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Comparative study of lignin fractionation by ultrafiltration and selective precipitation

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ABSTRACT

The present work presents two different methods to fractionate the lignin resulting from the black liquor of the pulping process of *Miscanthus sinensis* (7.5% (w/w) NaOH, 90 min, 90 °C). The first method consists of selective precipitation, which is achieved by the gradual acidification of the black liquor, getting different precipitates according to the pH. The second employed technique is the ultrafiltration, which uses ceramic membranes of different cut-off (5, 10 and 15 kDa) to obtain different liquors containing lignins with specific molecular weight.

Using both methods, different lignin fractions have been obtained and characterized by the following analysis techniques: FTIR, thermal analysis, GPC and NMR. Obtained results have shown that the fractionation process applied affects the properties of the obtained lignin. Ultrafiltrated fractions are less contaminated by lignin–carbohydrate complex than the fractions obtained by selective precipitation. Ultrafiltration process also allowed controlling the molecular weight of the obtained fractions.

1. Introduction

Nowadays, life is based on petroleum. Nevertheless, as fossil fuel reserves are decreasing, the exploration of feasible pathways for the conversion of abundant and renewable biomass into clean fuels and high value added chemicals to supplement or gradually replace the petroleum-based industry is highly desirable [1].

The main components of lignocellulosic biomass are cellulose, hemicelluloses and lignin. Cellulose is the most abundant natural polymer. It has a linear structure and is made up of glucose monomers. Hemicelluloses are heteropolysaccharides and have an amorphous structure. The third main component of biomass is lignin. Lignin has a complex phenolic polymeric structure. Its structure results from the condensation of phenylpropane units. The precursors for lignin are p-hydroxyphenyl alcohol (H), guaiacyl alcohol (G) and syringyl alcohol (S). The structure of lignin varies depending on its origin and the extraction method used to obtain it. Lignin molecules are very heterogeneous; therefore, fractionation has become one of the best ways to obtain specific lignins. The aim of fractionation is to obtain specific molecular weight fractions with defined properties; so they can be then used as high added value products. Yang et al. [2] and Matsushita et al. [3] proposed the use of lignin as dispersant in cement and gypsum blends, Boeriu et al. [4] as emulsifier, Sena-Martins et al. [5] as a chelating agent for removing heavy metals from industrial effluents, Mohan et al. [6] found excellent adsorbent in lignin, even compared with the activated carbons and El Mansouri et al. [7] and Tejado et al. [8] proposed its use as a component of phenol–formaldehyde resins.

Different methods have been proposed to fractionate lignin. Mörck et al. [9] fractionated both softwood and hardwood Kraft lignins by successive extraction with organic solvents. Thring et al. [10] divided Alcell® hardwood lignin into three fractions by successive extraction with organic solvents increasing hydrogen-bonding capacity. They obtained similar results as Mörck et al. [9] concluding that the low molecular weight fractions had a lower polydispersity but a higher content of guaiacyl structures with saturated side chains than the higher molecular weight fractions. Yuan et al. [11] studied different procedures of fractionation by selective solvent.

Another possibility to fractionate lignin is the selective precipitation. Sun et al. [12] obtained and characterized five lignin fractions by precipitation from the black liquor of oil palm empty fruit bunches (EFB) fibre pulping after isolation of the polysaccharide degradation products. One lignin fraction was obtained directly from the black liquor by lowering the pH until 2 and was characterized prior to the isolation of the polysaccharide degradation products. Mussatto et al. [13] described the precipitation of lignin by acidification of the black liquor. The lignin mass precipitated for each pH condition was determined. The obtained liquors were evaluated in terms of their colouration and the concentration of soluble lignin, suggesting that each lignin-derived compound was differently affected by the pH alteration. Garcia et al. [14] studied

