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Combined organosolv and ultrafiltration lignocellulosic biorefinery process

M. González Alriols, A. García, R. Llano-ponte, J. Labidi *,[1]

Chemical and Environmental Engineering Department, University of the Basque Country, Escuela Politécnica de San Sebastián, Plaza de Europa, 1, 20018, Donostia-San Sebastián, Spain

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ABSTRACT

Non-woody lignocellulosic feedstock (*Miscanthus sinensis* L.) was fractionated by a biorefinery process to obtain cellulose, different molecular weight lignin fractions and an hemicelluloses enriched liquor following economically and environmentally sustainable criteria. An integrated process composed by ethanol organosolv pre-treatment followed by a membrane ultrafiltration system was used to extract the different fractions. Products physico-chemical characterization (FTIR, GPC, ^{1}H NMR) was done to evaluate their potential possible industrial applications. Obtained experimental data were used to develop a simulation of the process using Aspen Plus software in order to establish mass and energy balances and optimize the process in terms of yield, solvent recovery and energy consumption. Finally, production costs of the obtained ultrafiltrated lignin were estimated resulting in 52 €/tonne of lignin for the studied process conditions.

1. Introduction

In the last decades, renewed interest has been put on biomass as an alternative to fossil fuels to produce products and energy. While the former may be produced from several alternative sources and technologies, wind, sun, water, biomass or nuclear energies, substances obtaining depends basically on biomass [1]. Nevertheless, in order to become an actual alternative to fossil fuels and petroleum derivate products, biorefinery processes must face the challenge of being competitive and cost-effective, which is highly dependent on raw materials costs. The 'Whole Crop Biorefinery', based on processing cereals or grain (maize), uses expensive feedstock with fluctuant prices; the 'Green Biorefinery' system, process green grass and immature cereal whether the 'Lignocellulose Feedstock Biorefinery' makes use of 'nature-dry' raw material such as wood, straw and forest or agricultural lignocellulosic residues. The latter group is predicted to have the highest success due to the abundance (estimated annual worldwide production of 10–50 billion dry tonnes, accounting for about half of the global biomass yield) and variety of available raw materials and the good position of the conversion products on the market [1,2].

Another clue point in the process profitability is the selection of the technology required to alter the structure of lignocellulosic biomass, where native cellulose is protected by lignin and hemicelluloses [3]. Several bioconversion schemes have been proposed, including enzymatic fractionating by cellulases or chemical hydrolysis (with hot water and dilute or concentrated acid), steam explosion, alkaline treatment and organosolv processes [4]. The latter group, which consists on using mixtures of water and organic alcohols or acids to fractionate the biomass, is well known in the pulp and paper industry. These processes allowed overcoming some of the main drawbacks of traditional pulping processes by using sulphur free delignifying agents, which could be recovered by distillation after the pulping process [5,6].

Ethanol organosolv process, already used biofuel production and in the pulp and paper industry as the Alcell® process [7], has gained new relevance for biomass biorefining (Lignol process). This technology has been successfully applied to fractionate softwoods [4] and hardwoods [8] allowing the obtaining of multiple co-products (cellulose, lignin, hemicelluloses and extractive components of the lignocellulosic biomass) with versatile uses.

Cellulose obtained from biomass as a solid fraction presents many interesting applications: paper and board production, anticake 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 [9]. Furthermore, hydrolytic enzymes can be used to convert the cellulose in lignocellulosic biomass to glucose for fermentation and ethanol production.

Lignin structure, an intricate combination of phenyl propanoid units linked by different ether and carbon–carbon linkages, is

* Corresponding author. Tel.: +34 943017166; fax: +34 943017140.
E-mail addresses: maria.gonzalez@ehu.es (M.G. Alriols), jalel.labidi@ehu.es (J. Labidi).
[1] Tel.: +34 943017178; fax: +34 943017140.

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highly dependent on its origin and the method used for its extraction [10]. Organosolv lignins present low molecular weight values and high solubility in most common solvents [11]. The high percentage of phenolic hydroxyl groups and oxidized groups present in their composition allow their use for polymer formulation and their chemical modification [12]. Hardwood Alcell lignins, extracted through acidic ethanolysis, have been successfully transformed into filament form suitable for carbon fibres without any chemical modification [13] and Alcell lignin/poly(vinyl chloride) composites have been reported to present higher mechanical properties than kraft or sodium lignosulphonate-based materials [14]. Within their ability to undergo chemical modification, organosolv lignins have been found to be an appropriate raw material for producing LMW compounds [15] 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 [16].

Furthermore, oligomers and monomers hydrolyzed from the hemicelluloses as well as the degraded hemicellulosic polymers are associated with specific properties and diverse applications, as films and coatings, polyelectrolytes, food emulsifiers or rheology modifiers, as well as drugs [17,18].

In this study, organosolv ethanol treatment was combined with membrane ultrafiltration technology to treat non-woody biomass feedstock (*Miscanthus sinensis*). Organosolv technology enabled the fractionation of the raw material in different products (cellulose hemicellulose-derived sugars and lignin) allowing the subsequent recovery of the solvents by distillation with high yields and low energy consumption. Membrane ultrafiltration was used to obtain specific molecular weight lignin fractions as it proportioned excellent fractionation capability with low chemicals consumption and low energy requirements.

The combination of the abovementioned technologies present the novelty of allowing to obtain lignin with defined properties, particularly specific molecular weight and low polydispersity, which could be used in high added value applications, as polymer formulation or low molecular weight compounds.

