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Miscanthus sinensis fractionation by different reagents

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ABSTRACT

Miscanthus sinensis L. was fractionated by different reagents (ethanol, soda and soda–ethanol) in order to obtain cellulose, hemicelluloses and lignin. Characterization of original *M. sinensis* fibres (66.6% holocellulose, 36.1% α-cellulose, and 15.5% lignin) was done and compared with other biomass species chemical composition (alternative raw materials, agriculture residues, coniferous and leafy plants). Obtained solid fractions were chemically characterized and compared with solid fractions from other biomass products (palm oil empty fruit bunches (EFB) and rice straw) generated by similar fractionation processes (soda and organosolv). Soda process produced the solid fraction with the highest content in α-cellulose and lowest content in lignin revealing a strong fractionation effect. On the contrary, soda–ethanol process was found to present low fractionation capability. Obtained cellulose samples were characterized by FTIR to complete the chemical structure analysis. Lignin samples isolated from the liquid fractions were submitted to FTIR, ^{1}H NMR, GPC, DSC and TGA in order to suggest suitable applications for the products based on their properties.

1. Introduction

The use of renewable feedstock as an alternative to fossil sources to produce both products and energy is an economic and environmental objective in the scientific and political agenda of the last years. There are different non-fossil sources and technologies to generate energy (wind, sun, water, biomass, and nuclear), but chemicals and goods can only be obtained from biomass [1].

Among the different types of available biomass, the use of agricultural crops, non-woody materials, annual plants or grasses have roused special interest as they represent an inexpensive and abundant feedstock to work with, particularly in countries with scarcity of forest resources [2–5].

The fractionation of biomass into its crystalline part (cellulose) and the non-crystalline carbohydrates (hemicelluloses) and lignin have been already carried out by the pulp and paper industry. However, the main objective of these processes was to isolate cellulose-rich solid fractions (about half of the starting raw material) without taking care of the rest [6]. An efficient fractionation performance requires selectivity in the separation of constitutive components, accessibility to each of them after fractionation, high yields, good quality of obtained products and process economic viability [7,8]. The conversion of cellulose, lignin and hemicelluloses into high value products is necessary to fulfil the above-mentioned requirements.

Several reagents have been used to fractionate lignocellulosic biomass. Soda is one of the most relevant and widely solvents used for delignification of non-woody materials [9]. Organic alcohols and acids have been used in the pulp and paper industry (organosolv technology) and they are gaining new relevance for biomass biorefining as they allow the obtaining of multiple co-products (cellulose, lignin, hemicelluloses and extractive components of the lignocellulosic biomass) with versatile uses [10,11].

Cellulose, a linear polymer formed by 1,4-β-anhydroglucopyranose units, is the major constituent of all plant materials and constitutes the most abundant, renewable polymer resource available today worldwide [12,13]. Cellulose constitutes a vast potential feedstock for a number of industries [14] and it presents many interesting applications as paper and board production, as anti-cake agent, emulsifier, stabilizer, dispersing agent, thickener or gelling agent, although its main industrial use is to produce water-soluble derivatives with pre-designed and wide-ranging properties dependent on involved groups and the degree of derivatization [15,16].

Lignin is a heterogeneous and highly crosslinked macromolecule built up by phenyl propanoid units linked together to a three-dimensional network by different ether and carbon–carbon linkages [17]. The major chemical functional groups presented by lignin are aromatic rings, phenolic and aliphatic alcohol groups and methoxy groups in various amounts, whose contents depend on the botanic origin and the applied extraction processes [18]. Lignin is the most abundant source of aromatic compounds in nature and can substitute petro-based chemical compounds in polymer formula-

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Table 1
Black liquor characterization.

Reagent	pH	Density (g/mL)	TDS[a] (%)	MI[b] (%)	MO[c] (%)	Lignin (%)
NaOH	13.02	1.09	10.02	7.05	2.97	2.21
NaOH–EtOH	12.83	1.07	9.17	7.33	1.84	3.03
EtOH	4.63	0.92	3.40	0.20	3.20	1.20

[a] TDS: total dissolved solids.
[b] MI: inorganic matter.
[c] MO: organic matter.

tion [19,20], as adhesive [21], dispersant agent [22], emulsifier [23], chelating agent [24] or adsorbent [25].

