



Lignin depolymerization for phenolic monomers production by sustainable processes

Javier Fernández-Rodríguez, Xabier Erdocia, Cristina Sánchez, María González Alriols, Jalel Labidi*

Chemical and Environmental Engineering Department, University of the Basque Country UPV/EHU, Plaza Europa, 1, 20018 San Sebastián, Spain

ARTICLE INFO

Article history:

Received 30 November 2016
Revised 20 February 2017
Accepted 21 February 2017
Available online 10 March 2017

Keywords:

Organosolv
Lignin
Depolymerization
Phenolic
Catalyst
Catechol

ABSTRACT

Biomass wastes (almond shell and olive tree pruning) were used in this work as raw materials for the extraction of high purity lignin by different delignification methods. A pretreatment stage was carried out to remove the major hemicelluloses content in the solid feedstocks. Afterward, two sulfur-free pulping processes (soda and organosolv) were applied to extract the largest fraction of lignin. The extracted lignin contained in the liquors was isolated using selective precipitation methods to design a tailor-made technique for obtaining high-purity lignin (in all cases more 90% of purity was reached). Soda process allowed the extraction of more lignin (around 40%–47%) than organosolv process (lower than 20%) regardless of the lignocellulosic source employed.

Once the different lignin samples were isolated and characterized, they were depolymerized for the obtaining of small phenolic compounds. Three main streams were produced after the reaction: phenolic enriched oil, residual lignin and coke. After the purification of these fractions, their quantifications and characterization were conducted.

The most abundant product of the reaction was residual lignin generated by the undesirable repolymerization of the initial lignin with yields around 30%–45%. The yield of the stream enriched in phenolic oil was higher than 20%. Coke, the lowest added-value product, presented a yield lower than 12% in all the cases. Lignin from organosolv presented higher phenolic oil yields, mainly due to their lower molecular size. This parameter was, thus, considered a key factor to obtain higher yields.

© 2017 Science Press and Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by Elsevier B.V. and Science Press. All rights reserved.

1. Introduction

Lignocellulosic biomass is attracting more and more interest due to its potential as renewable carbon source for chemicals, materials and energy production for the partial substitution of fossil

resources [1]. Biomass is mainly composed by three macromolecular components, cellulose, hemicellulose and lignin, whose quantities within plants depend on the species, age, harvest season, etc. [2]. Among these compounds, lignin has traditionally been considered as a byproduct obtained during the cellulose extraction process, being burnt for energy recovery purposes [3]. Lignin is a three-dimensional amorphous polymer made up by the combination of three different phenylpropane monomer units: guaiacyl alcohol (G), *p*-coumaryl alcohol (H) and syringyl alcohol (S), linked mainly by (β -O-4) aryl ether bonds in a randomized way [4]. Depending on the source of the raw material, the ratio between these monomers may vary significantly. G and S monomer units appear in different quantities in the composition of hardwood species lignins, although S units tend to be the most plentiful. In softwood species, G units are the most abundant ones while, in herbaceous lignin, G, H and S units are usually present [5].

The availability of lignin in the biosphere exceeds 300 billion tons and increases by about 20 billion tons every year [6]. Nevertheless, although lignin is produced worldwide in amounts close

Abbreviations: A, almond shell; O, olive tree pruning; AS, almond shell soda lignins; AO, almond shell organosolv lignins; OS, olive tree pruning soda lignins; OO, olive tree pruning organosolv lignins; AS pH = 6, almond shell-soda lignin precipitated at pH = 6; AS pH = 4, almond shell-soda lignin precipitated at pH = 4; AS pH = 2, almond shell-soda lignin precipitated at pH = 2; AO 1 vol, almond shell-Organosolv lignin precipitated adding 1 volume of water; AO 2 vol, almond shell-Organosolv lignin precipitated adding 2 volumes of water; AO 4 vol, almond shell-Organosolv lignin precipitated adding 4 volumes of water; AS pH = 6, olive tree pruning-soda lignin precipitated at pH = 6; AS pH = 4, olive tree pruning-soda lignin precipitated at pH = 4; AS pH = 2, olive tree pruning-soda lignin precipitated at pH = 2; OO 1 vol, olive tree pruning-Organosolv lignin precipitated adding 1 volume of water; OO 2 vol, olive tree pruning-Organosolv lignin precipitated adding 2 volumes of water; OO 4 vol, olive tree pruning-Organosolv lignin precipitated adding 4 volumes of water; ALL, acid insoluble lignin; ASL, acid soluble lignin.

