ultrafiltration technique can be used as a first step for autohydrolysis liquor hemicellulose fractionation and purification.

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Table captions

Table.1 pH, Inorganic Matter, Organic Matter and Total Dissolve Solids of Original Autohydrolysis Liquors and Ultrafiltrated Fractions

Table.2 Sugar Monomer Quantifications and Characterization at Different Times of Posthydrolysis, P0, P30, P60, and P90 min (Sugars at 0, 30, 60, and 90 min of Posthydrolysis Time), of Brute Hydrolysate and Ultrafiltrated Fractions

Table 3. Analysis of GPC Results of the Different Fractions Obtained by Ultrafiltration of Corn Waste Autohydrolysis Liquor

Table 4. CHNS-O Elemental Analysis of Precipitated Hemicelluloses

Table 1

Fraction	pH	TDS[a] (%)	IM[b] (%)	OM[b] (%)
Brute liquor (TDS)	4.6 ± 0.05	1.64 ± 0.04	0.27 ± 0.03	1.37 ± 0.01
Permeates				
1 kDa	5.10 ± 0.03	1.36 ± 0.06	0.44 ± 0.04	0.92 ± 0.02
5 kDa	4.60 ± 0.05	0.90 ± 0.05	0.29 ± 0.04	0.61 ± 0.01
10 kDa	5.70 ± 0.04	1.32 ± 0.04	0.33 ± 0.03	0.99 ± 0.01
retentate (>10 kDa)	4.75 ± 0.03	2.21 ± 0.08	0.38 ± 0.06	1.83 ± 0.02

[a] Total dissolved solids (TDS). [b] Inorganic and organic matter (IM) and organic matter (OM) referred to TDS content.

Table 2

fraction	posthydrolysis time (min)	glucose (g/L)	xylose (g/L)	arabinose(g/L)	total sugars (g/L)	acetic acid (g/L)
brute liquor	P0	0.03 ± 0.01	0.84 ± 0.04	0.30 ± 0.03	1.17 ± 0.08	0.59 ± 0.02
	P30	0.14 ± 0.01	1.95 ± 0.04	0.25 ± 0.02	2.34 ± 0.07	0.67 ± 0.03
	P60	0.17 ± 0.02	2.62 ± 0.05	0.32 ± 0.03	3.11 ± 0.09	0.54 ± 0.03
	P90	0.19 ± 0.05	2.36 ± 0.05	0.36 ± 0.02	2.91 ± 0.12	0.68 ± 0.04
permeates						
1 kDa	P0	0.14 ± 0.03	0.46 ± 0.05	0.43 ± 0.03	1.03 ± 0.11	0.59 ± 0.03
	P30	0.16 ± 0.03	1.82 ± 0.04	0.52 ± 0.01	2.50 ± 0.08	0.57 ± 0.04
	P60	0.14 ± 0.02	2.23 ± 0.05	0.49 ± 0.02	2.86 ± 0.09	0.57 ± 0.04
	P90	0.13 ± 0.01	2.22 ± 0.06	0.31 ± 0.03	2.66 ± 0.10	0.58 ± 0.05
5 kDa	P0	0.03 ± 0.01	0.24 ± 0.03	0.38 ± 0.02	0.65 ± 0.06	0.56 ± 0.02
	P30	0.01 ± 0.01	0.92 ± 0.05	0.39 ± 0.02	1.32 ± 0.08	0.58 ± 0.01
	P60	0.09 ± 0.02	1.10 ± 0.06	0.40 ± 0.03	1.59 ± 0.11	0.54 ± 0.02
	P90	0.10 ± 0.01	1.10 ± 0.06	0.37 ± 0.03	1.57 ± 0.10	0.64 ± 0.03
10 kDa	P0	0.01 ± 0.01	0.25 ± 0.03	0.40 ± 0.02	0.66 ± 0.06	0.48 ± 0.01
	P30	0.19 ± 0.03	2.26 ± 0.05	0.62 ± 0.05	3.07 ± 0.13	0.56 ± 0.02
	P60	0.20 ± 0.02	2.49 ± 0.04	0.53 ± 0.05	3.22 ± 0.11	0.53 ± 0.02
	P90	0.16 ± 0.02	1.94 ± 0.06	0.31 ± 0.06	2.41 ± 0.14	0.56 ± 0.04
retentate (>10 kDa)	P0	0.09 ± 0.01	0.42 ± 0.03	0.43 ± 0.01	0.94 ± 0.05	0.55 ± 0.02
	P30	0.25 ± 0.02	2.96 ± 0.06	0.74 ± 0.03	3.95 ± 0.11	0.65 ± 0.02
	P60	0.34 ± 0.01	5.03 ± 0.06	0.71 ± 0.03	6.08 ± 0.10	0.67 ± 0.02
	P90	0.12 ± 0.03	4.28 ± 0.07	0.68 ± 0.04	5.08 ± 0.14	0.68 ± 0.03