In order to maximize process efficiency, a simulation of the biorefinery process based on experimental laboratory results was carried out using Aspen Plus software. Solvent consumption recovering section was designed to recycle ethanol and water to the different process units reducing their fresh input. Mass balance and stream compositions were calculated and adjusted as well in order to minimize the operation costs of the process and reduce its environmental impact.

2. Materials and methods

2.1. Materials

Characterization of original *M. sinensis* fibres was done according to standard methods (see Table S1 in the Supporting Information Section).

2.2. Biorefinery process

M. sinensis biorefinery process (Fig. 1) consisted of several stages: raw material organosolv ethanol pre-treatment, solid fraction (SF) washing and separation, membrane ultrafiltration of the liquid fraction (LF), lignin precipitation and isolation and solvents recovery. This last step consisted on the evaporation of an ethanol–water stream which was sent to a distillation column to separate and reuse both components and the obtaining of a concentrated liquid fraction enriched in hemicelluloses.

2.3. Laboratory experiments

2.3.1. Ethanol organosolv pre-treatment

Lignocellulosic raw material was milled and treated in aqueous ethanol, in a laboratory scale 20 L batch reactor with temperature and pressure control. Experimental conditions (selected after an extensive series of laboratory experiments) used were defined as follows: solvent concentration: ethanol–water 60/40 w/w; temperature: 160 °C; reaction time: 90 min; liquid/solid ratio: 6:1. Contents were stirred by rotating the reaction vessel via motor connected through a rotary axle to the control unit. After cooking, the reactor content was cooled to room temperature. SF and LF were then separated using a nylon mesh. The former was washed three times with 5 L aqueous ethanol (60/40 w/w) at 40 °C and the filtrates were mixed with the LF from the reactor forming the total liquid fraction (TLF) stream. SF was separated from uncooked material by screening through a sieve of 1 mm mesh.

2.3.2. Membrane ultrafiltration unit

Ultrafiltration module used to fractionate the TLF was a Pall Membralox XLab5 pilot unit equipped with a 3L 316 stainless steel tank with water jacket for temperature control, a recirculation pump and a set of tubular ceramic membranes of different cut-offs in the interval 5–15 kDa manufactured by IBMEM (Industrial Biotech Membranes, Germany). Four different cut-off fractions were obtained: less than 5 kDa fraction; 5–10 kDa fraction; 10–15 kDa fraction and more than 15 kDa fraction. The diameter of the membrane tubes was 6 mm, the length was 250 mm and the area of each membrane tube was 110 cm^2. The retentate and permeate were recirculated to the feed tank for 2 h before samples of permeate and retentate were withdrawn. The pressure was measured at the inlet and at the outlet of the membrane tube. As the pressure on the permeate side was atmospheric, the TMP is the average of the inlet and outlet pressure on the feed side. The experiments were done at the following experimental conditions: TMP: 300 kPa; cross-flow velocity: 5.6 m/s and temperature: 60 °C.

2.3.3. Organosolv lignin

Lignin contained in the obtained ultrafiltrated fractions was precipitated by dilution with 1.5 volumes of acidified water (pH 3) [19]. Precipitated lignin samples were allowed to settle over a 24-h period, centrifuged at 3500 rpm for 12 min, washed with water twice to remove sugar and other impurities and finally dried in a vacuum oven at 65 °C and −60 cmHg. Lignin concentration was then calculated gravimetrically, and isolated lignin samples were stored for subsequent characterization.

2.4. Process simulation

Aspen Plus was used to design and simulate the process on the basis of experimental results in order to optimize solvents recovery and calculate stream material balances and compositions. Lignin, cellulose and hemicelluloses were defined by their chemical structure and physical properties which were obtained from the National Renewable Energy Laboratory (NREL) database (NREL/MP-425-20685; task number BF521004), whereas other conventional components were selected from the ASPEN PLUS data bank. NRTL-RK (Non-Random, Two Liquids—Redlich-Kwong) model was used to simulate the thermodynamic properties of solutions. This route includes the NRTL equation, obtained by Renon and Prausnitz, for the liquids activity coefficients calculation, Henry's law for the dissolved gases and RKS (Redlich-Kwong-Soave) equation of state for the vapour phase.

The simulation process was developed using the following inlet streams to the reactor: 1000 kg/h of dry raw material with the abovementioned composition and 6000 kg/h of ethanol–water