* Corresponding author.

E-mail address: jalel.labidi@ehu.eus (J. Labidi).

to 70 million tones, only 1%–2% is used as precursor for chemicals and materials production [7].

Currently, most of the efforts in biorefinery industries are focused on the sugar platform (cellulose and hemicellulose) for chemicals and biofuels production, such as bioethanol, xylitol, succinic acid, and many others. However, the development of lignin platform is also essential for the economic sustainability of this industry [8]. In this sense, raising the portfolio of biorefineries would improve their feasibility to be considered as an actual alternative to partially replace petro-chemical industries in the future [9].

Lignin can be extracted from lignocellulosic biomass by several methods. Traditionally, the processes widely used in the industry for lignin separation have been the sulfate (Kraft) process and the sulfite process. However, the lignin obtained by these methods presents several impediments for its valorization in high value-added applications, such as no uniform structure, unique chemical reactivity, and the presence of various organic and inorganic impurities [10].

Among the sulfur-free delignification methods, soda and organosolv pulping processes are the most relevant methods. Soda process is an alkaline treatment that leads to mitigate some environmental problems caused by the sulfur used in the Kraft and sulfite cooking liquors. In addition, soda lignin could be successfully used for the production of phenolic resin, the synthesis of polymers and the obtaining of low-molecular weight substances [11]. Organosolv processes are based on the use of mixtures of organic solvents and water as cooking liquor. The low viscosity of these solvents favors the penetration into the chips causing the solubilization of lignin and, as a consequence, its structure is barely modified, reaching high homogeneity in comparison with the rest of the lignin samples; boosting its further valorization process [12]. Furthermore, the organosolv process enables the solvent recovery after the lignin extraction by distillation, fulfilling the green chemistry principles. The most common solvents used for this purpose are ethanol, acetic acid and formic acid [13].

Lignin samples from alkaline processes (Kraft or soda) are commonly isolated by precipitation with the acidification of the liquor, filtration and washing, being the LignoBoost® process the most current useful method for this purpose [14]. However, the commercial precipitated lignin presents high heterogeneity that hinders its further transformation. Hence, more selective technologies for lignin isolation have been proposed to enhance the purity of final lignin [15]. In this sense, selective precipitation could play an important role for the obtaining of lignin with certain parameters, such as purity or molecular weight distribution, which would facilitate its further valorization. On the other hand, the isolation of the organosolv lignin is carried out by the addition of an antisolvent that reduces the solubility of the lignin in the liquor. The most common method is based on the addition of water due to the high hydrophobicity of the organosolv lignin samples, besides the simplicity and low-cost of this method [16].

The great potential of lignin is based on its possibilities to be used in multiple applications. The fractionation of the lignin structure into small molecules, using advanced techniques such as pyrolysis or hydrogenation, is necessary for chemicals as well as for energy and fuels production [17,18]. Nevertheless, these methods are energy demanding. Depolymerization of lignin based on its thermochemical decomposition enables the production of low molecular weight compounds, like vanillin, simple and hydroxylated aromatics, aldehydes, aliphatic acids, and many others [19]. Different mechanisms have been tested for carrying out this process, mainly divided in supercritical or subcritical conditions [20]. Among subcritical conditions, one of the commonly used method is base catalyzed depolymerization (BCD), which has been widely studied for the phenolic monomers obtaining, based on the heterolytically cleavage of the most common lignin linkage, the (β -

O-4) ether bond, which represents around 60% of the lignin linkages [21]. This cleavage is conducted by means of the formation of a sodium phenolate derivative and a carbenium ion-like transition state, which is instantly neutralized by a hydroxide ion. The sodium cations catalyze the reaction by forming cation adducts with lignin and hence, polarizing the ether bond. This step increases the negative partial charge of the oxygen and, consequently, the energy necessary for heterolytic bond cleavage is reduced [22]. As a result, phenolic monomers-rich oil is obtained in a quantity of not higher than 20%–23%, regardless at which conditions lignin is exposed. This value is limited by the repolymerization reactions that occur during the process, when highly reactive phenolic and catechol derivative monomers undergo polymerization reactions instead of staying as monomeric products, generating residual lignin and coke as undesirable products [23]. This reaction is happening due to a delocalization of the charge in phenolate ions present in the alkaline media. The phenolate ion also exists as carbanion with negative charge in *ortho* or *para* position of the phenolic hydroxyl groups as a reason of resonance stabilization [24]. Therefore, the interaction of the carbanion species to other phenolic compounds with ketone groups will induce facile formation of carbon–carbon bonds between these compounds, leading to repolymerization of lignin.