In this work, *Miscanthus sinensis*, an alternative non-wood raw material, was fractionated by different reagents (soda, ethanol and soda–ethanol) to obtain cellulose, hemicelluloses and lignin as valuable products.

M. sinensis, or elephant grass, belongs to the Monocotyledoneae group and to the Gramineae family and presents some interesting characteristics to be considered for several applications: a C4 metabolism, which allows it to photosynthesize and use water and nutrients with a great efficiency, easy adaptation, high resistance to low temperatures, pests and diseases and high production yields [26]. Apart from the utilisation of *Miscanthus* as fuel (combined heat and power generation facilities or biogas plants), non-energy use of the fibres is possible. The fibres can be used to replace peat, to produce composites or insulating materials. The latter alternative could enter the market of natural insulations which have established themselves besides conventional products from mineral wool or polystyrene (PS) [27].

Original raw material fibres as well as the solid and liquid fractions obtained from the fractionation processes were characterized. Lignins obtained from the liquid fractions were also analyzed by different techniques (FTIR, NMR, GPC, TGA and DSC) in order to suggest suitable applications for the products based on their properties.

2. Materials and methods

2.1. Conditioning of the raw material

M. sinensis used in the experiments was kindly supplied by the company Straw Pulping Engineering (SPE), S.L. (Zaragoza, Spain). *Miscanthus* was acconditioned up to constant moisture; bark and core were ground in a hammer mill and sieved to obtain the 4–6 cm size fraction, free of impurities such as stones, sand and dust.

2.2. Characterization of the raw material and obtained solid fractions

Characterization of *M. sinensis* fibres and the obtained solid fractions were done according to standard methods [28] and bibliographic procedures [29,30]. Moisture content was determined after drying the samples at 105 °C for 24 h (TAPPI T264 cm-97); holocellulose by the Wise et al. method [29]; α-cellulose and hemicellulose contents by the Rowell method [30]; ashes content (TAPPI T211 om-93), hot water soluble matter (TAPPI 207 om-93), aqueous NaOH soluble matter (1%) (TAPPI T212 om-98), ethanol–benzene extractives (TAPPI T204 cm-97) and lignin (TAPPI T222 om-98). All determinations were performed three times and the mean value with standard deviation was reported.

2.3. Fractionation processes

The raw material was treated with the reagents (soda, ethanol and soda–ethanol) in a 25 L stirred, equipped with a cooling system and heating by an outer jacket controlled by an automatic control system. Ethanol process was carried out in a 4 L stirred reactor, equipped with temperature control system and data acquisition.

Experimental conditions of soda process were 7.5% (w/w) NaOH solution, in a solid:liquid ratio of 1:20, at 90 °C for 90 min. Ethanol process was performed using 60% (v/v) ethanol–water solution, in a solid:liquid ratio of 1:10, at 180 °C for 90 min. Finally, soda–ethanol process included 7.5% (w/w) NaOH and 60% (v/v) as reagents, in a solid:liquid ratio of 1:20, at 90 °C for 90 min.

After the reaction time, the solid fraction was separated from the liquid one by filtration and washed to remove residual liquor.

2.4. Liquid fraction characterization

The main physico-chemical properties of obtained liquid fraction were determined according to standard methods (Table 1): pH was measured with a digital SELECTA pH-meter “pH-2005”. Density was determined measuring the weight of the black liquor in a known volume previously weighed and moisture free. Total dissolved solids (TDS) were measured after keeping a weighed sample at 100 °C until constant weight. Inorganic matter was determined after combustion of the sample at 525 °C (TAPPI T211 om-93). Organic matter was defined as the difference between total dissolved solids and inorganic matter. Lignin content was balance weighted after precipitation from the liquid fraction (see Section 2.5).

2.5. Lignin recovery from the liquid fraction

Obtained liquid fractions were treated to precipitate the dissolved lignin. Ethanol liquid fraction was mixed with two volumes of water and the pH of the solution was lowered to 2 by sulphuric acid (72%, w/w) addition [31]. After that, precipitated lignin was separated by filtration, washed with acidified water and then vacuum dried at 50 °C until constant weight. Soda–ethanol and soda liquid fractions were just acidified until pH 2 with sulphuric acid (72%, w/w) to precipitate the lignin content [31].

