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EFFECT OF ALKALINE AND AUTOHYDROLYSIS PROCESSES ON THE PURITY OF OBTAINED HEMICELLULOSES FROM CORN STALKS

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Abstract

A study of the potential of autohydrolysis and alkaline extraction processes from corn stalks was performed for high purity hemicellulose extraction. The influence of process parameters on the purity of obtained hemicelluloses was analyzed. An experimental design was developed for the autohydrolysis treatments to determine the optimal conditions to solubilise the hemicelluloses with lowest content in contaminants. On the other hand, alkaline extraction, including raw material pretreatment (dewaxing and delignification step) was carried out analyzing the effectiveness of this processes for maximum pure hemicellulose recovery. The maximum yield (54% of the raw material hemicelluloses) and the best physicochemical properties (highest hemicellulose content free of lignin) were obtained with these pretreatments in alkaline extraction. Moreover, the effect of lignin removal by sulphuric acid from the autohydrolysis liquors before hemicellulose precipitation was studied. This purification step has allowed to obtain lignin-free autohydrolysis hemicellulose but with the presence of sulphur as predominant contaminant.

Keywords: corn residues, autohydrolysis, alkaline extraction, hemicelluloses, purification

1. Introduction

Before the 20th century, the economic development was sustained by the biomass and minerals, being an essential energy source of humans. However, due to the enormous petroleum reserves discovery and the development of economically efficient methods for its extraction, the energy based on biomass was replaced by petroleum products, losing importance as energy resources. Woody biomass was mainly used at industrial level for pulp and paper production. In recent years, the uncertainty in the supply, price of fossil fuels and environmental pollution generated make necessary the investigation of new alternatives. As a result, the lignocellulosic materials become again an important resource to provide and support a sustainable and environmentally friendly system (Reddy and Yang, 2005; Sun and Cheng, 2002). These renewable materials (consisting mainly of cellulose, hemicellulose and lignin) can be processed to produce energy, chemicals products with high added value and precursors of biopolymers, opening new fields in the chemical industry transforming petroleum refinery on biomass biorefinery (Cherubini and Ulgiati, 2010).

Polysaccharides are fascinating polymers possessing magnificent structural diversity and functional versatility. Although the cellulose is the main polysaccharide actively used in commercial products, the application potential of hemicelluloses is emphasized many times by scientists, converted them today an important no exploited fraction that can be used in a variety of promising applications. The xylo-oligosaccharides can be used for synthesis of biopolymers (polyols, lactic acid, alditols, aldonic acids and lactones), polyurethanes, polyesters and polyamides (Glasser et al., 1995). Moreover, they can be used to produce water soluble films, coatings, capsules, for production of chemicals such as xylitol (Rivas et al., 2002), furfural (useful to produce paints, solvents, plastics and resin) (Mansilla et al., 1998) and surfactants (Hass et al., 1990; Parker et al., 1973).

The hemicellulose fraction is a branched polysaccharide which is associated with cellulose and lignin in plant cell walls (Bian et al., 2010). Hemicelluloses have a higher hydrolysis rate and solubility in alkaline medium than cellulose, but hemicelluloses have higher resistance to oxidation than lignin. Hemicelluloses are monomers of pentoses (xylose and arabinose) and hexoses (glucose, mannose and galactose), but they have different substituent such as uronic acids, acetyl groups (Gírio et al., 2010) and phenolic acids. The functional groups present in the structure of hemicelluloses are composed of a carbonyl group in the first carbon and hydroxyl groups in other carbons. As a result of this structure, reaction occurs between the carbonyl group and fifth carbon hydroxyl group (Pradhan et al., 2009) giving more favourable cyclic structures in aqueous solutions. With carbonyl functional group, oxidation reactions can occur (oxidizing to carboxyl group, being the pentoses reductors of mild oxidants agents) whereas the hydroxyl groups give esterification reactions (acetylation). The main polymers that form hemicelluloses are xylans, mannans, galactans or other heteropolymers as glucans, xyloglucans, and other pectic substances.

In this work, corn stalks were studied as hemicellulose source material. These agricultural wastes are usually burned without value. Many experiments have focused on the use of this residue due to the high content of hemicelluloses, specially used for ethanol production by dilute acid and enzymes treatments (Kazi et al., 2010). But only a small part is used for producing chemicals such as furfural, additives for pulp and paper and for composite elaboration (Kadam and McMillan, 2003).

The fractionation of biomass can be carried out by using catalyzed chemical hydrolysis (Lavarack et al., 2002; Qiabi et al., 1994; Chamy et al., 1994), physical treatments such as steam explosion technologies (Montane et al., 1998; Teng at al., 2010) and their combination (Zimbardi et al., 2007). Recently, more environmental-friendly technologies such as autohydrolysis process, which uses water as only reagent, have gained interest for hemicellulose recovery (Carvalheiro et al., 2004; Garrote et al., 2002), being the autohydrolysis of xylan-rich lignocellulosic biomass an effective fractionation process for the production of xylo-oligosaccharides. The autohydrolysis process is very interesting fractionation because it can achieve hemicellulose solubilisation without any additional catalyst. The protons generated by the autoionization of water act as catalysts, mainly attacking the acetyl groups present in the form of esters in xylans. This process reduces the environmental impact, avoids corrosion problems (comparing mainly with acid hydrolysis processes) and reduces the hydrolysis process cost (Carvalheiro et al., 2008). On the other hand, taking into account the high solubility of hemicelluloses in alkali solutions, in this work, alkaline extraction was also studied as alternative for hemicellulose extraction from corn stalks. In this context, aqueous solutions of potassium and sodium hydroxide are mostly used to isolate hemicelluloses. In this work, the usage of NaOH was used following the method proposed by Sun et al. (2003).

In autohydrolysis and alkaline extraction processes, non-desirable reactions occur, such as solubilisation of extracts, dissolution of phenolic compounds, neutralizations of the ashes etc. Hence, it is essential the application of purification processes for hemicelluloses subsequent utilization. Therefore, in the autohydrolysis process an experimental design was performed to analyze the influence of temperature and process time on the purity of obtained hemicelluloses. On the other hand, the influence of lignin removal from autohydrolysis liquor as purification step before hemicellulose precipitation has also been studied. Acid precipitation is the most common method for lignin recovery from black liquor (Ghatac, 2008). Conventionally, the lignin has been recovered with addition of mineral acids like sulphuric, hydrochloric acid or phosphoric acid. In this study sulphuric acid was used to precipitate lignin before hemicellulose precipitation due to the high lignin recovery yield (Ibrahim and Chua, 2004), the solid phase obtained by autohydrolysis process, rich in cellulose and lignin, could be used for future applications (Behin and Zeyghami, 2009). Following the same objective, the alkaline extraction includes multi-stage pretreatments to remove impurities, consisting mainly in the removal of extractives, hydrolysis pretreatments at low temperature, following the isolation of holocellulose about delignification and the application of the alkaline extraction for hemicellulose recovery. This procedure has been used in many studies to obtain native hemicellulose from different raw materials (Sun et al., 2003; Egüés et al., 2010).