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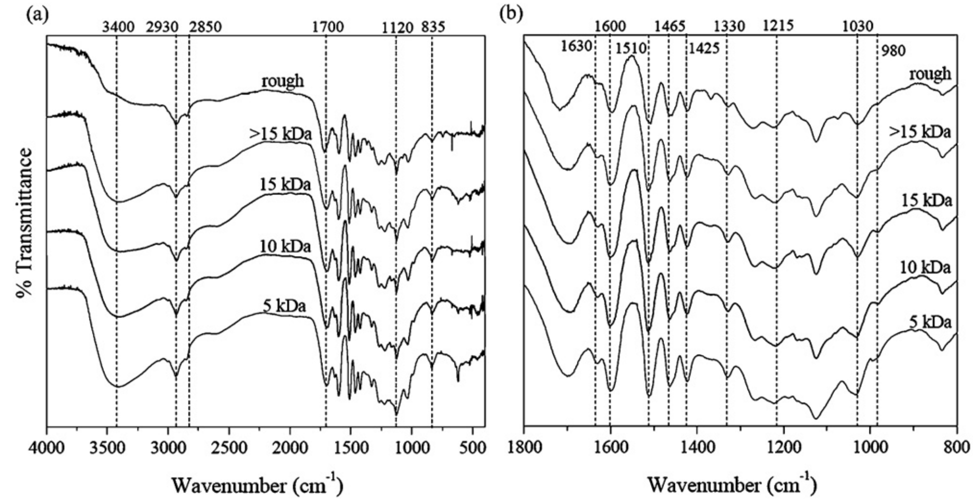

Fig. 1. (a) FTIR spectra of the fractions obtained by ultrafiltration. (b) Magnified region of FTIR spectra of the fractions obtained by ultrafiltration.

the characteristics of the lignin obtained by selective precipitation and the physico-chemical properties of the different lignin fractions obtained.

Membrane technology is another fractionation technology that can be considered because it allows obtaining lignin fractions with defined molecular weight distributions by free-reagent treatment. The effectiveness of the fractionating process using membrane technology lies on the selection of the proper cut-off. Ultrafiltration allows the separation of macromolecular solutions, so, theoretically, it is suitable for lignin fractionation as lignin is a macromolecule. Jönsson et al. [15] studied the influence of membrane cut-off, transmembrane pressure and cross-flow velocity during ultrafiltration of cooking liquor and black liquor. Colyar et al. [16] focused their study on the ultrafiltration of the liquid stream containing a variety of soluble lignin species, taking into account permeance decline, total organic carbon recovery (TOC) sodium recovery and the average molecular mass of organic compounds rejected and permeated.

In the present work, lignin was obtained from black liquor resulting from the soda pulping process of *Miscanthus sinensis* (7.5% (w/w) NaOH, 90 min, 90 °C). Two different processes were considered to fractionate lignin: selective precipitation and ultrafiltration. Obtained lignin fractions by both procedures were characterized to establish the relationship between lignin properties and the fractionation method applied.

2. Materials and methods

2.1. Black liquor obtaining

Black liquor was obtained by pulping *M. sinensis* in a 20 L glass reactor, at a temperature of 90 °C for 90 min, with 7.5% sodium hydroxide solution (w/w), a solid/liquid ratio of 1/18 (w/w) and a constant stirring rate. After reaction, the separation of liquid and solid fractions was carried out, and the resultant black liquor was characterized. The raw material, *M. sinensis*, was kindly supplied by SPE – Straw Pulping Engineering (Zaragoza, Spain).

2.2. Fractionation processes

The first fractionation method used was ultrafiltration (UF) membrane technology. The UF module used in the present work was supplied by IBMEM – Industrial Biotech Membranes (Frankfurt, Germany). The membranes (5, 10 and 15 kDa) are made of