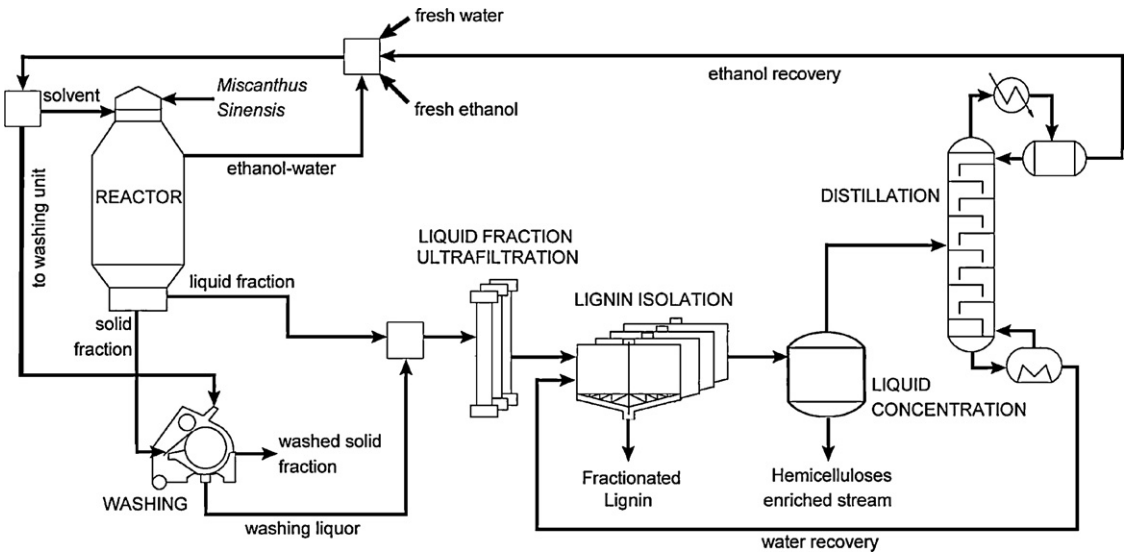

Fig. 1. Biorefining process scheme: ethanol organosolv pre-treatment and membranes ultrafiltration process.

(60% w/w), which corresponded to a liquid/solid ratio (w/w) of 6. As solvents were recovered at the end of the process and recycled to reaction unit, solvent input to reaction stage was the sum of the recovered solvent stream and a fresh solvent stream.

2.5. Products characterization

Products (solid fraction, lignin, liquid fraction) characterization procedures (FTIR spectroscopy, Gel Permeation Chromatography (GPC), ^{1}H NMR spectrometry, Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), High Performance Liquid Chromatography (HPLC)), are described in the Appendix B.

3. Results

3.1. Products characterization

3.1.1. Solid fraction characterization

3.1.1.1. Solid fraction chemical composition. Lignin content in pulp was 10.8 ± 0.3% and hollocellulose 72.3 ± 0.1% (cellulose: 55 ± 0.3%, hemicelluloses: 17.3 ± 0.3%), results given on an oven dry solid fraction weight basis. Lignin and hemicellulose percentages on the solid fraction were considerably lower than in the raw material composition (lignin: 20%; hemicelluloses: 32%) indicating a considerable removal of lignin and hemicelluloses during pre-treatment process which were recovered in the water-soluble stream. The solid fraction cellulose percentage (55%) was, as a consequence, higher than in the raw material (48%).

High cellulose and low lignin contents in the solid fraction made this material optimal to apply enzymatic hydrolysis to convert cellulose in glucose and obtain ethanol by further fermentation of the latter. Higher lignin percentages (about 27%) in solid fractions resulted in very low hydrolysis performances due to the enzymes impediment to attack cellulose in lignin presence [4].

3.1.1.2. FTIR spectroscopy. Cellulose obtained from the solid fraction was analysed by FTIR spectroscopy (Fig. 2a: 4000–500 cm^{-1} region and Fig. 2b: magnification of 1500–500 cm^{-1} region). Commercial microcrystalline cellulose (Avicel) spectrum was also included with the aim of comparison. The following typical cellulose bands were observed [20]: hydrogen-bonded OH stretching at 3400 cm^{-1}; CH stretching at 2900 cm^{-1}; OH bending of adsorbed water at 1640 cm^{-1}, CH deformation (asymmetric) at 1430 cm^{-1};

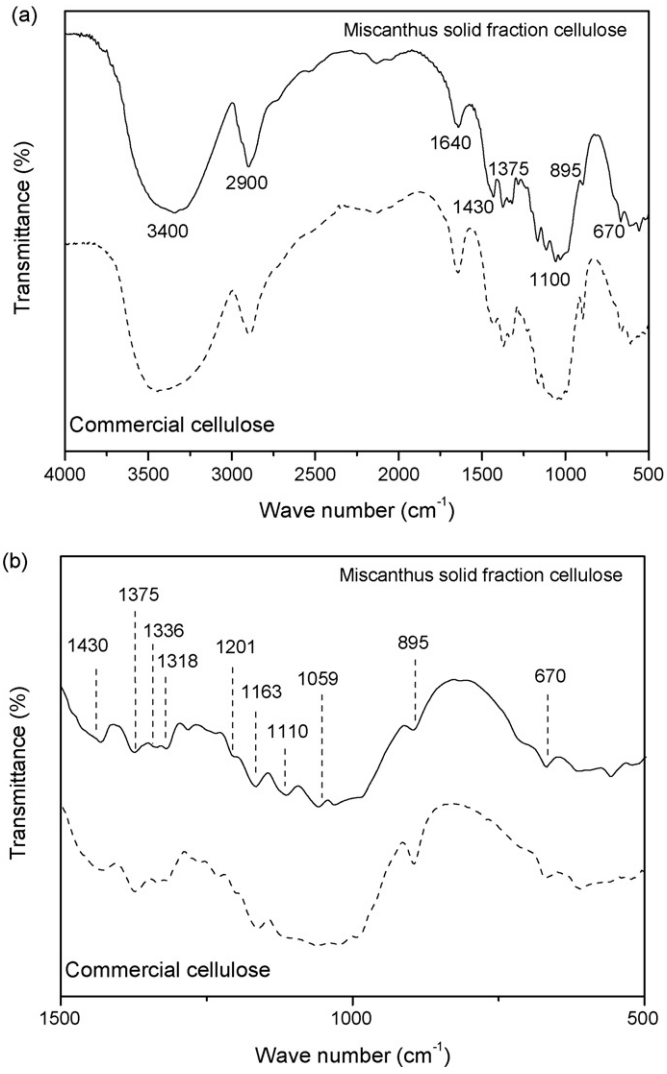

Fig. 2. (a) Miscanthus solid fraction cellulose and commercial cellulose FTIR spectra (4000–500 cm^{-1} region). (b) Miscanthus solid fraction cellulose and commercial cellulose FTIR spectra (magnification of 1500–500 cm^{-1} region).