Autohydrolysis and alkaline extraction were compared in terms of extraction yield and purity of obtained hemicelluloses (characterized by Fourier Transform Infrared Spectroscopy FT-IR, Thermo-gravimetric Analysis TGA, Gel Permeation Chromatography GPC, elemental analysis and Inductively coupled plasma mass spectrometry ICP-MS), the most important variables for hemicelluloses industrial application.

2. Methods

2.1 Raw material conditioning and characterization

The corn stalks used in the experiments was kindly supplied by the company Straw Pulping Engineering (SPE), S.L. (Zaragoza, Spain). The residue was dried up to constant moisture, and then it was ground in a mill and sieved to obtain the 4–6 mm size fraction.

The chemical composition was analyzed following standard methods and procedures found in the literature: ash (TAPPI T211 om-93); ethanol–toluene extractives (TAPPI T204 cm-97); lignin (TAPPI T222 om-98); α-holocellulose (Wise et al., 1946), α-cellulose (Rowell, 1983) and hemicelluloses content.

2.2 Fractionation process

The corn wastes were treated by autohydrolysis and alkaline extraction. In the case of autohydrolysis an experimental design was performed to observe the influence of process variables (such as temperature and cooking time) in the yield and composition of the obtained liquors. In the case of alkaline extraction, various pretreatments were applied to study their effects on the purity of the obtained hemicelluloses.

2.2.1 Autohydrolysis experimental design and severity parameter analysis

The autohydrolysis treatments were carried out in 4 L batch reactor (EL0723 Iberfluid) with electronic control unit for pressure and temperature control. The experimental design was realized under the operational conditions usually used in autohydrolysis process (below 230 ºC) (Garrote et al., 2002), in this case the selected temperatures were 160 ºC, 180 ºC, 190 ºC and 200 ºC. The cooking time was varied between 30, 45, 60 and 75 min after reaching the desired temperature. A constant solid/ liquid ratio of 1:20 was used for all experiments. Finally, the experimental design consisted in 16 different experiments.

Different severity factors were calculated in order to summarize in one variable the main autohydrolysis treatment parameters effects. The log severity values were calculated as defined by Overend and Chornet (1987), as shown in Eq. (1), where t represents the reaction time in minutes, T_H is the process temperature and T_R is a reference temperature value of 100 ºC (Lloyd and Wyman, 2005), respectively.

$$R_0 = t * \exp\left[\left(T_H - T_R\right)/14.75\right] \tag{1}$$

2.2.2 Alkaline extraction

The pretreatments carried out to the raw material consisted mainly in the removal of undesirable compounds such as extractives, inorganic compounds and a delignification step before hemicellulose extraction. Fig.1 shows the flow diagram corresponding to this refining procedure. Corn residues were dewaxed by ethanol–toluene extraction (1:2; v/v, 6 h) and treated with hot water (1:20; w/v, 80 ºC, 2 h). Water-soluble polysaccharides were precipitated from the obtained filtrate by adding 3 volumes of ethanol and were stored for further characterization. On the other hand, the water soluble free solid was treated with sodium chlorite in acid solution (pH 4.0, adjusted by 10% acetic acid, 75 ºC, 2 h) in order to remove lignin and to obtain the holocellulose fraction. Hemicelluloses were extracted from holocellulose by alkaline treatment (10% NaOH, 1:20; w/v, 10 h, 20 ºC). The filtrate was neutralized with 6 M HCl at pH 5.5 and hemicelluloses were precipitated in three volumes of ethanol and washed with ethanol–water (70:30; v/v), dried and stored for further characterization.

2.3 Liquors characterization

The autohydrolysis liquors were characterized in terms of density, pH, inorganic matter content (IM), organic matter content (OM), monomeric sugars concentration, acetic acid and acid insoluble lignin content.

Density was determined measuring the weight of the black liquor in a known volume previously weighed and moisture free. IM was determined after combustion of the liquor at 525 ºC (TAPPI T211 om-93) and OM was defined as the difference between TDS and IM.

2.3.1 Quantification of monosaccharide sugars and acetic acid

Sugars composition of hemicelluloses present in hydrothermal liquors were quantitatively determined in a high performance liquid chromatograph (HPLC) Jasco LC Net II /ADC (column oven and quaternary gradient pump) equipped with a refractive index detector and a photodiode array detector. 0.005 N H_2SO_4 prepared with 100% deionised and degassed water was used as mobile phase (0.35 mL/min flow, 40 ºC and injection volume 20 µL). High purity glucose, xylose, arabinose and acetic acid were used for calibration curve.

For quantification of monomeric sugars, the autohydrolysis liquors were subjected to post-hydrolysis process. The selection of the operation conditions was based on the maximum depolymerisation of hemicelluloses with minimum loss of sugars. The best operation conditions obtained for this study were the utilization of sulphuric acid (5% w/w) at 100 ºC for 60 min at a ratio of liquor: acid 4:1 (v/v). It should be noted that the acetic acid was the main hemicellulose decomposition product considered in this study.

2.3.2 Acid insoluble lignin in autohydrolysis liquors

Acid precipitation was used to quantify approximately the acid insoluble lignin present in autohydrolysis liquors. This fraction could be precipitated together with hemicelluloses causing impurities. For that purpose the autohydrolysis liquids were acidified until pH 2 with sulphuric acid (72%, w/w) and the acidic insoluble fraction was collected by filtration and vacuum dried at 50 ºC until constant weight.

2.4 Precipitation of autohydrolysis hemicelluloses

The precipitation of hemicelluloses was achieved using two different methods. The first method was direct precipitation of hemicelluloses adding three volumes of ethanol in the autohydrolysis liquor. The second method was firstly the acid precipitation of lignin before hemicelluloses precipitation. The application of these methods aimed to determine the effect of lignin removal before hemicellulose precipitation on the purity of subsequent precipitated hemicelluloses.

2.5 Characterization of precipitated hemicelluloses

2.5.1 Fourier transform infrared spectroscopy

Measurements were performed in a Perkin-Elmer 16PC instrument by direct transmittance using KBr pellet technique. Each spectrum was recorded over 20 scans, in the range from 4000 to 600 cm^{-1} with a resolution of 4 cm^{-1}. KBr was previously oven-dried to avoid interferences due to the presence of water, and background spectra were collected before every sampling.

2.5.2 Thermogravimetric analysis

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

2.5.3 Molecular weight

The molecular weights of the samples were determined by gel permeation chromatography (GPC). A GPC Jasco LC-Net II /ADC equipped with a photodiode array detector, refractive index detector and PDA detector were used. The column was PL aquagel-OH MIXED-H 8 μm. As the mobile phase, an acid solution of 0.005 N H_2SO_4 and deionised and degassed water was used (0.6 mL/min flow, 40 ºC and injection volume of 20 μL). Pullulan polysaccharides with different molecular weights (between 180 and 805000 Daltons) were used for the calibration curve.