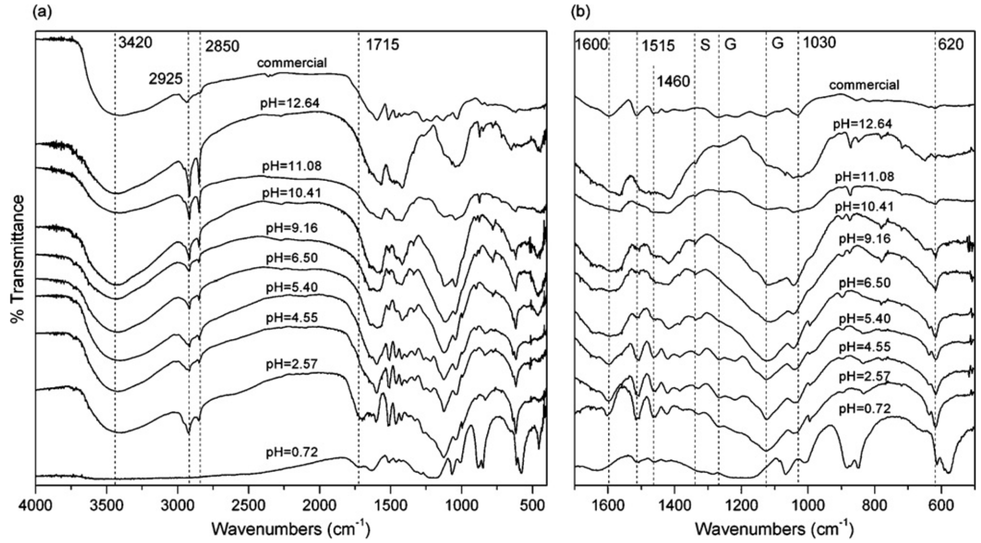

Fig. 2. (a) FTIR spectra of the fractions obtained by selective precipitation. (b) Magnified region of FTIR spectra of the fractions obtained by selective precipitation.

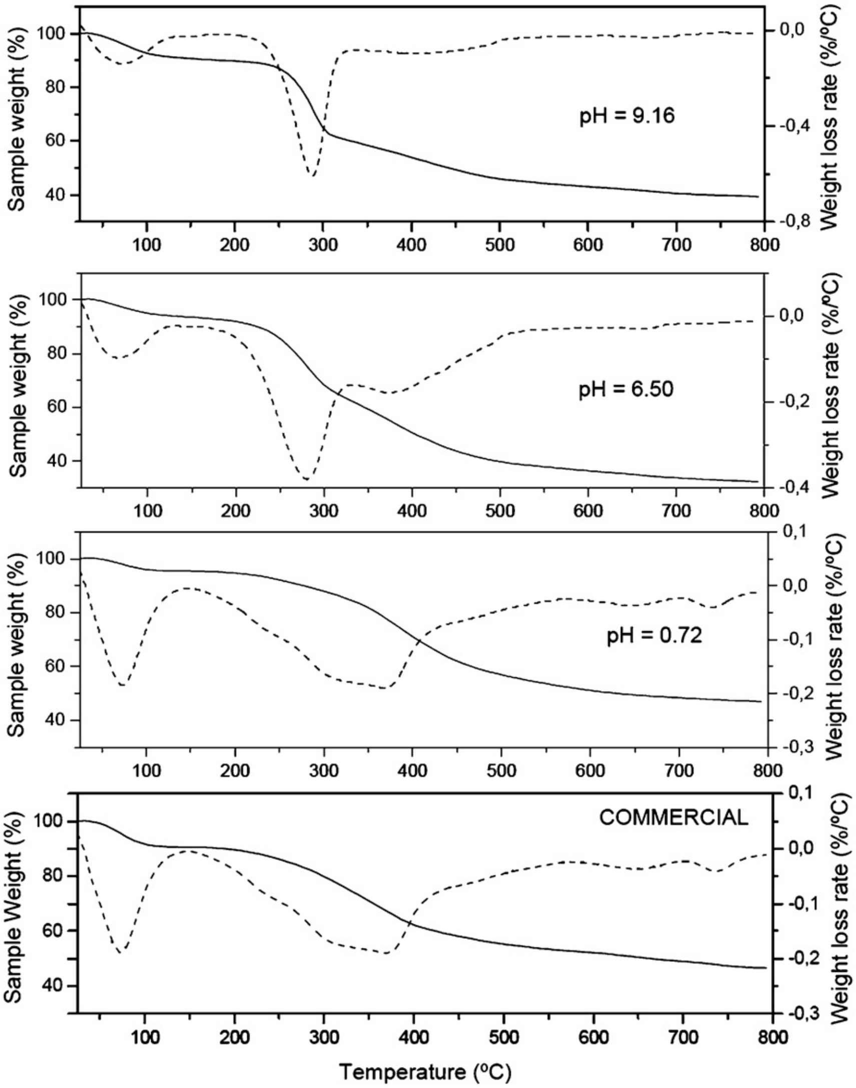

Fig. 3. Thermogravimetric analysis of the samples obtained by selective precipitation.