Almond shells (A) as well as olive tree pruning (O) were the chosen raw materials to work with due to their abundance, availability as well as their high lignin content. A pretreatment stage of autohydrolysis was conducted for the hemicellulose content removal to avoid lignin contamination. For the delignification stage, two sulfur-free methods were applied and compared: soda and organosolv ones. The black liquors obtained after the delignification stage were subjected to a selective precipitation following the same principle of reducing the solubility of lignin in the liquor, although the procedure varied from soda to organosolv liquors, as it will be depicted below. Therefore, different lignin samples were obtained and classified in terms of their source, pulping or delignification process and precipitation level, being assessed by its production yield as well as its physico-chemical properties.

Afterward, all the lignin samples were intended to their depolymerization by BCD reaction to generate lignin monomers and small phenolic compounds that could be valorized as chemical building blocks. As a result, three main products were obtained: an oil enriched in small phenolic compounds; residual lignin from the undesirable repolymerization of lignin; and coke, formed as decomposition product provoked by the harsh conditions at which the reaction was conducted. Moreover, downstream stages were applied to separate all these reaction products. Finally, the obtained products were characterized and compared with the different initial lignins.

2. Experimental

2.1. Feedstocks

Almond shells (A), obtained from *Prunus amygdalus* tree, were provided by a local farmer and olive tree pruning (O), from *Olea europaea* species, which were kindly supplied by local farmers.

Both materials were conditioned and grounded to obtain size particles between 0.25 cm and 0.40 cm.

2.2. Lignin extraction and isolation

2.2.1. Autohydrolysis pretreatment

Both raw materials were firstly pretreated by means of autohydrolysis process, an environmental friendly procedure which uses water as unique reagent at high temperature and pressure. This process tends to remove a high percentage of the hemicelluloses

present in the original composition, fact that could reduce the sugar impurities in the further lignin samples. Autohydrolysis was carried out in a 4 L batch reactor (EL0723 Iberfluid) equipped with a pressure and temperature PC-controller. The reaction conditions were optimized in previous studies [25], being 180 °C, 30 min and solid:liquid ratio of 1:8 the most favorable conditions for dissolving the highest quantity of hemicellulosic sugars. After the autohydrolysis step, liquid fractions were filtered and separated from solid fractions, which were chemically characterized prior to be sent to the delignification stage. The yield of this stage was gravimetrically determined.

2.2.2. Delignification processes: organosolv and soda pulping

Solid fractions derived from autohydrolysis process, were subjected to the delignification process. Organosolv and alkaline treatments were compared using the same reactor that the one which was used for the autohydrolysis processes.

The organosolv process was accomplished at optimal conditions of 200 °C, 90 min; using a mixture ethanol:water of 70:30 (v/v) as solvent reagent, and a solid:liquid ratio of 1:6; conditions optimized by Toledano et al. [26]. On the other hand, the applied conditions in the soda process were selected from the work of Uruzola et al. [27] as follows: NaOH 7.5 wt.% was used as solvent at 121 °C, during 90 min with a solid:liquid ratio of 1:6.

After finishing the pulping processes, the obtained solid fractions were washed until neutral pH and then chemically characterized, whereas the black liquors were intended to the lignin precipitation.

2.2.3. Selective lignin precipitation

Lignin from black liquor was isolated using a precipitation process at different levels.

Organosolv lignin was isolated in three fractions adding different amounts of acidified water (HCl 37 wt.% to reach pH 2) to decrease the solubility of lignin in the black liquor. Specifically, ratios of 1 volume, 2 volumes, and 4 volumes of acidified water were added to one volume of the black liquor. Instead of this, soda lignin was precipitated by dropping the pH level of the black liquor by means of the addition of sulfuric acid (96 wt.%). Three fractions of different pH levels (6, 4 and 2) were obtained. Hence, 12 different lignin samples were used as raw material for the depolymerization reaction study, whose compositions were chemically characterized as it is described below.

2.3. Lignin depolymerization

2.3.1. Base catalyzed depolymerization reaction

The depolymerization reaction was conducted in a batch reactor (5500 Parr reactor) with a 4848 Reactor controller. The volume of the reactor vessel is 100 mL. The reaction conditions were fixed, according to the previous study conducted by Erdocia et al. [28], at 300 °C during 80 min, reaching pressures around 90 bar, under constant stirring. The solid–liquid ratio was 1:20 (wt/wt). The catalyst (NaOH) concentration was set at 4 wt.%.