2.5.4 Elemental analysis

Elemental analysis for carbon, hydrogen, nitrogen, sulphur and oxygen content for the precipitated fractions was performed to determine the purity of obtained hemicelluloses. Total oxidation of the samples (10 mg) was conducted at 1020 ºC and the combustion products were separated in a chromatographic column.

2.5.5 Inductively coupled plasma mass spectrometry

Semiquantitative analysis was performed by ICP-MS to determine inorganic elements present in the raw material and precipitated hemicelluloses. For that purpose, the corn wastes and hemicellulose ashes were digested by microwave using 100 mg of the sample adding different acids in the following proportion: 5 mL 65% HNO_3, 1 mL

40% HF and 10 mL of 5% H_3BO_3. The microwave digestion was carried out at 200 ºC, at 1450 W and 90% of the power.

3. Results and discussion

3.1 Composition of corn residues

Raw material presented the following chemical composition (% on a dry basis): ashes content: 9.27 ± 0.20; ethanol-benzene extractives: 1.08 ± 0.10; Klason lignin: 17.18 ± 2.40; holocellulose: 70.79 ± 3.50; α-cellulose: 49.22 ± 2.70 and hemicelluloses: 25.57 ± 0.70.

Comparing the hemicellulose percentages found in other lignocellulosic residues such as barley straw (27.00%) (Reddy and Yang, 2005), rice straw (25.10%), wheat straw (33.30%) and corn stover (29.60%) (Wartelle and Marshall, 2006), the percentage found suggested the suitability of this material as source for sugars extraction. However, high ashes content which can be solubilised in the hydrolysis liquors was detected. The ashes were formed by inorganic impurities such as silicates and mineral components that could be precipitated and cause impurities. Extractives of ethanol-toluene showed a low content that indicated small amounts of waxes, resins, tannins, etc. In relation to the lignin and cellulose content, these values were in the range found in other agricultural wastes.

3.2 Solid yield, pH and density of the autohydrolysis liquors

The recovered solid residue (Table 1) decreased from values around 61.66% at log10 (R_0) = 3.42 to a value of 41.46% at log (Ro) = 4.72 due to higher solubilisation of the components in the hydrolysis liquor. At 180 ºC, 50% of the solubilisation was obtained. On the other hand, the pH of the hydrolysis liquors decreased with the severity of the treatment, which can be due to the presence of higher acetic acid content originated by the higher decomposition of the hemicelluloses and the breakdown of the present acetyl groups. However, the density values were maintained without significant changes.

3.3 Liquors characterization

Fig. 2 represents the content in IM and OM for the studied conditions. The liquor with higher content of organic matter, 1.30% OM, was obtained at 180 ºC and 30 min with severity factor of 3.8 followed by the treatment at 190 ºC and 30 min, 1.29% OM, with severity of 4.1. The minimum organic matter was reached under mild conditions, at 160 ºC and 30 min corresponding to a severity of 3.24 with 0.73% OM. On the other hand, the maximum solubilisation of inorganic matter was achieved at severity value of 4.1, at 190 ºC and 30 min with 0.64% IM.

It can be concluded that the optimal condition, respect to the relation of maximum content of OM and minimal content of IM, was the hydrolysis liquor obtained at 180 ºC and 30 min, with 1.30% of OM and 0.34% of IM.

3.4 Quantitation of monosaccharide sugars and acetic acid

The liquors obtained at severity of 4 to 4.2, of 4.3 to 4.5 and 4.6 to 4.8, corresponding to 45, 60 and 75 min autohydrolysis time, contained less sugars compared with those obtained at severity of 3.8, 4.1 and 4.4 corresponding with 30 min of the hydrolysis time (Fig. 3). The longer reaction time of the autohydrolysis process (except the liquor obtained at 160 ºC 75 min that showed more sugars at severity of 3.6), caused more degraded compounds in post-hydrolysis process. The predominant monomer present in all liquors was xylose (the main component present in agricultural residues), with small quantities of glucose and arabinose. The concentration of these sugars indicated that the hemicelluloses in corn residues were mainly composed of xylan and arabinoxylan type polysaccharides.

The highest sugars content in autohydrolysis liquor was obtained at severity factor of 3.8, at 180 ºC and 30 min with 3.94 g/L of total monomeric sugars whereas 84% was constituted by xylose. At this severity, the total sugars constituted about 27.74% of the hemicelluloses present in the raw material. In the case of 190 ºC and 30 min autohydrolysis liquor with 4.1 severity factor, the amount of hemicellulose present was 3.19 g/L constituting about 19.96% of the raw material hemicelluloses. On the other hand, for the liquor obtained at 200 ºC 30 min with severity of 4.4, the amount of sugars was 2.11 g/L constituting about 13.48% of the raw material hemicelluloses. The acetic acid content increased with the severity of the process (according to the results obtained from pH measurements) reaching a maximum value of 0.84 g/L at 200 ºC and 30 min respectively.

In conclusion, it was observed that the optimum condition for obtaining maximum available hemicellulosic sugars in liquid phase was reached at 180 ºC and 30 min of treatment.

3.5 Acid insoluble lignin in autohydrolysis liquors

According to the results shown in Fig. 4, the greater amount of lignin precipitated was obtained from 160 ºC and 75 min autohydrolysis liquors (severity of 3.6) while at most severe conditions of the treatment the precipitate decreased. The liquors with minor quantities of precipitated lignin were obtained at treatment severity 4.4, at 200 ºC and 30 min, respectively. However, the lower content in hemicelluloses, higher content in acetic acid and IM presence, converted again the 180 ºC 30 min as optimal condition for maximum available hemicellulose extraction with lower amounts of dissolved impurities.

On the other hand, the organic matter is composed mainly of lignin and hemicelluloses and it was observed in this study that the lignin plus hemicelluloses was not equivalent to the total OM measured. Maybe, this difference can be due to the not quantified hemicelluloses fraction because of existing C-C linkages of lignin-carbohydrates complex that were not broken in the post-hydrolysis process. In addition, it is well known that acid precipitation below pH 3 provides the highest lignin precipitation but soluble lignin remain in the solution. Other possible reason of this difference could be due to the non-quantified components like pectins and proteins.

3.6 Precipitation of hemicelluloses and physicochemical characterization

The hemicellulose recovery from autohydrolysis liquor was made on two selected autohydrolysis liquors: those obtained at 180 ºC 30 min (the optimum autohydrolysis liquor) and at 190 ºC 30 min (with higher amount of IM).

The precipitated hemicelluloses for 180 ºC 30 min autohydrolysis liquor after lignin removal showed white colour. Instead for the hemicellulose precipitated in presence of lignin presented a brownish aspect.