ceramic material, tubular and multichannel type, with an external and hydraulic diameter of 10 and 2 mm, respectively, and a surface of 110 cm^2. The black liquor solution was filtered successively by increasing the membrane cut-off and the permeates were collected. H_2SO_4 (95–98% purity, Panreac) was added to the permeates until reaching a pH around 2 to precipitate the lignin. The obtained mixture was vacuum filtered with a glass fibre filter of 1.2 μm (FVC-110, Albet), washed twice with acidified water to drag possible impurities (hemicelluloses, silicates, rest of reagents, etc.) and finally, vacuum dried at a temperature of 60 °C.

Selective precipitation was the second process carried out to produce specific lignins. To obtain different fractions at different pH by selective precipitation, a 20 mL sample of the black liquor was treated with different amounts of concentrated sulphuric acid (98%, w/w). Then, the sample was centrifuged and the precipitated lignin was filtrated and washed with acidified water and vacuum dried at 50 °C until constant weight. The remaining liquid fraction was kept at $-27\,^{\circ}C$ after what was centrifuged again. The lignin thus precipitated was treated by the same procedure explained above. The total precipitated lignin mass was considered as the sum of the mass recovered after the acid addition and the mass recovered after cooling [17].

2.3. *Lignin characterization*

The Fourier Transform Infrared Spectroscopy (FTIR) study was developed in a Nicolet spectrometer of direct transmittance. The region between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1} and 20 scans were recorded. Each sample was prepared according to the potassium bromide technique.

To study the thermal characteristics of the different fractions differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used. The differential scanning calorimetry (DSC) analysis was carried out in a thermal analyzer DSC 821 of Mettler Toledo, making dynamic scans of temperature from 30 to 250 °C with a constant heating rate of 10 °C/min. The tests were made under nitrogen atmosphere. The thermogravimetric analysis (TGA) was carried out in a TGA/SDTA RSI analyzer of Mettler Toledo. The samples were heated from 25 up to 800 °C at 10 °C/min. A constant nitrogen flow has been used, which provided an inert atmosphere during the pyrolysis.

Size exclusion chromatography (SEC) was used to determine lignin number-average ($\bar{M}_n$), weight-average ($\bar{M}_w$) molecular weight and polydispersity ($\bar{M}_w/\bar{M}_n$) in a Perkin-Elmer instrument equipped with an interface (PE Series 900). Three Waters Styragel columns (HR 1, HR 2 and HR 3) ranging from 100 to 5×10^5 and a

Table 1
FTIR structure correspondence for the lignin fractions obtained by both fractionation methods.

Wavelength (cm^{-1})	Structure correspondence
3450–3400	O–H stretching
2940–2820	C–H stretching in methyl and methylene groups
1715–1700	Carbonyl stretching in unconjugated ketones and conjugated carboxylic groups
1675–1660	Carbonyl stretching in conjugated ketone groups
1605–1425	Aromatic skeletal vibrations
1330–1235	Syringyl ring breathing with C–O stretching
1275–1230	Guaiacyl ring breathing with C–O stretching
1100 approx.	C–H inplane deformation in guaiacyl and syringyl
835	Aromatic C–H out-of-plane deformation

refractive index detector (Series 200) were employed, with a flow rate of 1 mL/min. Lignin samples were acetylated before the analysis in order to enhance their solubility in THF [18]. Calibration was made using polystyrene standards.

^{1}H NMR analysis was carried out to know the chemical structure of the different fractions of lignin through spectrometry using a Bruker 500 MHz spectrometer at a frequency of 250 MHz with an acquisition time of 0.011 s at 25 °C. DMSO-d6 has been used as solvent. Lignin samples were acetylated before the analysis in order to enhance their solubility [18].