Table 1
Chemical composition of the remaining liquid stream after lignin precipitation (LS) and after acid hydrolysis process (PHS). Results are expressed in mg/mL.

Sample	Glucose	Xylose	Mannose	Galactose	Arabinose	Total sugars	Furfural
LS	0.182	0.276	0.022	0.065	0.094	0.639	0.343
PHS	0.334	0.358	0.055	0.123	0.134	1.004	0.510

CH deformation (symmetric) at 1375 cm^{-1}; OH in-plane deformation at 1336 cm^{-1}; CH_2 wagging at 1318 cm^{-1}; OH deformation at 1201 cm^{-1}; COC asymmetric vibration at 1163 cm^{-1}; Glucose ring stretch (asymmetric) at 1110 cm^{-1}; CO stretching at 1059 cm^{-1}; β-glycosidic linkages between glucose units in cellulose at 895 cm^{-1}; C–OH out-of-plane bending mode at 670 cm^{-1}. No lignin-associated bands were observed at 1600 and 1510 cm^{-1} [21].

Obtained spectrum was very similar to Avicel commercial microcrystalline cellulose indicating that cellulose sample was free of lignin and hemicelluloses contamination.

3.1.2. Liquid stream characterization

Remaining liquid stream after lignin precipitation and solvents recovery was analysed in terms of hemicellulosic sugar concentration (Table 1) before submitting it to acid hydrolysis (sulphuric acid 0.1 M, 180 °C, 60 min). Sugar composition of the hydrolyzed stream is also included in Table 1.

Xylose, glucose and arabinose were the main soluble sugars representing 43.2%, 28.5% and 14.7% of total sugars content in the liquid stream and 33.2%, 35.6% and 5.5% in the acid hydrolysates. Mannose and galactose were also present in smaller amounts. The difference between liquid stream and hydrolysates monomeric sugars concentration corresponded to oligomeric sugars that were degraded by the acid hydrolysis. Sugars concentration in the hydrolysates was found to be 1.2–2.5 times higher indicating this proportion of oligomeric sugars present in the remaining liquid stream.

Measured furfural concentration was 0.343 and 0.510 mg/mL in the liquid stream and hydrolysate respectively. This product was generated by pentose sugars degradation, xylose and arabinose. Values were similar to published data for hardwoods [2] and higher than softwoods ones, as they contain lower levels of pentoses than hardwoods and non-woody lignocellulosic feedstock [4].

3.1.3. Lignin characterization

In lignin FTIR spectra (Fig. 3a: 4000–500 cm^{-1} region and Fig. 3b: magnification of 1500–500 cm^{-1} region) the following structure signals were found: aromatic phenylpropane skeleton vibrations (1600, 1515 and 1425 cm^{-1}), aromatic and aliphatic hydroxyl groups (3400, 1030 cm^{-1}), C–H aliphatic bonds (2925, 2850 and 1460 cm^{-1}), ether bridges (1220 cm^{-1}) and stretching of conjugated (1660 cm^{-1}) and non-conjugated (1710 cm^{-1}) carbonyl groups with the aromatic ring.

Besides these typical lignin structure bands, other signals were associated with syringyl (S) and guaiacyl (G) structures. S-type aromatic C–H in-plane and out-of-plane deformations gave a signal at 1118 and 833 cm^{-1} respectively while S ring breathing with C–O stretching was found at 1330 cm^{-1}.

G ring breathing with C–O stretching (1265 cm^{-1}), G-type aromatic C–H in-plane and out of the plane bending was found at 1033 cm^{-1}, the former and at 915 and 855 cm^{-1}, the latter.

The presence of S and G bands could be observed in all lignin samples. Nevertheless, it was noticed that signals intensity was dependent on lignin fraction cut-off. S band intensity was higher as the lignin sample cut-off decreased, corresponding the maximum intensity to the <5 kDa lignin sample.

The opposite behaviour was found in G signal intensity, which was found to be higher as the lignin fraction cut-off increased, being maximum in the >15 kDa lignin sample.