2.3.2. Downstream processes for product separation

After finishing the depolymerization process, the reaction mixture was treated to separate the different products, following the method described by Toledano et al. [29], graphically depicted in Fig. 1. In the first stage, the mixture was acidified with HCl (37 wt.%) dropping the pH = 2 to precipitate the residual lignin formed during the reaction as undesirable reaction product. The solid phase (residual lignin and coke) was separated from the mixture by filtration using MN 640 w filters and washed with acidified water (pH 2 with HCl as the acidic agent) to remove residual liquid. After that, the separation of residual lignin from the

coke was carried out washing the solid content of the filters with tetrahydrofuran (THF), stirring the dissolution for 3 h, and filtrating again later. The non-solubilized solid (coke) remained in the filter, whereas the residual lignin goes throughout the filter due to its solubility in the THF, solvent which is finally evaporated under vacuum to recover the residual lignin.

On the other side, liquid phase produced after the filtration of residual lignin and coke was subjected to a liquid–liquid extraction to separate the phenolic-enriched oil from the aqueous phase using ethyl acetate as organic solvent. Residual aqueous phase was completely removed from the organic phase by an extraction process with sodium sulfate anhydrous. After a filtration step for the solid separation, the organic solvent was removed by evaporation, remaining the phenolic oil in a liquid phase. The yield of each product was calculated gravimetrically referring to the initial lignin weight introduced in the reactor.

2.4. Analytical methods

The chemical characterization of the feedstocks (A and O) was carried out following TAPPI standard methods [30] in terms of moisture (TAPPI T264-97), ash (TAPPI T211 cm-93), ethanol–toluene extractives (TAPPI T204 cm-97), Klason lignin (TAPPI T222 cm-98), holocelluloses [31], cellulose [32] and hemicelluloses, which were determined as the difference between holocellulose and cellulose contents. After the autohydrolysis and pulping processes, the solid fractions were also characterized by the same methods.

The purity of the precipitated lignin was assessed by the measurement of the acid insoluble lignin (AIL) content as well as acid soluble lignin (ASL) content; following the TAPPI UM250 um-83 standard.

High performance liquid chromatography (HPLC) was used to determine the presence of impurities in form of monomeric sugars in the isolated lignin samples, using a Jasco LC-Net II/ADC equipped with a Rezex ROA–Organic Acid H⁺ (8%) column, photodiode array detector and refractive index detector. Samples were analyzed with a 0.005 N H₂SO₄ dissolution with 100% deionized and degassed HPLC water at 30 °C, 0.35 mL/min flow and 40 µL as injection volume. For calibration, high purity standards of arabinose, xylose, and glucose were used.

Additionally, TGA/SDTA RSI analyzer of Mettler Toledo was used as thermogravimetric analysis (TGA) to determine the ash contents. Around 6–7 mg of lignin samples were heated from 25 up to 800 °C at a rate of 10 °C/min using air atmosphere with constant flow.

The precipitated lignin samples, as well as the residual lignin samples obtained after the depolymerisation reaction were subjected to gel permeation chromatography (GPC) to evaluate the average molecular weight (M_w) of solutes and the polydispersity index (M_w/M_n) using a Jasco instrument unit equipped with an interface (LC-NetII/ADC) and a refractive index detector (RI-2031Plus). Two PolarGel-M columns (300 mm × 7.5 mm) and PolarGel-M guard (50 mm × 7.5 mm) were employed. The flow rate was 0.7 mL/min at 40 °C and *N,N*-dimethylformamide (DMF) was used as mobile phase. The analyses were carried out at 40 °C. Calibration was made using polystyrene standards (Sigma-Aldrich) ranging from 70,000 to 266 g/mol.