Finally, lignin samples were characterized by different techniques (FTIR, DSC, TGA, GPC and ^{1}H RMN).

2.6. Cellulose obtaining from solid fractions

Cellulose was extracted from obtained solid fractions by the Rowell method [30] and samples were characterized by FTIR.

2.7. Instrumental methods

Fourier transform infrared spectroscopy (FTIR) spectra were obtained in a PerkinElmer 16PC instrument by direct transmittance using KBr pellet technique.

^{1}H NMR spectrometry was carried out after subjecting samples to acetylation in order to enhance their solubility in dimethyl sulphoxide (DMSO), used in this technique as solvent [32]. The chemical structure of acetylated samples was studied through ^{1}H NMR spectrometry using a Bruker 500 MHz spectrometer at a fre-

Table 2
Chemical properties of *Miscanthus sinensis*, EFB and rice straw solid fractions.

	Solid fraction type								
	Soda			Soda–ethanol	Ethanol	Ethyleneglycol		Diethyleneglycol	
Raw material	*Miscanthus*	EFB[a]	Rice straw[a]	*Miscanthus*	*Miscanthus*	EFB[a]	Rice straw[a]	EFB[a]	Rice straw[a]
Hot water solubles	14.4	3.8	5.1	4.2	6.3	2.5	3.6	2.8	4.7
1% soda solubles	14.0	32	47	45.5	35	26	22	27	19
Ethanol–benzene extractables	2.4	4.3	3.2	1.85	4.4	7.1	8.3	10	12
Ash	8.7	2.3	6.7	5.1	4.04	1.8	13	1.9	13
Holocellulose	75.3	82	85	61.6	72.3	66	69	68	70
α-Cellulose	58.5	67	75	58.2	54.9	62	62	62	64
Hemicellulose	16.8	15	10	3.4	17.4	4	7	6	6
Lignin	12.5	18	17	16.7	10.8	19	15	17	14

[a] Ref. [33].

quency of 250 MHz with an acquisition time of 0.011 s at 25 °C. DMSO-d_6 has been used as solvent.

Gel permeation chromatography (GPC) was used to determinate samples molecular weight (M_w). Acetylated samples were examined through tetrahydrofurane (THF) eluted GPC technique, using a PerkinElmer 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 refractive index detector (Series 200) were employed, with a flow rate of 1 mL/min. Calibration was made using polystyrene standards.

Glass transition temperature (T_g) of samples was determined using a Mettler DSC20 differential scanning calorimeter linked to a TC 15 TA processor and medium pressure pans. The scan was run at 10 °C/min under a nitrogen flow rate of 10 mL/min. T_g was defined as the mid-point of the temperature range at which the change in heat capacity occurred.

The thermal stability of the samples was studied in terms of thermogravimetric analysis (TGA). A dynamic scan from 30 to 800 °C at 10 °C/min was done under helium atmosphere employing a TGA-92 thermobalance from Setaram.

3. Results and discussion

3.1. Chemical characterization of M. sinensis

Table S1 (see the Supporting Information) shows the results of chemical analysis of *M. sinensis* and other alternative raw materials, agricultural residues, coniferous and leafy woods from the literature. A comparison of these results revealed the following:

- *M. sinensis* water soluble content was higher than other alternative raw materials studied and also higher than pine and eucalyptus wood contents. On the contrary, was lower than studied agricultural residues percentages with the exception of olive prunings, sugarcane bagasse and cotton stalks contents and very similar to wheat straw one. Hot water percentage is related with the content in soluble salts, starch, proteins, gums, tannins, etc.
- Hot alkaline solutions dissolve low molecular weight carbohydrates, mainly hemicellulose and degraded cellulose. The content in 1% NaOH soluble of *M. sinensis* was higher than contents found in pine and eucalyptus wood and other alternative raw materials but Phragmites presented similar values. Furthermore, obtained content was lower than those of the agricultural residues except for olive prunings, sugarcane baggase and cotton stalks.
- Ethanol–benzene extractions are used to remove waxes, fats, some resins and some glue fractions in the wood. The content in ethanol–benzene extractables of *M. sinensis* was higher than those of pine, eucalyptus wood, studied alternative raw materials (but similar to *Arundo donax*) and agricultural residues (except for olive prunings, that presented lower content and similar to sorghum stalks one).
- Ash content in raw material is composed of silicates and mineral components (Na, Fe, Mn, K, etc.). High ashes percentages could cause problems during recovery of products from the liquid fraction. *M. sinensis* ash content was higher than Tagasaste, *Chamaecytisus*, pine and eucalyptus wood ones; it was lower than those of studied agricultural residues except for olive prunings, sugarcane bagasse, vine shoots and cotton stalks.
- Holocellulose is the moiety of cellulose and hemicellulose in the fibres. The holocellulose content of *M. sinensis* was lower than those of pine and eucalyptus wood, studied alternative raw materials, except for Phragmites and *Prosopis* and agricultural residues except for olive prunings, sorghum stalks and very similar to sunflower stalks contents.
- The α-cellulose content in *M. sinensis* was lower than those of alternative raw materials and very similar to *Prosopis*, lower than those of agricultural residues except for olive prunings and than those of pine and eucalyptus wood.
- The lignin content in *M. sinensis* was lower than those of pine and eucalyptus wood, studied alternative raw materials and agricultural residues with the exception of sunflowers stalks contents and very similar to sorghum stalks percentages.

3.2. Solid fraction chemical composition

Table 2 shows the values of chemical composition of the solid fractions obtained from the applied fractionation processes. Chemical composition of EFB and rice straw solid fractions obtained with soda and organosolv processes was also included for comparison.

Soda solid fraction of *M. sinensis* presented medium–high percentages of holocellulose, α-cellulose and low lignin content in comparison with other soda solid fractions (EFB and rice straw). Holocellulose and α-cellulose percentages were higher than those obtained by ethanol and soda–ethanol processes and lignin content was lower, revealing the stronger effect of this treatment on the raw fibres and suggesting its suitability for cellulose derivatives production. Nevertheless, higher ash contents were found as well in soda solid fractions, which could cause problems during recovery of the products dissolved in the liquid stream. On the other hand, *M. sinensis* ethanol (organosolv) solid fraction characterization showed intermediate percentages of holocellulose, α-cellulose and lignin while soda–ethanol process showed the lowest percentages of holocellulose and hemicellulose and the highest percentage of lignin. The comparison with EFB and rice straw organosolv (ethyleneglycol and diethyleneglycol) solid fractions revealed higher holocellulose content in *M. sinensis* fraction than in EFB and rice straw ones. Furthermore, *M. sinensis* ash content was lower than rice straw one but higher than EFB percentage.

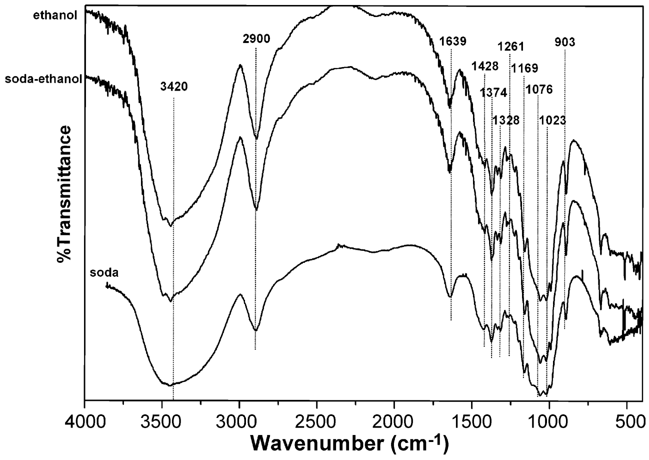

Fig. 1. FTIR spectra of celluloses from soda, soda–ethanol and ethanol solid fractions.

3.3. *Instrumental characterization*

3.3.1. *Raw material*

FTIR absorption spectra of *M. sinensis* fibres, lignin and cellulose were recorded in the 4000–400 cm^{-1} region. As shown in Fig. S1 (see the Supporting Information), spectra of fibres could be considered as the sum of lignin and cellulose spectra. Observed band around 3400 cm^{-1} is characteristic of the OH vibration stress. Bands at 2800–2900 cm^{-1} were attributed to methyl and methylene groups vibration stress.