Table 3

fraction	M_n[a]	M_w[b]	IP[c]	(%)[d]
brute liquor	1651	1815	1.09	87.71
	335	345	1.03	12.29
permeates				
1 kDa	1670	1839	1.10	85.00
	329	341	1.03	15.00
5 kDa	2844	2772	1.01	74.33
	412	404	1.05	25.67
10 kDa	2834	2872	1.01	80.18
	347	385	1.03	19.82
retentate (>10 kDa)	2699	2880	1.02	100.0

[a] M_n, number-average molecular weight. [b] M_w: weight-average molecular weight. [c] IP: polydispersity (M_w/M_n). [d] %: percentage of the molecule in the liquor.

Table 4

sample	% N (RSD[a])	% C	% H	% S	% O
brute liquor	1.00 (0.2)	39.90 (0.9)	5.61 (0.01)	1	22.59 (0.5)
1 kDa	0.77 (0.01)	21.75 (1.0)	3.07 (0.1)	4	23.13 (0.5)
5 kDa	1.09 (0.02)	19.62 (0.3)	3.00 (0.3)	1	21.94 (2.0)
10 kDa	1.07 (0.05)	28.06 (0.3)	3.67 (0.01)	< 1	33.20 (2.0)
10 kDa retentate	0.99 (0.2)	39.44 (0.9)	4.74 (0.9)	< 1	36.12 (2.0)

[a] RSD, relative standard deviation.

Figure captions

Figure 1. Pilot plant employed (Membralox® XLAB 5) for ultrafiltration process.

Figure 2. GPC curves of brute liquor and 10 kDa retentate fraction.

Figure 3. IR spectrum of 1 kDa, 5 kDa, 10 kDa and 10 kDa retentate fractions.

Figure 4. Thermogravimetric analysis TGA (a) and its derivative DTG curves (b) of precipitated hemicelluloses from ultrafiltrated fractions.

Figure 5. ^{1}H NMR spectrum spectra of 10 kDa retentate precipitated hemicellulose.