3. Results and discussion

The FTIR spectra of both processes were obtained and are shown in Figs. 1a and 2a. In concordance with previous studies [19], typical lignin peaks were identified and, consequently, the structure correspondences are shown in Table 1.

In the magnified region (Fig. 2b) of the fractions obtained by differential precipitation, bands at 1030–620 cm^{-1} were observed, and attributed to hemicelluloses and silicates contribution. These peaks were not as intense as in the magnified region of the fractions obtained by ultrafiltration spectra (Fig. 1b) which suggested that fractions obtained by acid precipitation were more contaminated than ultrafiltrated fractions. Suspended lignin drags hemicelluloses and lignin–carbohydrate complex (LCC) when precipitating. This fact was more obvious when using selective precipitation as a fractionation process.

Differential scanning calorimetry (DSC) allows to determine the thermal effects associated with physical or/and chemical changes of a substance, which temperature increases or decreases at constant rate. Lignin glass transition temperature (T_g) is difficult to determine with reliability because of the strong electrostatic interactions and because it depends on diverse factors as the extraction process followed [8,19,20]. At the same time lignins are very much influenced by water presence. Fractions obtained by both fractionation processes presented a T_g between 100 and 110 °C. These results are in agreement with other authors' ones [18,21].

The thermogravimetric analysis is widely used to study how the organic polymers decompose. TG curves reveal the weight loss of substances in relation to the temperature of thermal degradation, while the first derivative of that curve (DTG) shows the corresponding rate of weight loss. Results corresponding to the different fractions obtained by selective precipitation are shown in Table 2 and Fig. 3. A peak representing weight loss can be observed around 90 °C, which corresponded to the absorbed water evaporation. The second peak, which appeared at relative low temperatures, was, in most of the cases, a wide peak. These observations suggested the presence of hemicellulose–lignin complexes in the selective precipitated fractions. Decomposition temperature of these products was found to be intermediate between hemicelluloses one (around 230 °C) and lignin, explaining the low DTG obtained value.

Table 2
Maximal mass loss rate temperature for the different precipitated fractions.

pH fraction	9.16	6.50	5.40	4.55	2.57	0.72
DTG (°C)	283.5	279.5	291.3	291.3	369.6	369.6

Table 3
Results of GPC analysis. Number-average ($\bar{M}_n$), weight-average ($\bar{M}_w$) molecular weight and polydispersity ($\bar{M}_w/\bar{M}_n$) of the different fractions obtained by ultrafiltration and by selective precipitation.

Fraction	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Ultrafiltration			
Rough	1879	5654	3.01
>15 kDa	2032	6300	3.10
15 kDa	1891	3544	1.87
10 kDa	946	2022	2.14
5 kDa	940	1806	1.92
Selective precipitation			
pH = 0.72	3501	2908	1.20
pH = 2.57	2432	1311	1.86
pH = 5.40	2120	1142	1.62
pH = 6.50	1990	1430	1.40
pH = 9.16	2160	1550	1.41

Obtained TG curves for ultrafiltrated fractions are shown in Fig. 4. The thermogravimetric analysis of ultrafiltrated fractions showed that the first weight loss (DTG$_{\max}$ = 75 °C) was due to the moisture of the sample, subsequently the second peak (DTG$_{\max}$ = 235 °C) could be ascribed to the degradation of polysaccharide (hemicelluloses) contamination [21] due to the extraction process followed. The maximum DTG at 380 °C belonged to lignin degradation. The thermal degradation of lignin takes place from 185 to 500 °C, being this fact associated to the complex structure of lignin with phenolic hydroxyl, carbonyl groups and benzylic hydroxyl, which are connected by straight links [22].