3.3.2. *Cellulose*

FTIR spectra of cellulose extracted from the different solid fractions (ethanol, soda and soda–ethanol) were recorded in the 4000–400 cm^{-1} region (Fig. 1). The absorption band at 3420 cm^{-1} was associated with stretching of C–H groups and the signal at 2910 cm^{-1} to C–H stretching. The band at 1639 cm^{-1} corresponded to the bending mode of the absorbed water. Signal at 1428 cm^{-1} could be attributed to CH_2 bending and this at 1374 cm^{-1} to OH bending. The absorbance at 1328 cm^{-1} could be related to C–C and C–O skeletal vibrations. Band at 1261 cm^{-1} is indicative of OH in-plane bending cellulose. The absorption band at 1169 cm^{-1} was associated with C–O antisymmetric bridge stretching. The C–O–C pyranose ring skeletal vibration occurs in the region 1076–1023 cm^{-1}. The peak at 903 cm^{-1} could be originated from β-glycosidic linkages between glucose units in cellulose [14]. All these bands were less intense in cellulose extracted from soda solid fraction and presented similar intensity in cellulose from ethanol and soda–ethanol solid fractions.

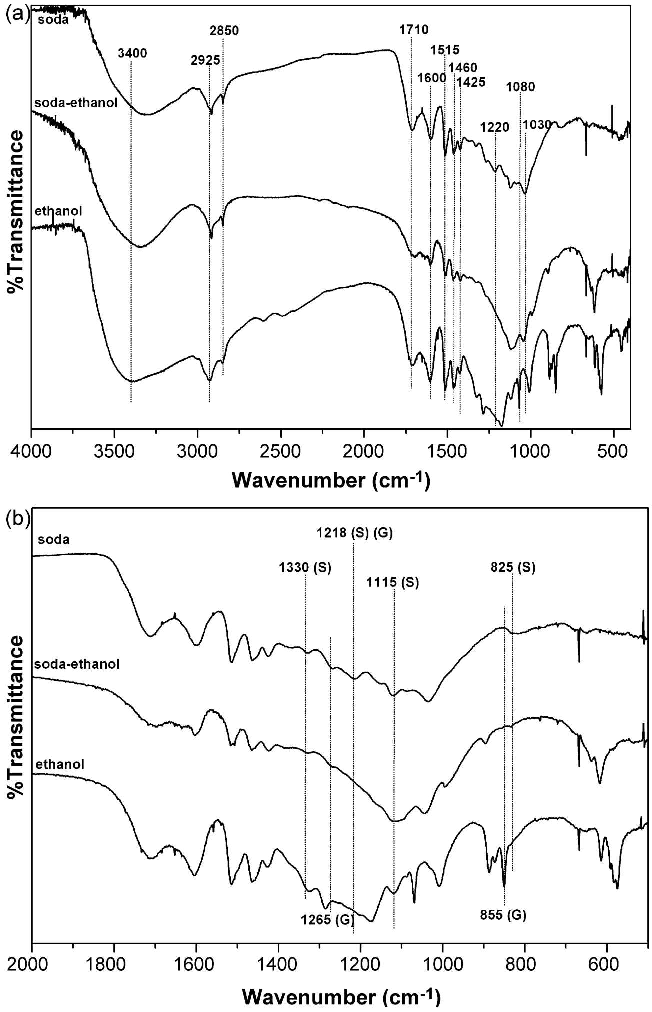

Fig. 2. FTIR spectra of *Miscanthus sinensis* lignin recovered from the black liquor (soda, soda–ethanol and ethanol) (a) 4000–400 cm^{-1} and (b) magnification 2000–500 cm^{-1}.