Figure 1

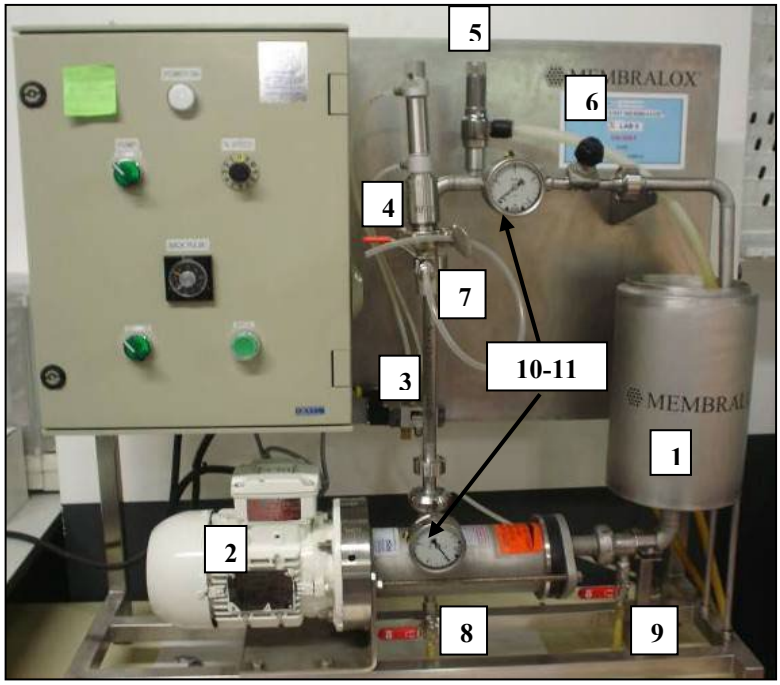


Figure 2

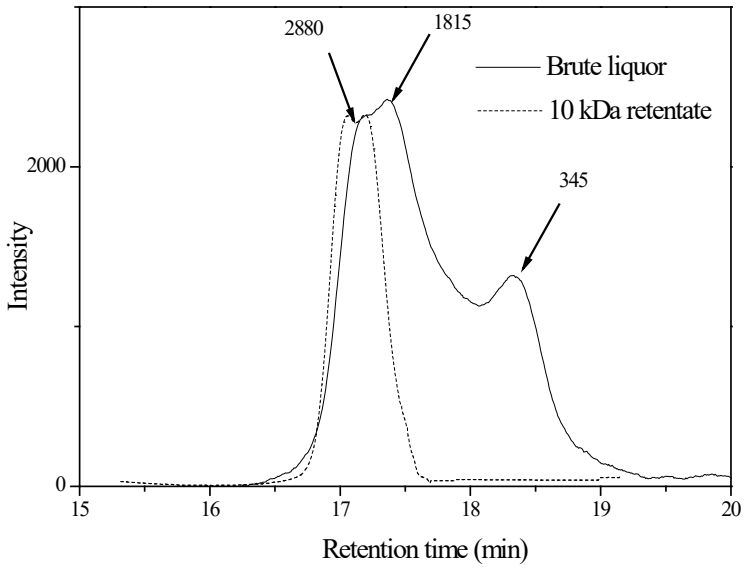

2880
1815
345
Brute liquor
10 kDa retentate
2000
0
Intensity
15
16
17
18
19
20
Retention time (min)