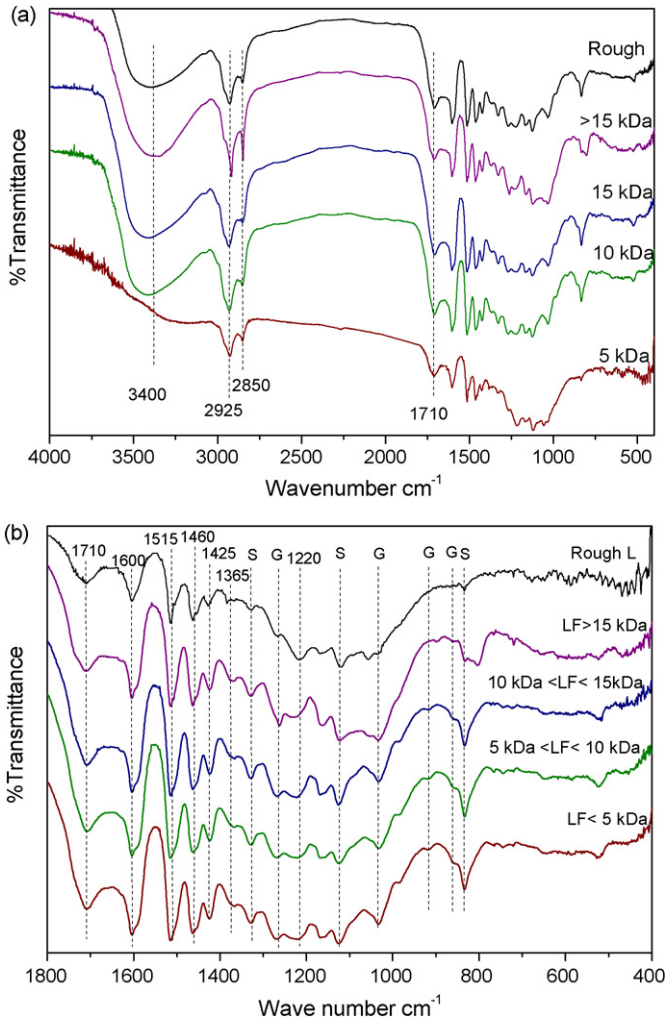

Fig. 3. (a) FTIR spectra of lignin samples (wave number: 400–4000 cm^{-1}). (b) FTIR spectra of lignin samples (magnification of 500–2000 cm^{-1} region).

These observations were associated with the different chemical bonds that S and G lignin structural units can develop. β-O-4 and C–C links are the most common bonds between lignin structural units (specially those involving C5 of the aromatic ring) and they are so stable that they are not cleaved during the fractionation process. G units can form C5 bonds, but this is impossible in the case of S units as they have C5 position substituted by a methoxy group. As a consequence, lignin with higher percentages of G units will present higher molecular weight than lignins with majority of S units [22]. This conclusion was in concordance with obtained results in this work, and demonstrated the effectiveness of the membrane ultrafiltration system to produce lignin groups with different cut-off.

3.1.3.1. ^1H NMR spectra. The ^1H NMR spectra of rough ethanol organosolv lignin and obtained fractionated samples are shown in Fig. 4a and b (magnification of the aromatic zone). Analysis of the ^1H NMR signal intensity in the range of 8.0–6.2 ppm provides an indirect method of monitoring the level of substitution on the aromatic ring of lignin. The integrals of signals between 0.8 and 1.5 ppm were related to the aliphatic moiety in the lignin. Signal at 3.3 ppm was related to protons in water in DMSO. Protons in DMSO gave also an intense signal at 2.5 ppm which is not shown in the spectra. Signal at 3.8 ppm was attributed to methoxyl protons ($-OCH_3$).

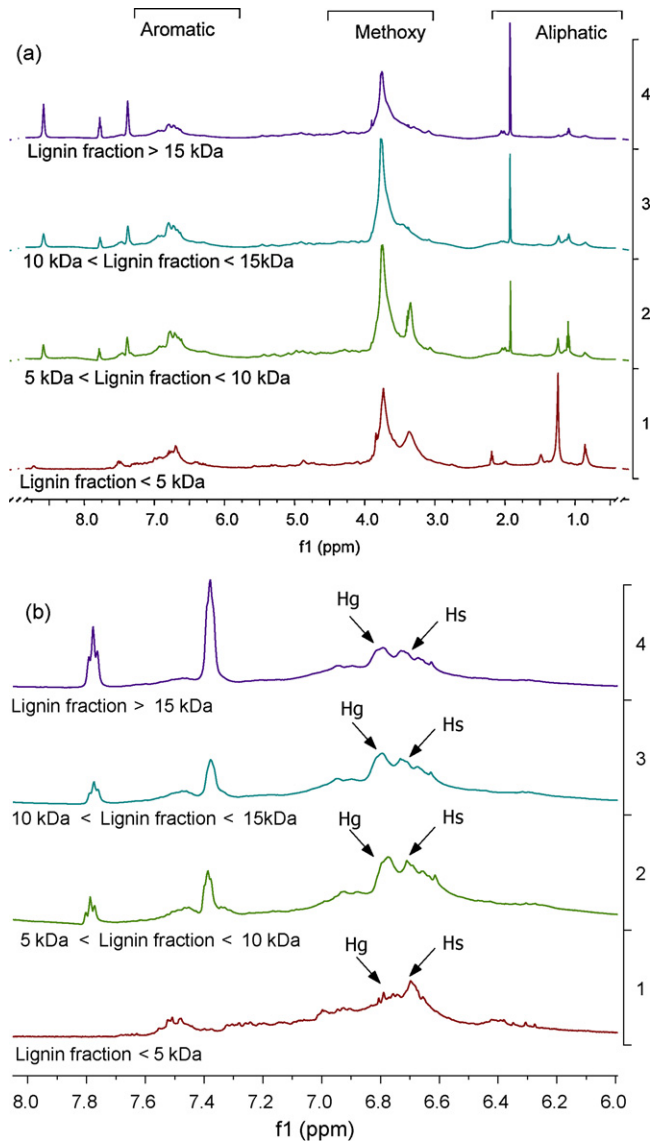

Fig. 4. (a) ^{1}H NMR spectra of fractionated lignin samples. (b) ^{1}H NMR spectra of fractionated lignin samples. Magnification of aromatic zone.

The integrals of signals between 6.2 and 6.8 ppm were attributed to aromatic protons in syringylpropane and guaiacylpropane structures [23,24]. As it can be seen, the relative contents of syringyl and guaiacyl units in the different lignin fractions varied proportionally to lignin molecular weight. Thus, the smaller was the molecular weight lignin fraction, the higher was S percentage in lignin composition, reaching the maximum percentage in lignin fraction <5 kDa and corroborating the obtained results by FTIR. Signals around 7.3–7.4 ppm were assigned to aromatic protons in *p*-hydroxyphenyl units, C_α=O groups and aromatic protons in *p*-coumaric and ferulic acids [24,25].