The yield obtained by alkaline process (% on a dry basis) was 54% extraction of sugars present in the raw material. It could be concluded that alkaline extraction process, has higher hemicellulose extraction yield than autohydrolysis process in the liquor (27.14%).

Fig. 5a shows FT-IR spectra of precipitated samples obtained from optimum autohydrolysis liquor: hemicellulose precipitated in presence of lignin (named as hemicellulose-lignin complex LCC), hemicellulose precipitated in absence of lignin (named as hemicellulose H) and the hydrolysis lignin (named as lignin L), respectively. As can be observed the bands found at 3400, 2920-2850 and 1460 cm^{-1}, which indicate the OH stretching and CH bond deformation of CH_2-CH_3 groups, respectively, were presented in all samples. In hemicellulose precipitate the absence of bands at 1520 cm^{-1} (typical of aromatic skeletal vibration of the carbonyl group) and 1330-1210 cm^{-1} (stretching of C=O group of siringyl ring), indicated the nonexistence of phenolic compounds in the sample. On the other hand, the hemicellulosic presence was observed in the bands at 1040 cm^{-1} originated from typical of xylans (indicating the predominance of this monomer, which is in agreement with sugar analysis) and at 890 cm^{-1} referred to the domain of β-glycosidic bonds between sugars. Alternatively, the peak found at 1640 cm^{-1} might be due to the presence of water (Sun and Tomkinson, 2002) or to the stretching of carboxylic acids forming intermolecular hydrogen bond (Sun et al., 2003). In the hemicellulose-lignin complex, the main characteristics bands found in lignin spectrum were observed, therefore justifying the lignin contamination in the sample. The Fig. 5b shows FT-IR spectra of alkaline extraction precipitates (water-soluble polysaccharides named as WSP) and alkaline hemicelluloses (named as AH), respectively. In the same way, the characteristics of vibration of OH groups at 3300 cm^{-1}, CH at 2920-2850 cm^{-1} and CH of CH_2-CH_3 groups were found in both samples. As in previous case, the presences of hemicellulose characteristics bands were found at 1160-1030 cm^{-1} and 899 cm^{-1}. The absence of bands at 1520-1330 cm^{-1} in the alkaline hemicellulose demonstrated the effectiveness of the sodium chlorite for lignin removal.

The thermogravimetric analysis result of all precipitates is summarized in Fig. 6. The hemicellulose precipitate of the optimum autohydrolysis (Fig. 6a and its derivative in Fig. 6b) showed three maximum weight losses: at 100 ºC due to sorbed moisture, at 250-300 ºC due to decarboxylation of hemicellulose (releasing CO, CO_2 and some hydrocarbons) and at 750 ºC possibly due to heavier volatile compounds ignition or carbonized combustion. The hemicelluloses represented approximately 26% of the total weight loss with a residue about 70% at 800 ºC. In the thermogram of the LCC the maximum weight loss rate was observed at 450 ºC, which confirms the presence of lignin in precipitated hemicellulose (in agreement with FT-IR results). In this case, the precipitate showed about 42% of the residue at 800 ºC. In addition, the analysis of TGA curve of precipitated hemicellulose from 190 ºC 30 min liquor (Fig. 6c and d), showed the highest level of residues, 87% in hemicellulose and 50% in LCC sample. The high levels of residues found in these autohydrolysis precipitates (mainly in hemicellulose precipitated after lignin removal), could be due to: (1) inorganic matter dissolved in the hydrolysis liquor can be dragged along with hemicelluloses in the precipitation process (Werther et al., 2000), (2) introduction of sulphuric acid in the second precipitation method could contribute to the formation of more salts through sulphate group, which were then precipitated together with hemicelluloses, (3) other authors justify the high residue formed by the hemicellulose (~25%) and lignin (~40%) due to the formation of char, compared to cellulose which leading to very few solid residues for its rapid devolatilization reactions (Yang et al., 2007). To verify these hypotheses, TGA measurements of commercial xylose (provided by Fluka, with ≥ 99% of purity named as Xy) under the same conditions were carried out (Fig.6e and f). At 800 ºC, 27% residue was obtained; this result suggests that part of the found residue may be due to the formation of char in the pyrolysis process.

In the case of the alkaline extraction precipitates thermograms (Fig. 6g and h), the AH showed a prominent peak at 250-300 ºC due to hemicellulose presence, representing 55% of the total weight loss. The absent of weight variation at highest temperature indicated the nonexistence of lignin in the sample. The residue in this case was about 30%.

3.7 Molecular weight

The precipitated hemicellulolisic fractions were further characterized by determination of their molecular mass. The weight-average (M_w) and number-average (M_n) molecular weights and polydispersity (M_w/M_n) are given in the Table 2.

As it could be observed, the 180 ºC hemicellulose-lignin complex sample was characterized by $M_w = 2183$ molecular weight whereas free of lignin the molecular weight is decreased to $M_w = 1267$. The same trend was observed in hemicellulosic precipitates with and without lignin at 190 ºC, so it could be concluded that lignin removal before hemicellulose precipitation offers hemicelluloses with lower molecular weight. However, in alkaline hemicellulose sample, besides the main fraction which was constituted by $M_w = 1141$ low molecular mass (probably produced by number of step used in its extraction), the presence of a second fraction with $M_w = 75208$ was detected. This high molecular weight fraction constituted only about 17.45% of total molecules in the sample. In general, the alkaline treatment of lignocellulosic substances disrupts the cell wall by dissolving hemicelluloses and lignin, hydrolyzing uronic and acetic esters, cleaving the α-ether linkages between lignin and hemicelluloses, as well as the ester bonds between lignin and/or hemicelluloses and hydroxycinnamic acids (Wen el al., 2011). In this case, the dewaxing and delignification treatments of the raw material carried out before the alkaline extraction, resulted in obtaining small percentage of high molecular weight oligosaccharide. It could be concluded that the use of high severities such as high temperature in autohydrolysis process causes relatively monodisperse polymers with small molecular weight molecules and the alkaline extraction including raw material pretreatment, provided two different molecular weight fractions.

3.8 Elemental analysis

Table 3 shows elemental analysis obtained values of precipitated fractions of the selected experimental design liquors (180 and 190 ºC at 30 min) and alkaline hemicelluloses.

High carbon, hydrogen and oxygen percentages (35.55%, 5.51% and 37.92%) were found in the 180 ºC LCC sample. However, the hemicellulose fraction precipitated after lignin removal presented less percentage of these elements and the presence of 14% of sulphur in the precipitates being observed. It seems to confirm that hemicelluloses precipitates were free of lignin but contaminated by the presence of sulphur. On the other hand, the precipitated hemicelluloses of 180 ºC hydrolysis liquor presented higher percentage of organic compound than 190 ºC hemicelluloses, verifying the influence of the autohydrolysis process conditions on the purity of the obtained hemicelluloses. The elemental analysis obtained for commercial xylose by Cagnon et al. (2009), showed approximately 38% C, 6% H and 48% O. Although for alkaline hemicelluloses fewer percentage of these elemental compounds were observed (compared with commercial xylose), it can be concluded that it was the most pure precipitated hemicellulose obtained in this study, with 20.49% of C, 3.32% of H and 34.74% O, free of sulphur and lignin content.