Figure 3

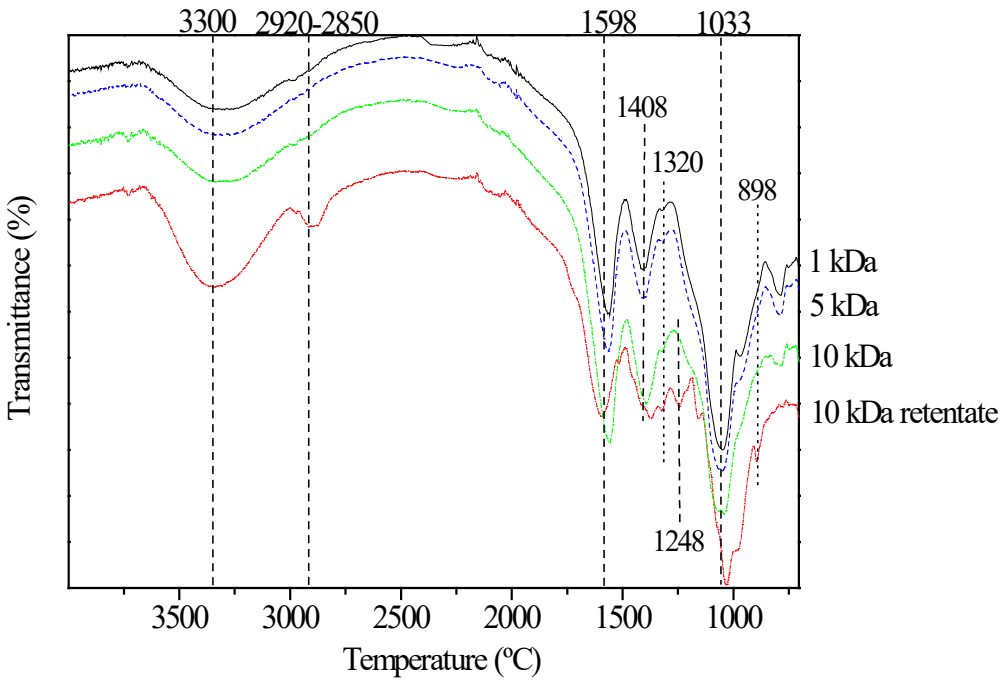
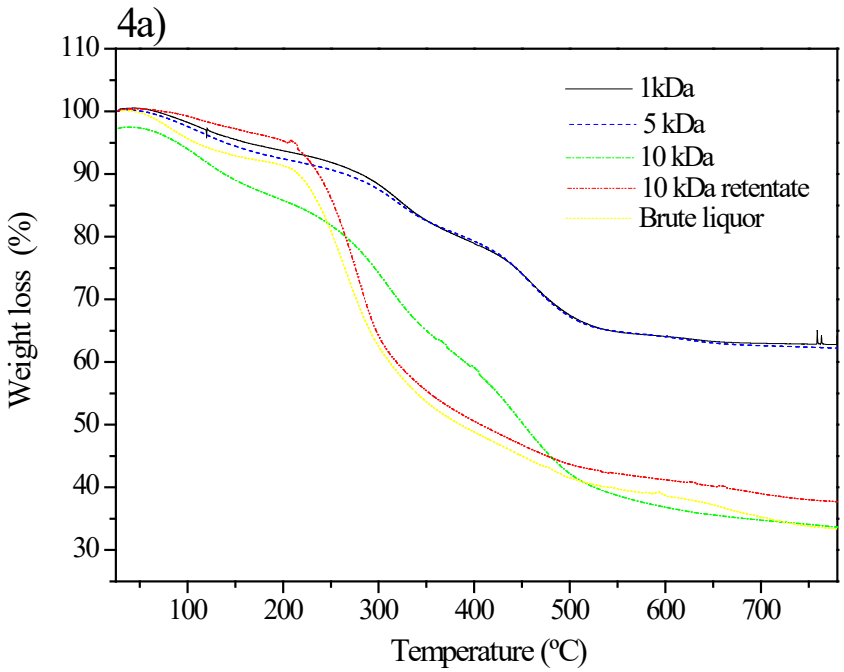

3300
2920-2850
1598
1033
1408
1320
898
1248
1 kDa
5 kDa
10 kDa
10 kDa retentate
Transmittance (%)
3500
3000
2500
2000
1500
1000
Temperature (ºC)

Figure 4


4a)
Weight loss (%)
Temperature (ºC)
1kDa
5 kDa
10 kDa
10 kDa retentate
Brute liquor