3.1.3.2. Gel Permeation Chromatography (GPC). Molecular weight (MW) distribution (weight average MW (M_w), number average MW (M_n) and polydispersity (M_w/M_n)) of lignin samples analysed by GPC is presented in Table 2, where obtained lignin fraction yields LF (dry lignin kg/dry lignocellulosic raw material kg) are also included.

As it can be observed, the lowest MW lignin fraction was obtained in less quantity finding higher lignin yields as lignin MW increased. Obtained values were in the range of organosolv lignin MW published data [26] and lower than those reported for kraft and soda lignins [22]. The four ultrafiltrated lignin fractions presented lower polydispersity than rough lignin, especially the smallest MW fraction, suggesting that the membrane filtration system would allow the purification of narrower lignin fractions with similar molecular weights which could be used in specific industrial applications as polymer formulation [12] or as antioxidants [27]. Furthermore, the smaller was the cut-off of the membrane, the lower were the M_w and M_n of the correspondent lignin fraction. As previously said, the relative contents of syringyl and guaiacyl units in the different lignin fractions varied proportionally to lignin molecular weight, meaning that lignin fractions with differences in their predominant structures were obtained and could be selected for different applications.

Table 2
Lignin yield (dry lignin kg/dry lignocellulosic raw material kg). Weight average MW (M_w) (g/mol), number average MW (M_n) (g/mol) and polydispersity (M_w/M_n) of lignin samples analysed by GPC.

Lignin fraction	Yield fraction	M_w	M_n	M_w/M_n
Rough	0.138	2180	1150	1.9
Lignin > 15 kDa	0.087	2390	1500	1.6
10 kDa < Lignin < 15 kDa	0.028	1900	1260	1.5
5 kDa < Lignin < 10 kDa	0.015	1780	1270	1.4
Lignin < 5 kDa	0.008	1357	1050	1.3

3.1.3.3. Differential Scanning Calorimetry (DSC). The percentage of structural units (S and G) present in the lignin sample and the fractionation method by which it has been extracted determine lignin Tg, corresponding the highest values to kraft softwoods and the lowest ones to organosolv lignins [28]. In general, lignin presents high glass transition temperature (Tg), from 90 to 180 °C, associated with hydrogen bonds between OH groups and its aromatic character [13,14,22].

Tg values of the lignin fractions obtained by membrane ultrafiltration are presented in Table 3. These values are in the range of organosolv lignins Tg published data; ethanol Leucaena Leucocephala lignin presented a Tg of 100 °C [22], while different raw materials fractionated by Alcell® process showed the following values [10]: hardwood, 97 °C; wheat straw: 106–122 °C and reed: 97 °C. Organosolv lignins usually present lower ash contents than lignins extracted by alkaline treatments (soda or kraft). This fact allows a better thermal mobility of the molecules and better thermal behaviour [12,13]. Published Tg values of alkaline lignins (kraft pine lignin: 141 °C [10,14]; soda rice straw lignin: 160–185 °C [10]) are higher than the obtained for organosolv ones.

Furthermore, it can be seen that ultrafiltrated lignin fractions Tg increases as the lignin MW does. This observation is in concordance with obtained results by other techniques, as FTIR, ^{1}H RMN and SEC where a relation between lignin MW and the percentage of S and G groups was established. The smallest MW fraction (Lignin < 5 kDa) presented the highest S content (units unable of

Table 3
Glass transition temperature (Tg) of lignin fractions obtained by ultrafiltration.

Lignin fraction	Tg (°C)
Rough lignin	106
Lignin >15 kDa	102
10 kDa < Lignin < 15 kDa	97
5 kDa < Lignin < 10 kDa	90
Lignin <5 kDa	85

creating C–C bonds) and the lowest MW, what is in concordance with a Tg lower than other fractions.

3.1.3.4. Thermogravimetric Analysis (TGA). Fig. 5 presents TG and DTG curves of ultrafiltrated lignin fractions. The former reveals the weight loss of substances in relation to the temperature of thermal degradation, while the latter, which is the first derivative of TG curve, shows the corresponding rate of weight loss. A peak representing weight loss can be observed around 90 °C, which corresponds to absorbed water evaporation. The peak around 225 °C is related to hemicelluloses content in the samples. These components have a degradation temperature between 200 and 300 °C [29,30]. It can be observed that hemicelluloses content in samples is low.