3.3.3. *Lignin*

FTIR absorption spectra of lignin isolated from the liquid fractions (ethanol, soda and soda–ethanol) were recorded in the 4000–400 cm^{-1} region (Fig. 2a). A magnification of 2000–500 cm^{-1} region is presented in Fig. 2b. A wide absorption band focused at 3400 cm^{-1} and the signal at 1030 cm^{-1} were assigned to aromatic and aliphatic OH groups. Bands at 2960, 2925 and 1460 cm^{-1} were related with C–H vibration of CH_2 and CH_3 groups. Bands in range 1705–1715 cm^{-1} could be attributed to non-conjugated carbonyl groups. Lignin samples showed bands at 1600, 1515 and 1425 cm^{-1} associated with aromatic ring vibrations of the phenylpropane skeleton. Bands at 1220 and 1080 cm^{-1} were identified with ether bridges vibration. In addition to these general bands, the spectrum also showed other signals attributed to syringyl (S) and guaiacyl (G) groups: syringil ring breathing with C–O stretching at 1330 cm^{-1}, syringil-type aromatic C–H in-plane deformations at 1115 cm^{-1}, syringil and guaiacyl ring breathing with C–O stretching at 1218 cm^{-1}, typical syringil band at 825 cm^{-1} and guaiacyl units at 1265 and 855 cm^{-1}. Results were in good agreement with reported data in previous studies [19]. The delignification method used for the isolation of lignin highly influenced the final structure. Soda fractionation process of non-woody materials produces the cleavage of aryl ether linkages through the formation of small quantities of phenolic hydroxyls [34]. This could be seen in soda spectrum, where there was practically no vibration at 1365 cm^{-1} and the signal of 1030 cm^{-1}, attributed to primary OH (among others), was less intense than in the ethanol and soda–ethanol lignin. In the organosolv method, the acid acetic released from the hemicelluloses is the chemical fractionation agent. This method promotes the acid hydrolysis of lignin generating new carbonyl groups (1715 cm^{-1}) in its structure [19].

Glass transition temperature (T_g) was determined by DSC scans after extensively drying the sample (60 °C, 24 h, vacuum-oven dried) in order to release all the moisture content. Different underivatized lignin preparations are reported to have T_g values between 90 and 180 °C [35,36], corresponding the higher values usually to softwood kraft lignins and lower ones to organosolv lignins [36]. Table 3 shows good agreement with these T_g ranges.

Thermal composition of lignins was determined by thermogravimetric analysis (TGA) under nitrogen atmosphere. DTG (weight loss rate) and TG (weight loss of lignins in relation to

Table 3
Values of glass transition temperature, maximal loss rate temperature and solid residue at 800 °C for all lignin preparations.

Lignin	T_g (°C)	DTG$_{max}$ (°C)	Residue (%)
NaOH	126	378	42
NaOH–EtOH	143	385	36
EtOH	106	200	35

the temperature of thermal degradation) curves are presented in Fig. 3 and results in Table 3. The results obtained by thermal analysis showed that that values reached in ethanol lignin could be influenced principally by the presence of hemicelluloses, being the melting temperature 200 °C. On the contrary, the higher values obtained in soda and soda–ethanol lignin (378 °C, 385 °C) were related to pyrolytic degradation in this region (350–425 °C) that involved fragmentation of inter-unit linkages, releasing monomeric phenols into the vapour phase. Obtained values were in agreement with those found in bibliography [36–38].

Molecular weight of acetylated samples was analysed through THF-eluted GPC. Data and chromatograms obtained for lignin preparations are shown in Table 4 and Fig. 4 respectively. Ethanol lignin was found to present the lowest molecular weight, followed by soda–ethanol lignin while soda lignin presented the highest value. Lignin molecular weight depends on the nature of the raw material and the method used for extraction. Structural units forming lignin, especially G and S ones, influences its molecular weight. S units cannot form C–C bonds between units in the ortho position of the aromatic ring, as they have both C3 and C5 positions substituted by methoxy groups. On the contrary, G units are able to form these linkages as they have C5 position free [39]. These C–C bonds are not cleaved during the wood fractionation due to their higher stability. For this reason, lignins mostly composed by G units are expected to show higher molecular weight than those presenting higher contents of S units [19,32]. As it was previously shown by FTIR, both groups were found in the composition of the studied samples but a low molecular weight suggests higher proportion of S units.