3.9 Inductively coupled plasma mass spectrometry

Table 4 shows the predominant elements found in the corn residues and the most contaminated sample of hemicelluloses obtained from 190 ºC and 30 min autohydrolysis liquor after lignin removal. As it can be observed, the main impurities in the hemicelluloses ashes (besides of sulphur content) were K, Ca and Si cationic elements.

Indeed, it can be concluded that the high residues found in TGA measurements for the hemicelluloses precipitates free of lignin were influenced by the presence of sulphur (introduced for precipitation of lignin) in addition of some other inorganic compounds. In contrast, the LCC precipitates were less contaminated due to the higher content of organic material caused by the presence of lignin in the sample.

The knowledge of these results might be used in further studies to determine appropriate purification process depending on the hemicellulose application.

4. Conclusions

In this work the potential of autohydrolysis and alkaline process for high purity hemicellulose extraction was studied. Autohydrolysis experimental design performed with corn residues has revealed that 180 ºC and 30 min was the optimal condition for maximum available hemicelluloses solubilization with minor quantities of undesirable compounds. On the other hand, the purification step carried out to remove lignin from autohydrolysis liquor before hemicellulose precipitation, has provided hemicelluloses precipitates free of lignin but contaminated by sulphur. On the other hand, the alkaline extraction process showed higher hemicellulose extraction providing hemicelluloses with better physicochemical properties. All hydrolysates constituted mainly by arabinoxylan type polysaccharides could be converted in different chemicals products such as xylitol but additional experimental work must be performed. Alkaline hemicellulose could be used also in polymeric material application.

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Table captions

Table 1. Solid yield (SY), pH and density of the experimental design liquors and the severity factor of the treatments.

Table 2. Molecular weight distribution of the samples.

Table 3. Elemental analysis of the precipitates.

Table 4. Predominant elements found in corn residues and 190 ºC 30 min autohydrolysis hemicellulose precipitates.

Table 1

Experiment	T (ºC)	t (min)	YS[a] (%)	pH	Density (g/cm^3)	Severity factor
1	200	75	44.46	3.81	0.99	4.82
2	200	60	41.46	3.82	0.99	4.72
3	200	45	45.13	3.79	0.98	4.60
4	200	30	45.40	4.17	0.98	4.42
5	190	75	44.13	3.79	0.99	4.52
6	190	60	44.72	3.93	0.99	4.43
7	190	45	46.03	4.09	0.99	4.30
8	190	30	45.61	4.29	0.99	4.13
9	180	75	48.44	4.39	0.98	4.23
10	180	60	48.46	4.49	0.99	4.13
11	180	45	50.57	4.60	0.98	4.01
12	180	30	52.56	4.88	0.98	3.83
13	160	75	60.25	4.99	0.99	3.64
14	160	60	60.96	5.17	0.98	3.54
15	160	45	61.66	5.35	0.99	3.42
16	160	30	61.03	5.48	0.98	3.24

[a] Solid residue recovered in the autohydrolysis process

Table 2

Sample	Mw[a]	Mn[b]	IP[c]	%[d]
180 ºC hemicellulose-lignin complex	2182	2093	1.04	100
180ºC hemicellulose	1267	1144	1.11	100
190 ºC hemicellulose-lignin complex	2390	2336	1.02	100
190ºC hemicellulose	1450	1054	1.37	100
Alkaline hemicellulose	75208	15898	4.73	17.45
	1141	1060	1.07	82.55

[a] Weight-average molecular weight.
[b] Number-average molecular weight.
[c] Polydispersity (M_w/M_n).
[d] Percentage of the molecule in the sample.

Table 3

Sample	% N (RSD[a])	% C	% H	% S	% O
180 ºC hemicellulose-lignin complex	0.34 (0.01)	35.55 (0.1)	5.51 (0.01)	< 4	37.92 (2.0)
180ºC hemicellulose	0.16 (0.01)	19.39 (0.3)	3.24 (0.01)	14.04	35.05 (1.0)
190 ºC hemicellulose-lignin complex	0.46 (0.02)	24.70 (0.3)	3.75 (0.2)	< 4	26.72 (2.0)
190ºC hemicellulose	0.09 (0.01)	5.06 (0.4)	1.34 (0.01)	14.36	10.72 (1.0)
Alkaline hemicellulose	0.06 (0.01)	20.49 (0.3)	3.32 (0.07)	< 3	34.74 (0.9)

[a] RSD: Relative Standard Deviation

Table 4

Element	Quantification (ppm)	
	Corn residues ashes	Hemicellulose ashes
Na	6.20	5.00
Mg	98.0	7.40
Al	11.0	0.57
Si	430	110
S	130	960
Cl	130	16.0
K	460	540
Ca	140	270
Fe	9.50	7.00
Mn	2.00	2.90
Sr	1.50	3.30

List of figures

Figure 1: Isolation of alkaline hemicelluloses by multiple pretreatments.

Figure 2: IM (%) and OM (%) of the experimental design liquors.

Figure 3: Quantification of monomeric sugars by posthydrolysis.

Figure 4: Representation of amount of precipitated lignin, hemicelluloses, OM and IM content of the liquors with higher content of sugars.

Figure 5: IR spectrum of 180 ºC 30 min autohydrolysis precipitates (a): H: hemicellulose, LCC: lignin-carbohydrate complex, L: lignin; and alkaline precipitates (b): AH: alkaline hemicellulose, WSP: water-soluble polysaccharides.

Figure 6: TG and DTG curves of 180 ºC 30 min autohydrolysis precipitates (a and b), 190ºC 30 min autohydrolysis precipitates (c and d) H: hemicellulose, LCC: lignin-carbohydrate complex, L: lignin, commercial xylose (Xy) (e and f) and alkaline precipitates (g and h) AH: alkaline hemicellulose, WSP: water-soluble polysaccharides.