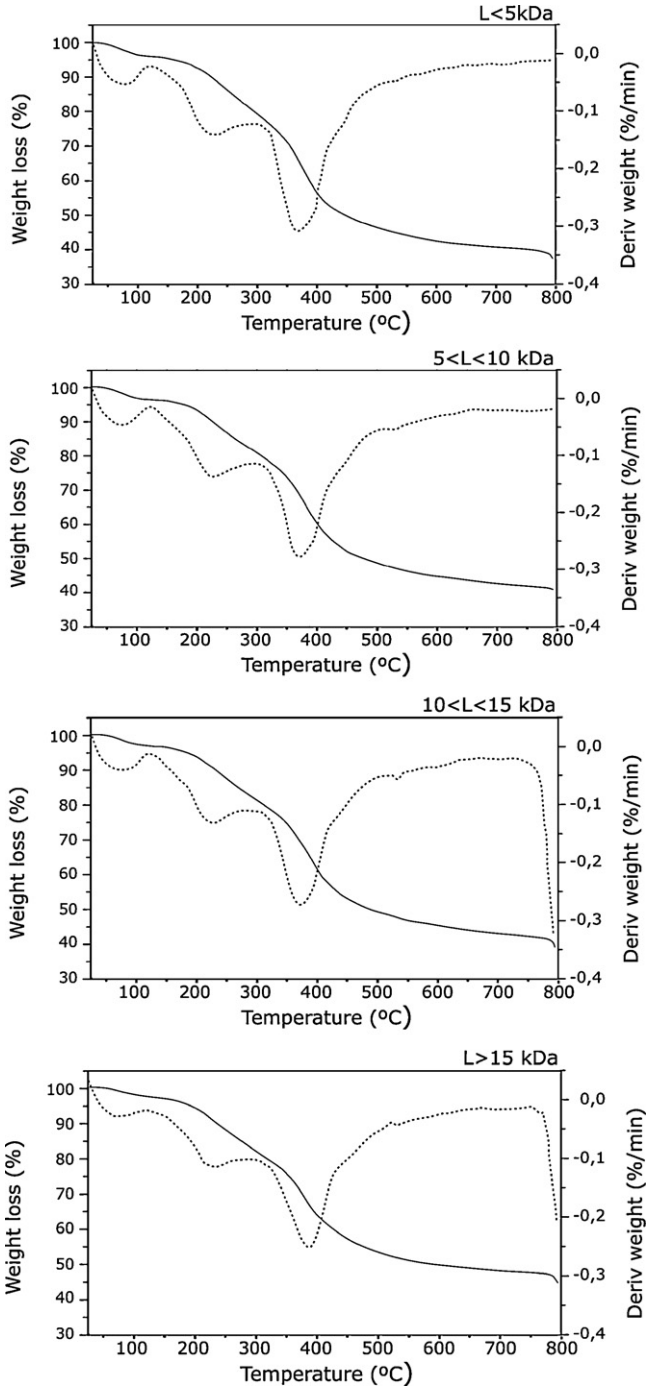

Fig. 5. TG and DTG (dashed line) curves presented by ultrafiltrated lignin fractions.

Table 4
Mass balances of reaction unit (kg/h). LF (liquid fraction); SF (solid fraction).

	Miscanthus	Solvent	Flash stream	LF	SF
Ethanol	0	3601	1061	1524	1016
Water	58	2399	387	1234	822.5
Cellulose	423.9	0	0	0	402.7
Lignin	235.5	0	0	84.8	150.7
Hemicelluloses	263.7	0	0	102	82.6
Glucose	0	0	0	14.13	9.42
Xylose	0	0	0	49.8	30.5
Furfural	0	0	0	4.15	5.5
Others	18.9	0	0	6.2	12.7
Total	1000	6000	1448	3019	2532

The most important degradation peak appears around 400 °C and it is assigned to the breakage of the bonds between lignin structural units [31,32].

The smallest MW lignin fraction (Lignin <5 kDa) presented its maximum DTG peak at 360 °C, which is the lowest value found for studied lignin fractions. The highest value, 395 °C corresponded to the lignin fraction >15 kDa, and the intermediate fractions presented similar DTG maximum values indicating a similar thermal degradation.

The peak around 550 °C was associated with aromatic rings decomposition [33].

The residual mass fraction that remained at 800 °C was found to be from 30 to 45% for the studied samples. This non-volatile fraction was related to the creation of highly condensed aromatic structures during thermal degradation.

Thermal decomposition temperatures found for studied lignin samples were in the range of published data for organosolv lignins [32,33]. Lignin thermal behaviour is important for their use in potential applications which require high thermal stability, as phenolic resins formulation for several uses (isolating and refractory materials, abrasive components, etc.) [22].

3.2. Simulation results

Process simulation allowed calculating mass balances and compositions of the streams in the different sections of the process.

3.2.1. Organosolv pre-treatment balances

Miscanthus (1000 kg/h) and solvent (6000 kg/h; ethanol–water 60% w/w) were fed to the reactor where lignin and hemicelluloses were partially dissolved. Reaction temperature was 160 °C and pressure was 10 bar. After reaction, a flash separation was done to recover a vapour fraction composed of ethanol (1060 kg/h) and water (387 kg/h) whose heat content was used to preheat the fresh solvent input. Obtained LF and SF were separated by filtration. Table 4 presents obtained mass balances for the organosolv pre-treatment reaction unit.

Table 5
Mass balances of solid fraction washing stage (kg/h). SF (solid fraction); WS (washing solvent); WSF (washed solid fraction); WL (washed liquors).

	SF	WS	WSF	WL
Ethanol	1016	1404	726	1695
Water	822.5	935.8	527.5	1231
Cellulose	402.7	0	402.7	0
Lignin	150.7	0	105.5	45.2
Hemicelluloses	82.6	0	46.8	35.8
Glucose	9.42	0	1.88	7.54
Xylose	30.5	0	7.19	23.3
Furfural	5.5	0	4.1	1.4
Others	12.7	0	5.3	7.4
Total	2532	2340	1827	3047

Table 6
Mass balances of ultrafiltration system (kg/h).

	TLF	LF < 5 kDa	5 kDa < LF < 10 kDa	10 kDa < LF < 15 kDa	LF > 15 kDa
Ethanol	3219	161	305.8	571.8	2180
Water	2465	123	234	442.3	1666
Cellulose	0	0	0	0	0
Lignin	130	7.8	14.6	26.8	80.8
Hemicelluloses	137.8	2.75	14.4	20.15	100.5
Glucose	21.67	0.35	1.46	2.34	17.52
Xylose	73.1	1.26	6.57	9.20	56.1
Furfural	5.5	0.11	0.48	1.08	3.8
Others	13.6	0.34	1.33	2.9	9.03
Total	6065	297	578.7	1077	4034

3.2.2. Solid fraction washing stage

SF was sent to washing stage where it was mixed with 2340 kg/h of washing solvent: WS (ethanol–water 60% w/w) at 40 °C which came from the solvent recovery stage at the end of the process. Thus, no fresh solvent was required in the solid fraction washing unit. Mass balances of washing stage are presented in Table 5. Washing liquor (WL) exiting this stage was mixed with the liquid fraction from the reaction unit (LF) forming the total liquid fraction (TLF) stream that was sent to ultrafiltration system.