Gel permeation chromatography was carried out to obtain the molecular weights distribution of the different acetylated fractions of lignin fractionated by ultrafiltration and selective precipitation. Number-average ($\bar{M}_n$), weight-average ($\bar{M}_w$) molecular weight and polydispersity ($\bar{M}_w/\bar{M}_n$) are shown in Table 3. Results showed that the fractionating of lignin was achieved using both methods. For the ultrafiltration fractionation process, there was a clear trend of the decrease of the weight-average molecular weight as the cut-off used to obtain the fractions was smaller. As a consequence, the polydispersity also decreased with the pore size. By differential precipitation, all the obtained fractions presented low polydispersity. When the pH was strongly acidic the highest weight-average molecular weight was reached. Ultrafiltration yielded fractions with more differentiated weight-average molecular weight than selective precipitation. Both fractionating techniques produced fractions with low polydispersity. The relatively low polydispersity indicated a high fraction of low molecular weight (LMW) in the different fractions. The low polydispersity was connected to the possibility of forming C–C bonds between units; this type of bonds is related to the structures involving C5 in the aromatic ring, guaiacyl-type unit and syringyl-type unit. Guaiacyl-type units are able to form this kind of bonds, so raw materials with high content of guaiacyl-type units are expected to show high fractions of high molecular weight (HMW). However, this is not possible for syringyl-type units as they have both C3 and C5 positions substituted by methoxy groups, so raw materials with high content of syringyl-type units are expected to show high fractions of low molecular weight (LMW) [23]. Other authors have suggested that lignins with high fraction of LMW are adequate to be used as an extender or as component of phenol–formaldehyde resins because of their high reactivity, comparing with lignins with high percentages of high molecular weight molecules [7,24,25].

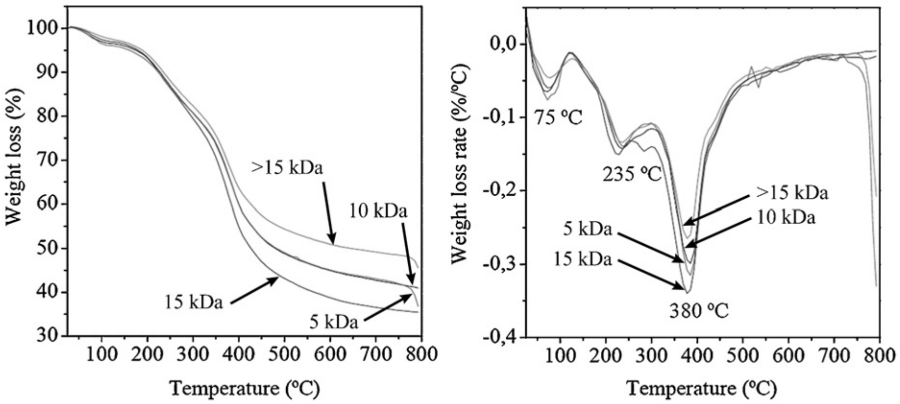

Fig. 4. Thermogravimetric analysis of the samples obtained by ultrafiltration.