Fig.1

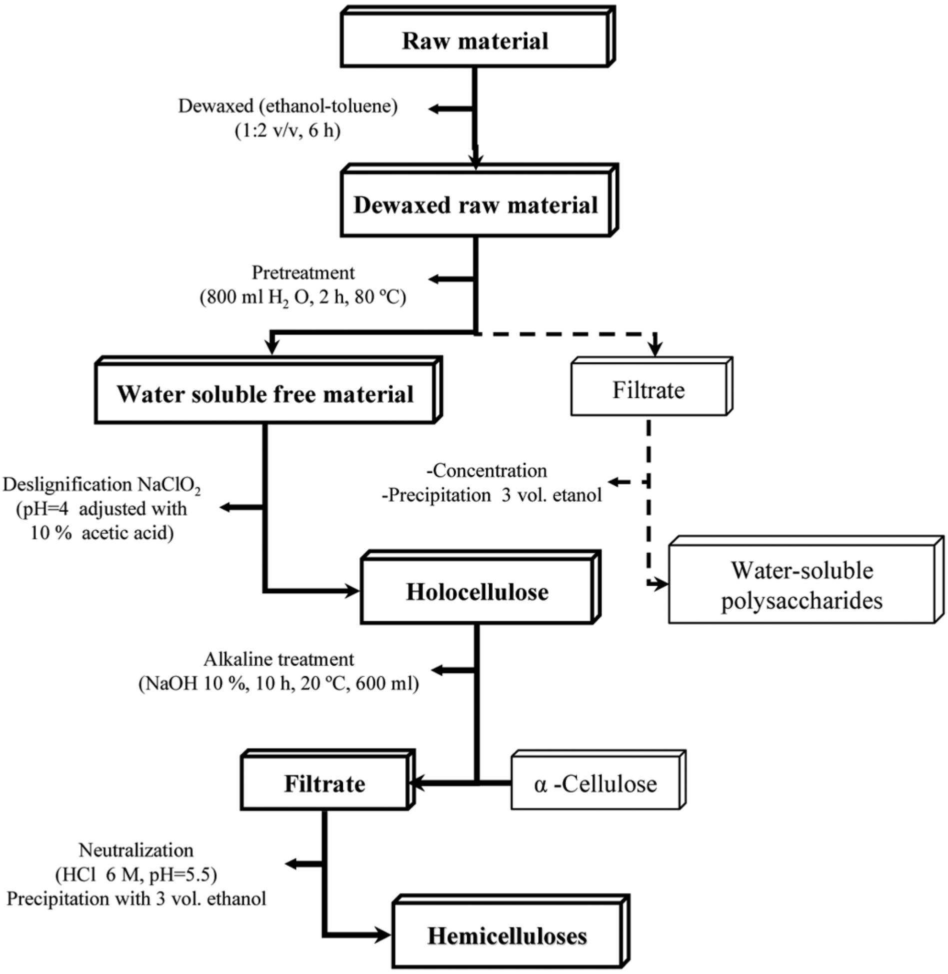

Raw material
Dewaxed (ethanol-toluene)
(1:2 v/v, 6 h)
Dewaxed raw material
Pretreatment
(800 ml H2 O, 2 h, 80 ºC)
Water soluble free material
Filtrate
-Concentration
-Precipitation 3 vol. etanol
Deslignification NaClO2
(pH=4 adjusted with
10 % acetic acid)
Holocellulose
Water-soluble
polysaccharides
Alkaline treatment
(NaOH 10 %, 10 h, 20 ºC, 600 ml)
Filtrate
α -Cellulose
Neutralization
(HCl 6 M, pH=5.5)
Precipitation with 3 vol. ethanol
Hemicelluloses

Fig.2

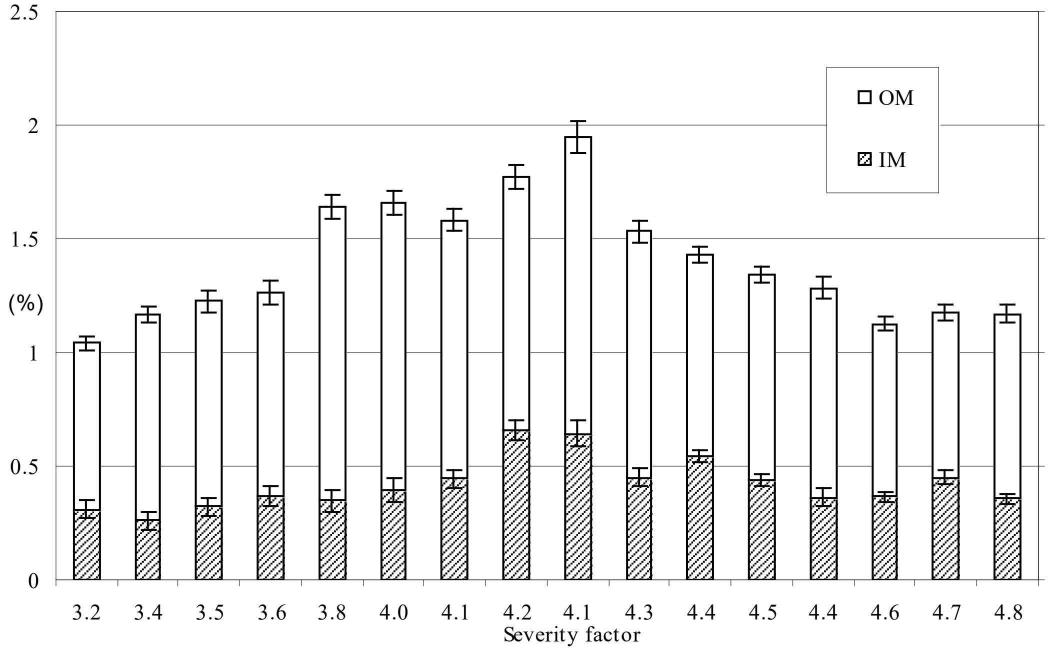

2.5
2
1.5
(%)
1
0.5
0
OM
IM
3.2
3.4
3.5
3.6
3.8
4.0
4.1
4.2
4.1
4.3
4.4
4.5
4.4
4.6
4.7
4.8
Severity factor