3.2.3. Membranes ultrafiltration system balances

Total LF was fractionated into four streams (Table 6 presents ultrafiltration system mass balances). The obtained liquid fractions (LF < 5 kDa, 5 kDa < LF < 10 kDa, 10 kDa < LF < 15 kDa and LF > 15 kDa) represented approximately 5%, 10%, 18% and 67% of the total liquid stream treated in ultrafiltration stage. The total lignin obtained was 138 kg/h. Lignin >15 kDa represented the 63%, the fraction between 10 and 15 kDa was found to be 20% while 11% and 6% where the percentages of the fraction between 5 and 10 kDa and the fraction <5 kDa respectively.

3.2.4. Solvents recovery

Solvents recovery step was designed to maximize both ethanol and water recovery. The filtrates obtained after lignin precipitation were concentrated by evaporation process. As a result, a liquid stream enriched in hemicelluloses was obtained as by-product while a clean ethanol–water condensate was recovered and sent to a distillation column in order to separate both components. This way ethanol fresh input was reduced from 3600 to 900 kg/h (75%). Furthermore, water recycling allowed an 80% reducing of this input (to 2100 fresh water kg/h). Water required in the reaction section was 2400 and 9800 kg/h were needed to precipitate lignin fractions.

3.2.5. Costs estimation of ultrafiltration process

Cost estimation of the simulated ultrafiltration process were based in some assumptions (Table 7) reported by other authors [34,35]. Considering a liquor flow of 6000 L/h in the simulated ultrafiltration process and supposing an average flux of 65 L/m^2 h, a total membrane area of 95 m^2 was estimated. The capital and operation costs associated to these assumptions are presented in Table 8.

Table 7
Assumptions for cost estimates of the ultrafiltration section.

Investment cost (€/m^2 membrane area)	3300
Annuity factor	0.1
Membrane cost (€/m^2)	1000
Membrane lifetime (years)	6
Electricity price (€/kWh)	0.04
Pump efficiency	0.85
Cleaning cost (€/m^2)	50
Cleaning (h/d)	1
Maintenance cost (% capital cost/year)	5
Operating time (h/year)	8000

Table 8
Cost estimates of the liquor ultrafiltration section.

Parameter	Cost	Units
Membrane area	95	m^2
Investment cost	313.5	k€
Capital cost	31.35	k€/year
Electricity requirement	1.94	kWh
Electricity cost	0.6	k€/year
Membrane replacement cost	15.8	k€/year
Cleaning cost	4.8	k€/year
Maintenance cost	1.6	k€/year
Operating costs	22.8	k€/year
Total cost	54.1	k€/year
Lignin production	1040	tonne/year
Production cost	52	€/tonne of lignin

As reported by Jönsson and Wallberg [35], the capital cost is the dominating cost for an ultrafiltration plant, being directly proportional to the total membrane area. The strategic scope of the ultrafiltration plant also plays a crucial role in the capital cost, because it determines the annuity factor. For the considered ultrafiltration stage, the capital cost was calculated according to an annuity factor of 0.1 respect to the total investment cost, resulting in 31.35 k€/year.

Operation cost of the simulated ultrafiltration system included the electrical consumption for liquor pumping, the cleaning and maintenance costs and the costs related to the replacement of the membranes. The electrical requirements for pumping liquid fraction in the ultrafiltration stage were calculated directly by Aspen Plus software utilities, resulting in a consumption of 1.94 kWh.

As a result, a total cost of 54.1 k€/year was obtained for the simulated ultrafiltration process. This means that, obtained lignin fractions entailed a cost of 52 €/tonne of product. This value is higher than that reported by Jönsson and Wallberg for kraft black liquor treatment (33 €/tonne of lignin). However, this process permitted the obtaining of several lignin fractions with determined characteristics, as specific molecular weight and functional groups, with the added value of being sulphur-free lignins. These characteristics make them optimal for their use in a wide variety of applications.

4. Conclusions

Combining organosolv technology with membranes ultrafiltration, a biomass refinery process was developed which economic fundamentals were based on the obtaining of different valuable products with actual industrial applications and the recovery and recycling of used solvents. A distillation unit allowed the recovery of significant amounts of ethanol at the proper concentration to be directly sent back to the digester unit and also the recovery of water to be used in the pulp washing stage and the lignin precipitation unit. A cost estimation of the obtained lignin fractions by ultrafiltration process resulted in 52 €/tonne of lignin, which was

found higher than reported costs of kraft lignin (33 €/tonne) but the high quality of the product related with its high purity and specific characteristics (low polydispersity, determined functional groups) convert it in a potential high added value product.

Supporting information section

Characterization of original *M. sinensis* fibres by standard methods and products (solid fraction, lignin, liquid fraction) characterization procedures: FTIR spectroscopy, Gel Permeation Chromatography (GPC), ^{1}H NMR spectrometry, Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), High Performance Liquid Chromatography (HPLC), are described in the Appendix B, available free of charge via the Internet.

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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.2009.10.058.

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