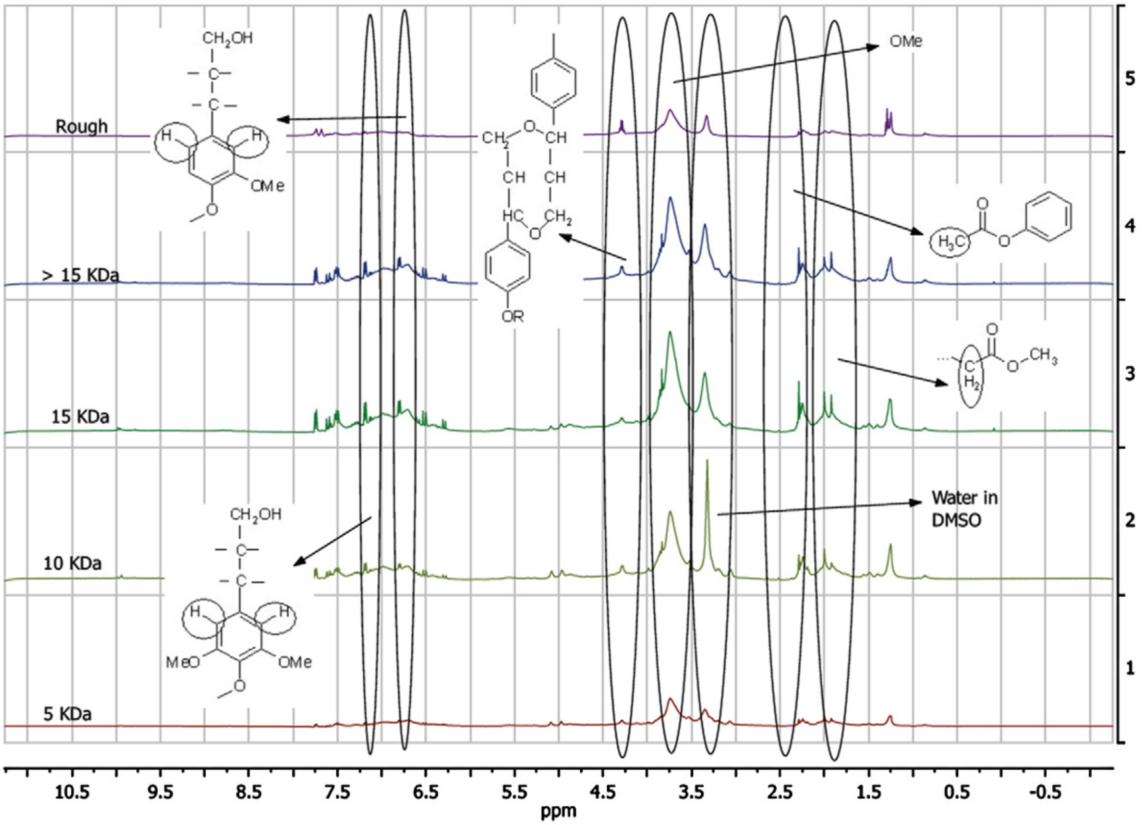

Fig. 5. ^{1}H NMR spectra of the fractions obtained by ultrafiltration.

The ^{1}H NMR experiment was carried out to obtain the chemical structure of the different fractions. The main identified structures are in accordance with other authors data (Figs. 5 and 6) [26,27]. Between 2.0 and 0.8 ppm, the signal was associated with protons in aliphatic groups such as in the side chains of lignin or in acetyl groups. Ultrafiltration ^{1}H NMR spectra showed peaks that did not exist in acid precipitation spectra because ultrafiltration technology slightly depolymerised lignin. Structure correspondence is shown in Table 4. As previously observed in the other analysis lignin obtained by selective precipitation was more contaminated than the one obtained by using membrane technology. That is the reason why the ^{1}H NMR spectra of both fractionation processes have different shape. The main structures were present in both cases. Between 2.3 and 0.8 ppm, the signal was due to protons in aliphatic and aromatic acetates. The signals around 4.0 ppm was due to protons in ether structures. The area from 6.0 to 7.5 ppm was related to structures with aromatic rings (syringyl and guaiacyl groups).

Table 4
Structure correspondence for ^{1}H NMR.

δH (ppm)	Structure
1.90	Protons of aliphatic acetates
2.25	Protons of aromatic acetates
3.60	OCH_3
4.15	$\gamma(\beta-\beta)$
6.70	S2,6
7.20	G2,6