Fig.3

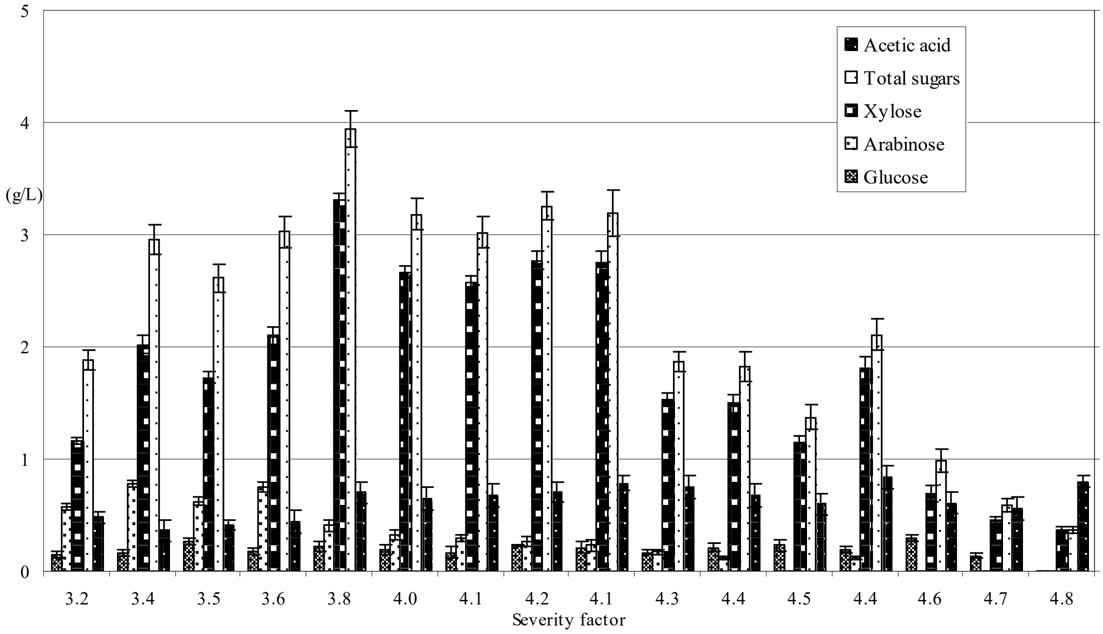
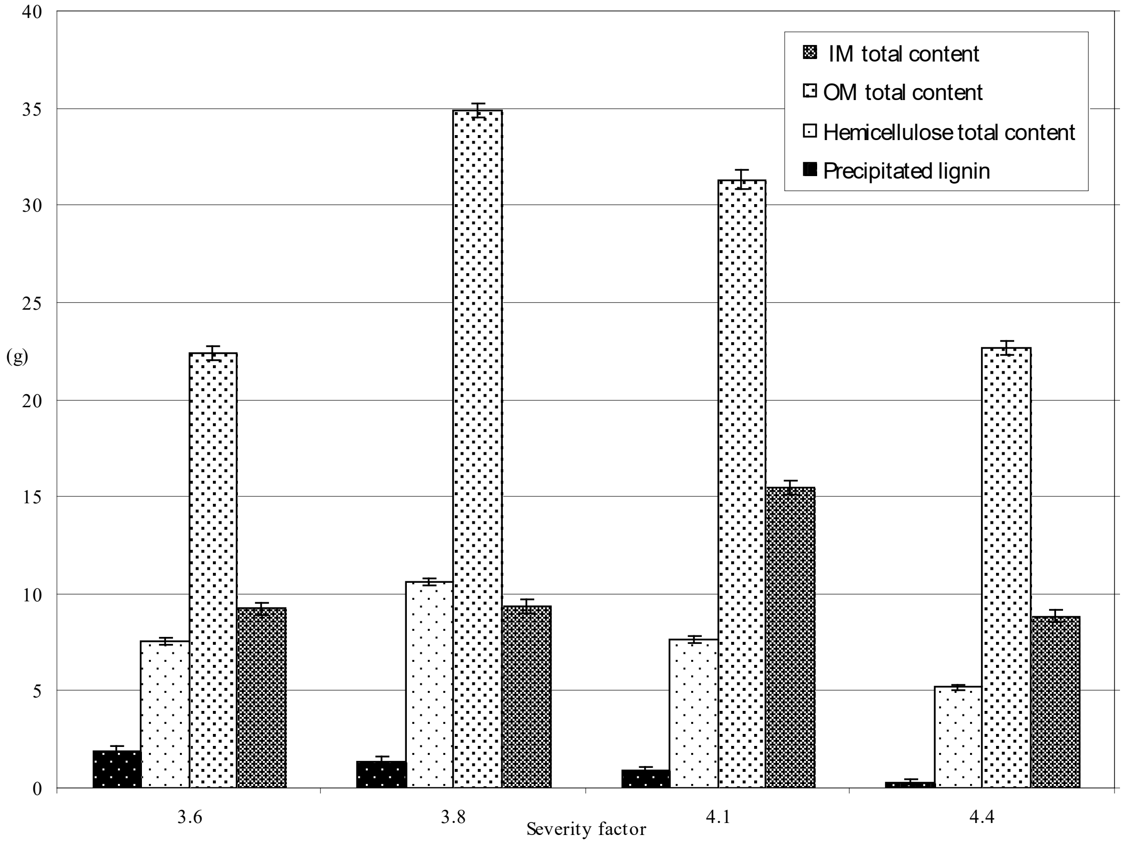

5
4
(g/L)
3
2
1
0
Acetic acid
Total sugars
Xylose
Arabinose
Glucose
3.2
3.4
3.5
3.6
3.8
4.0
4.1
4.2
4.1
4.3
4.4
4.5
4.4
4.6
4.7
4.8
Severity factor

Fig.4



40
35
30
25
(g)
20
15
10
5
0
IM total content
OM total content
Hemicellulose total content
Precipitated lignin
3.6
3.8
4.1
4.4
Severity factor