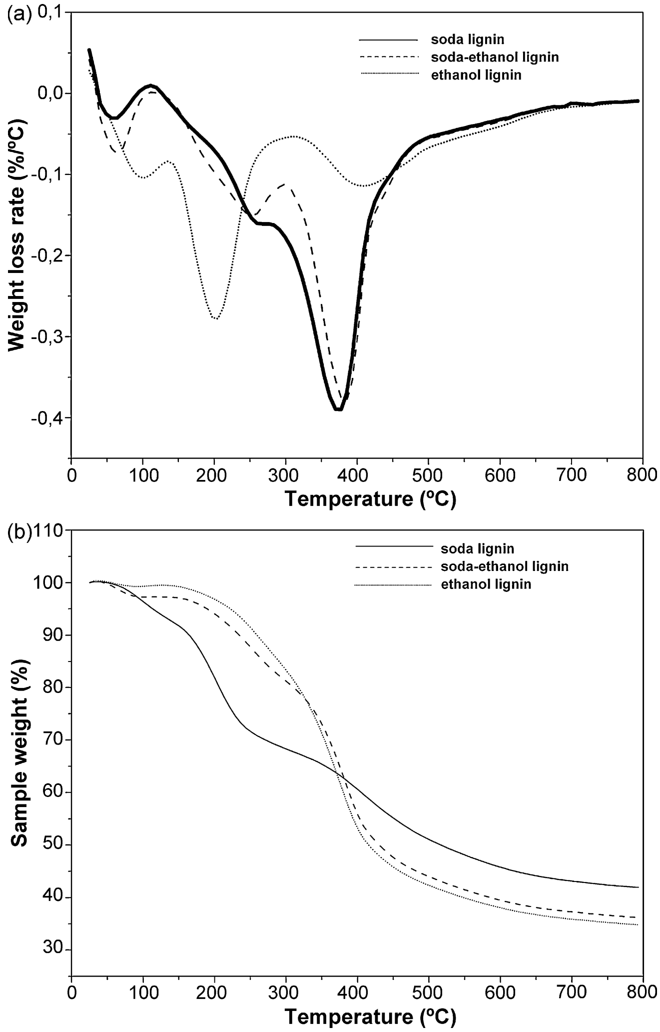

Fig. 3. (a) DTG and (b) TG curves of soda lignin, soda–ethanol lignin and ethanol lignin obtained from TGA analysis.

Table 4
Weight average ($\bar{M}_w$), number average ($\bar{M}_n$) and polydispersity ($\bar{M}_w/\bar{M}_n$) of acetylated lignins analysed by GPC.

Lignin	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
NaOH	5654	1879	3.0
NaOH–EtOH	1534	861	1.7
EtOH	1104	578	1.9

In relation with the extraction process, the severe conditions used during the soda treatment, caused the appearance of high molecular weight species ($\bar{M}_w = 5654$) due to repolymerisation reactions promoted during alkaline fractionation process. Under highly alkaline conditions some α-hydroxyl groups form quinone methide intermediates that react easily with other lignin fragments giving alkali-stable methylene linkages [19].

Soda–ethanol lignin presented a normal curve with a small fraction of low molecular weight oligomers. Ethanol and soda lignins presented a bimodal curve, indicating that there were two lignin fractions with different molecular weights. This shape has been previously reported for other organosolv lignin samples, but soda lignins usually presented curves with only a small fraction of low molecular weight oligomers [40,41].

The relatively low polydispersity found indicated the high fraction of low molecular weight lignin present in samples. Lignins with high fractions of low molecular weight have been reported to be adequate as an extender or as component of phenol-formaldehyde resins because of their high reactivity, in comparison with lignins with high percentages of high molecular weight molecules [40–43].

The chemical structure of acetylated samples was studied by ^{1}H NMR spectrometry. Fig. 5 shows ^{1}H NMR spectra of acetylated soda, soda–ethanol and ethanol lignin. As pointed out in

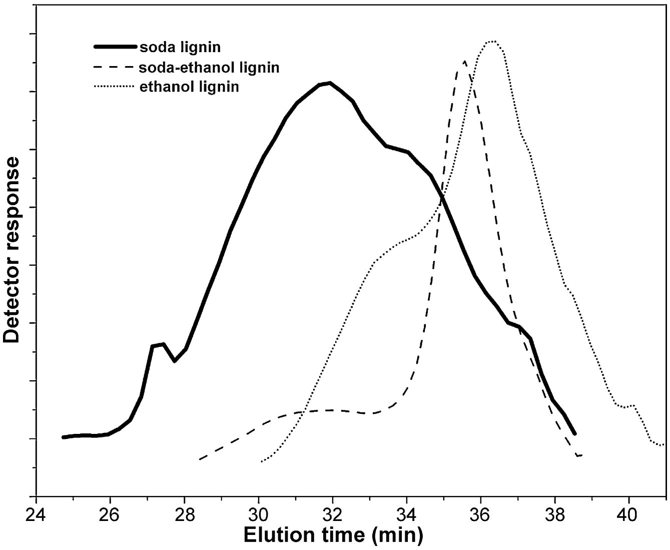

Fig. 4. GPC chromatograms of acetyled soda, soda–ethanol and ethanol lignins.