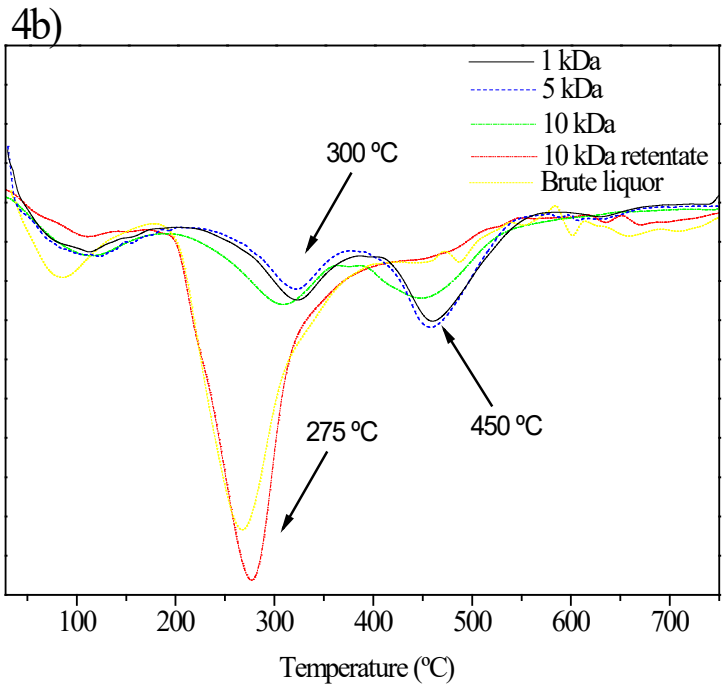
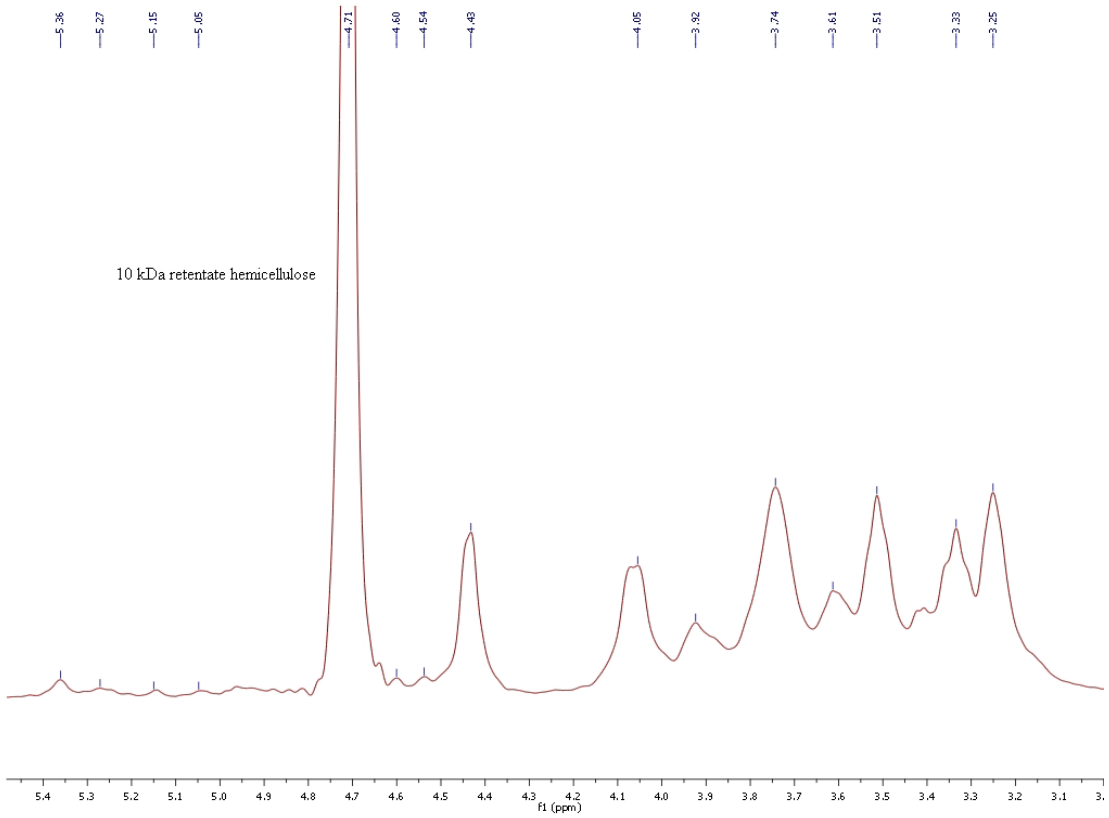

4b)
Temperature (ºC)
1 kDa
5 kDa
10 kDa
10 kDa retentate
Brute liquor
300 ºC
275 ºC
450 ºC

Figure 5


5.36
5.27
5.15
5.05
4.71
4.60
4.54
4.48
4.05
3.92
3.74
3.61
3.51
3.33
3.25
10 kDa retentate hemicellulose
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
f1 (ppm)