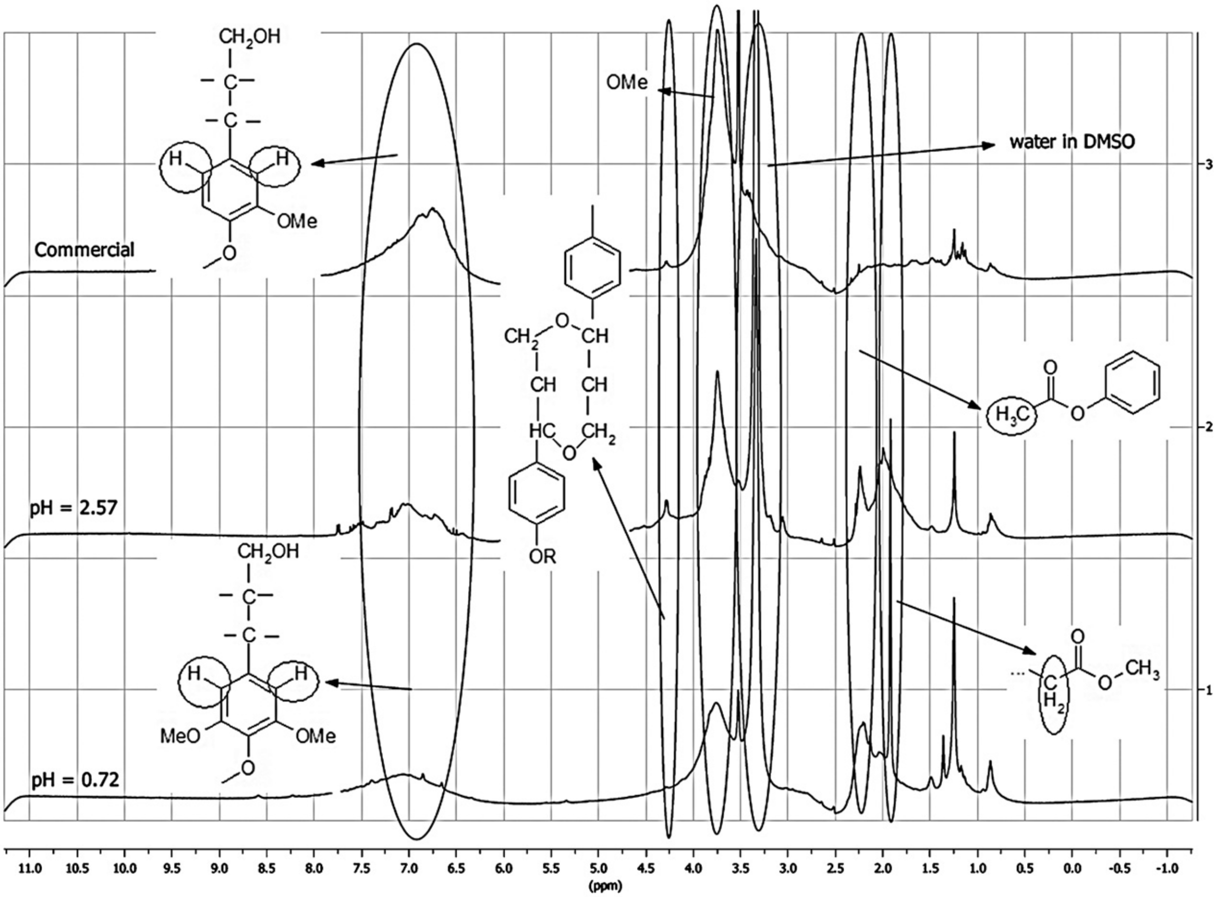

Fig. 6. ^{1}H NMR spectra of the fractions obtained by selective precipitation.

4. Conclusions

Selective precipitation and ultrafiltration were found to be effective techniques to fractionate and to extract lignin from the black liquor.

Ultrafiltration showed better results as the lignin obtained was less contaminated with hemicelluloses as it was confirmed by the thermal analysis and FTIR spectra. Selecting the right cut-off of the membrane, the weight-average molecular weight could be controlled. Also slightly depolymerisation was reached. Differential precipitation was an easier and simpler technique and less energy consuming than ultrafiltration, however the obtained lignin had lower quality since its weight-average molecular weight cannot be controlled easily and because the presence of lignin–carbohydrate complex (LCC) was higher. Thermal analysis and FTIR spectra confirmed the contamination and it was proved that LCC contamination affects degradation temperature. ^{1}H NMR spectra of the obtained fractions by the different fractionation processes used, agreed with the fact that lignin obtained by selective precipitation was more contaminated than the ultrafiltrated lignin.

Lignin fractionated by selective precipitation had higher molecular weight and was more contaminated; this type of lignin could be considered for usage as dispersant or as chelating agent. Ultrafiltrated lignin fractions (5 and 10 kDa fractions) could be used as adhesives where low molecular weight and purity are important factors to take into account. Depending on the future use of the lignin, the right technique to obtain the fractions has to be chosen.

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