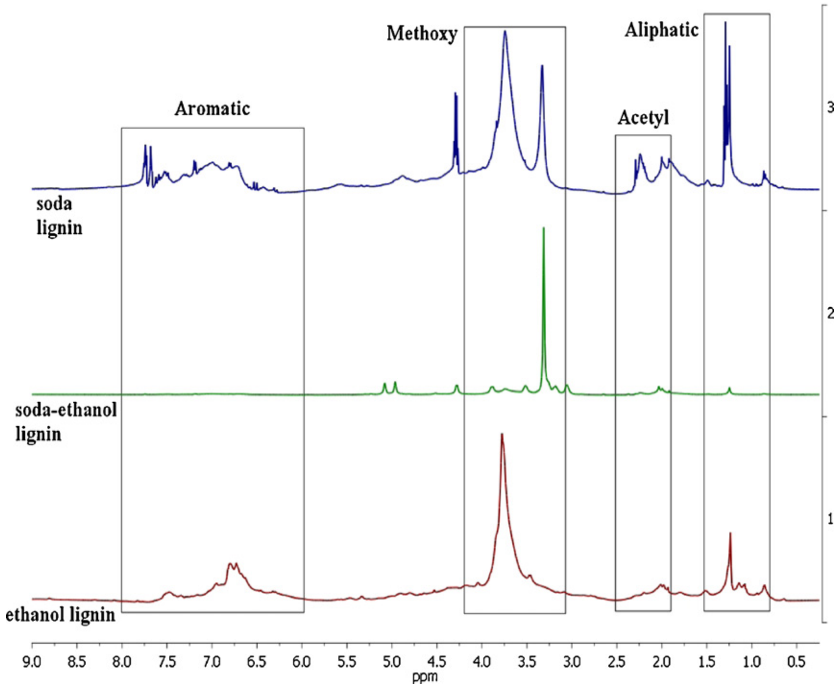

Fig. 5. ^{1}H NMR spectra of acetylated soda, soda–ethanol and ethanol lignins.

Table S2 (see the Supporting Information), the integral of all signals between 6.0 and 8.0 ppm could be attributed to aromatic protons in S and G units, while those between 0.8 and 1.5 ppm could be related to the aliphatic moiety. Methoxyl protons, closely related to G:S proportion, gave an intense signal centred at 3.74 ppm. Acetylation produced derivatives that displayed broad proton signals in regions with small interference with other hydrogen signals. In addition, aromatic and aliphatic acetyl groups were shifted differently (2.24 and 1.92 ppm, respectively) giving rise to separate peaks. Soda–ethanol lignin showed a spectrum with few signals and with low intensity, possibly due to a lower concentration of lignin structures.

4. Conclusions

M. sinensis chemical composition revealed medium α-cellulose and low lignin percentages that suggested its suitability as alternative source of these components for further valorisation. Applied fractionation processes (ethanol, soda and soda–ethanol) presented different yields and fractionation capabilities, being soda treatment the most effective one, followed by ethanol process and finding the lower separation capability for the soda–ethanol scheme. Obtained solid fractions presented high α-cellulose contents, specially the soda one, suggesting its suitability for cellulose derivatives production, as in membrane, paper, polymers and paints manufacturing. Ethanol process solid fraction presented acceptable α-cellulose contents and the lignin dissolved in the liquid fraction was easily extracted showing low molecular weights and suitable properties to be considered in several applications as low molecular weights compounds like vanillin, widely used in cosmetics, simple and hydroxylated aromatics, quinones, aldehydes, aliphatic acids and many others, for which the economic feasibility is being studied.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2009.09.032.

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