Fig.5

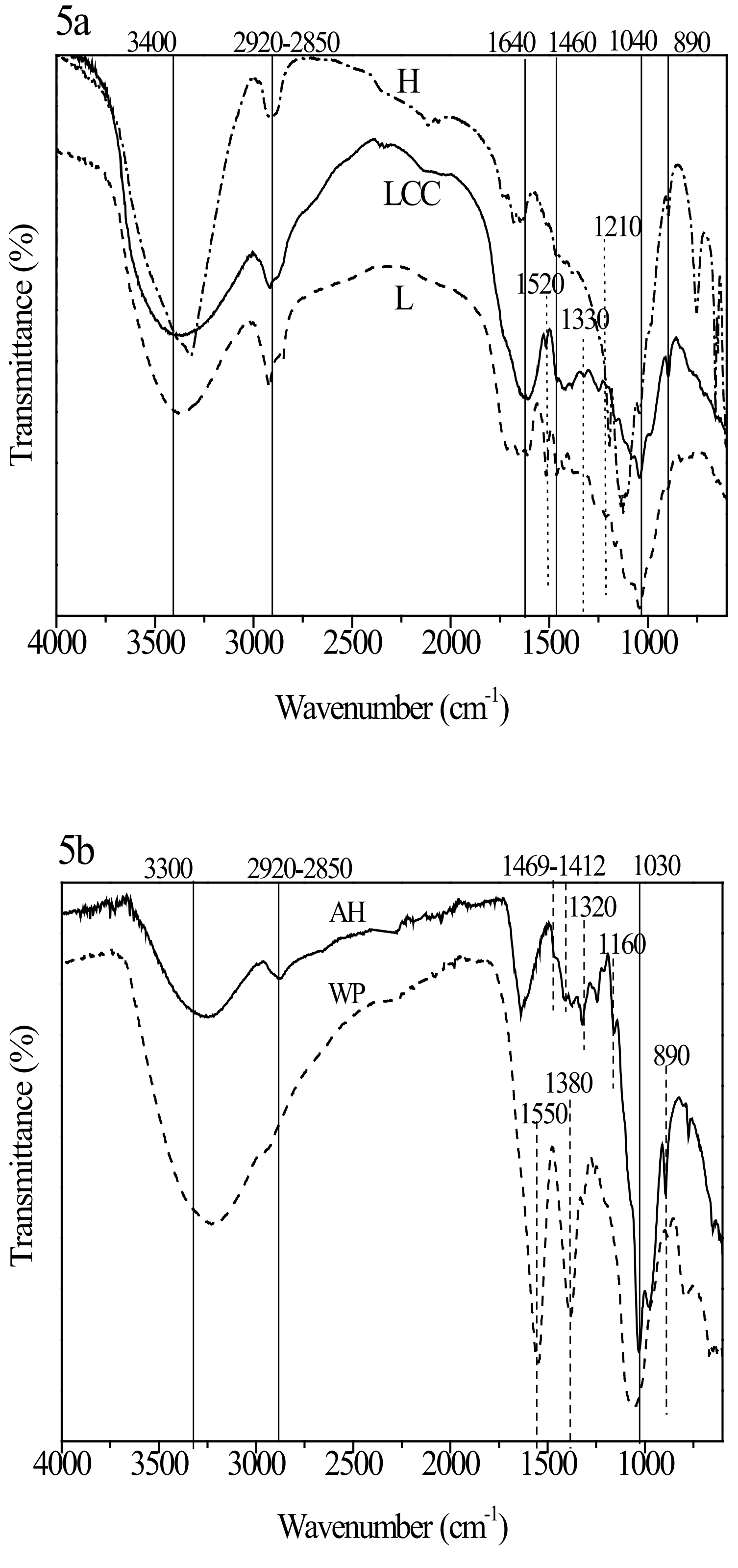
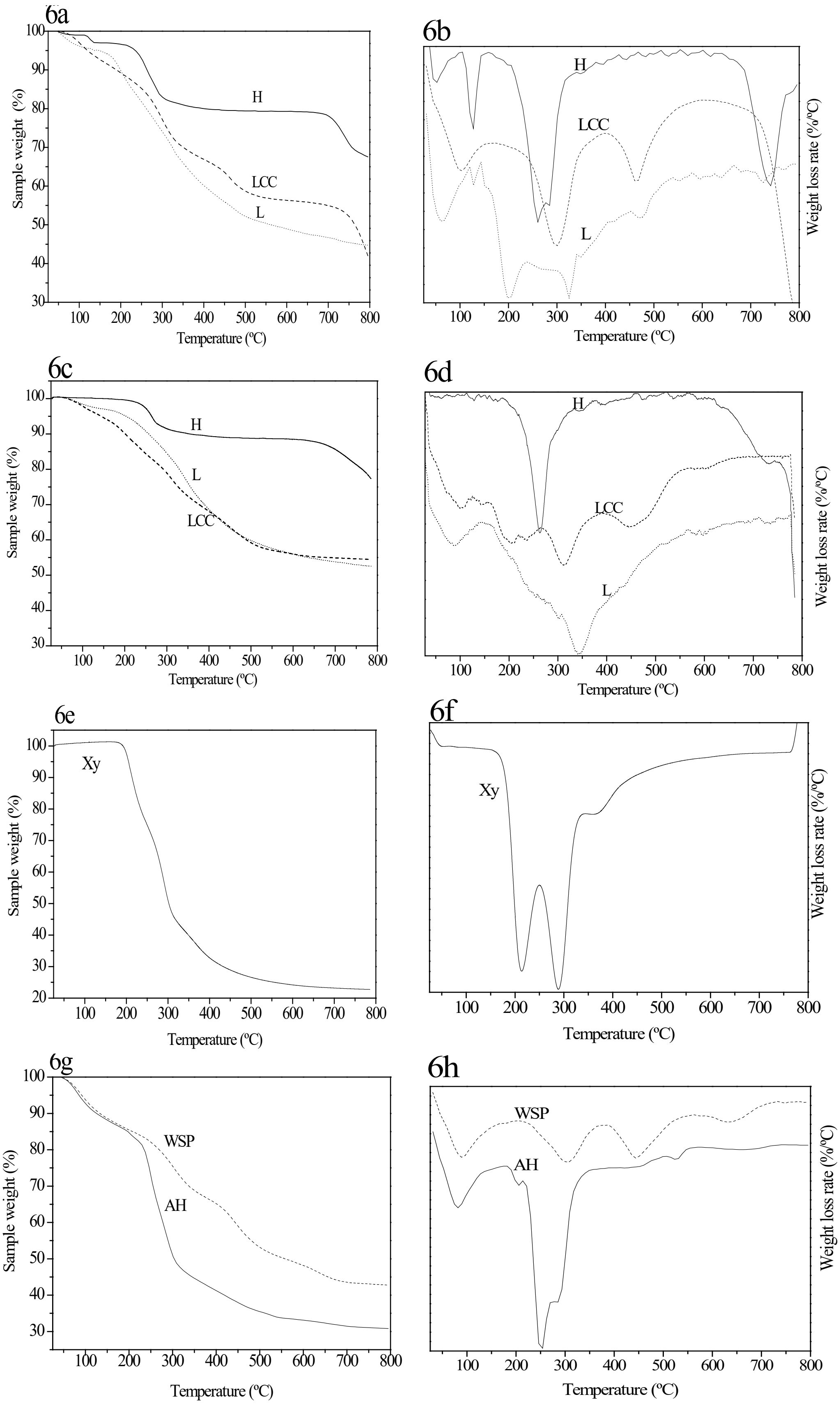

5a
3400
2920-2850
1640
1460
1040
890
H
LCC
L
1210
1520
1330
Transmittance (%)
4000
3500
3000
2500
2000
1500
1000
Wavenumber (cm^{-1})
5b
3300
2920-2850
1469-1412
1030
AH
1320
1160
WP
890
1380
1550
Transmittance (%)
4000
3500
3000
2500
2000
1500
1000
Wavenumber (cm^{-1})

Fig.6


6a
H
LCC
L
Sample weight (%)
Temperature (ºC)
30 40 50 60 70 80 90 100
100 200 300 400 500 600 700 800
6b
H
LCC
L
Weight loss rate (%/ºC)
Temperature (ºC)
100 200 300 400 500 600 700 800
6c
H
L
LCC
Sample weight (%)
Temperature (ºC)
30 40 50 60 70 80 90 100
100 200 300 400 500 600 700 800
6d
H
LCC
L
Weight loss rate (%/ºC)
Temperature (ºC)
100 200 300 400 500 600 700 800
6e
Xy
Sample weight (%)
Temperature (ºC)
20 30 40 50 60 70 80 90 100
100 200 300 400 500 600 700 800
6f
Xy
Weight loss rate (%/ºC)
Temperature (ºC)
100 200 300 400 500 600 700 800
6g
WSP
AH
Sample weight (%)
Temperature (ºC)
30 40 50 60 70 80 90 100
100 200 300 400 500 600 700 800
6h
WSP
AH
Weight loss rate (%/ºC)
Temperature (ºC)
100 200 300 400 500 600 700 800