The composition of the phenolic oil was determined based on its monomeric phenolic compounds. The oil was dissolved in ethyl acetate (HPLC grade) in a metric flask. The solution was injected in a GC (7890A)-MS (5975C inert MSD with Triple-Axis Detector) Agilent unit equipped with a capillary column HP-5MS ((5%-Phenyl)-methylpolysiloxane, 30 m × 0.25 mm). The temperature profile was defined as follows: starting at 50 °C, then raised to 120 °C at 10 °C/min, kept 5 min, raised to

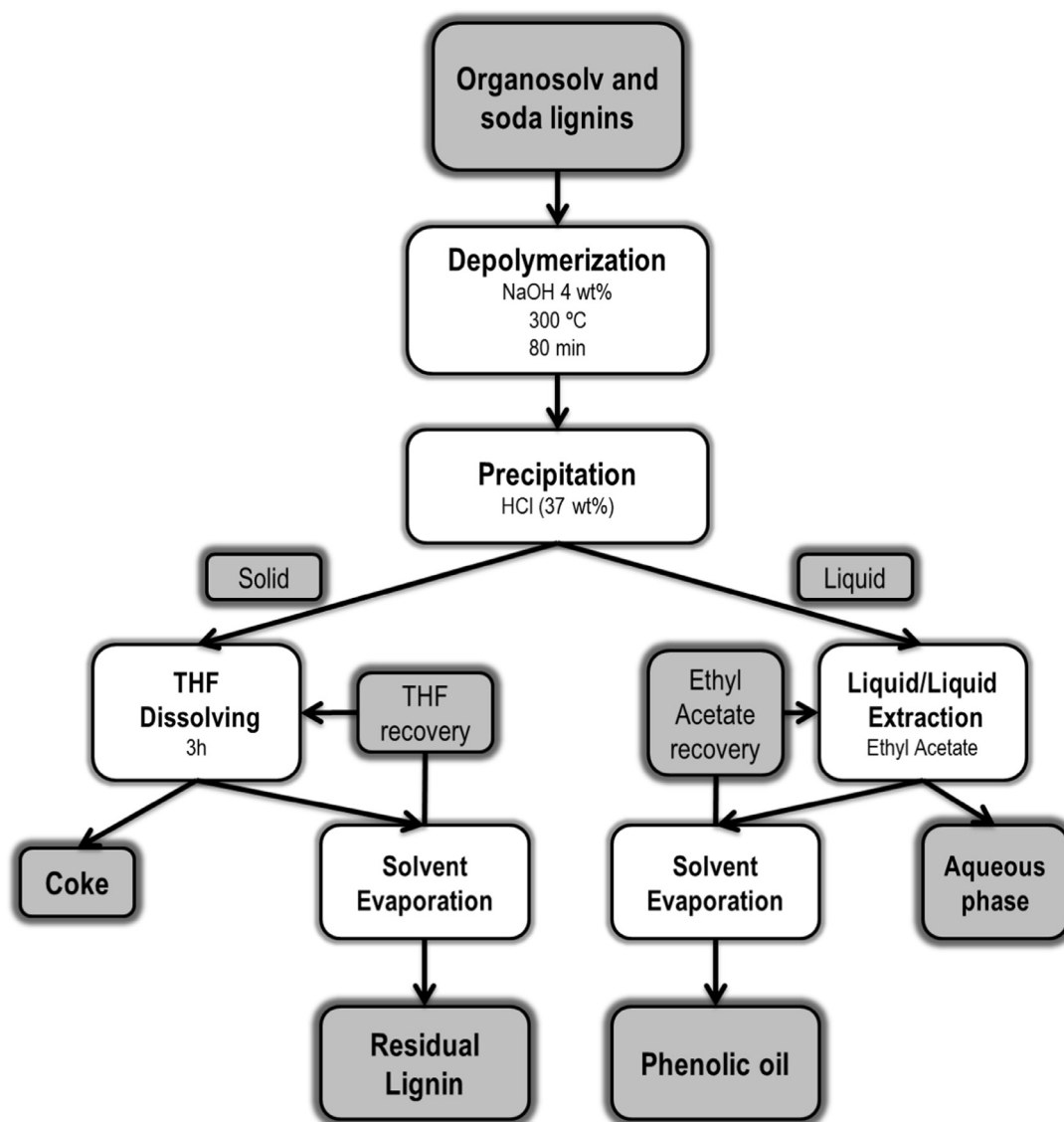


Fig. 1. Schematic process of the lignin depolymerization and separation of the reaction products.

280 °C at 10 °C/min, kept 8 min, raised to 300 °C at 10 °C/min and kept 2 min. Helium was used as carrier gas. Calibration was done using pure compounds (Sigma-Aldrich) phenol, *o*-cresol, *m*-cresol, *p*-cresol, guaiacol, catechol, 3-methylcatechol, 4-methylcatechol, 4-ethylcatechol, 3-methoxycatechol, syringol, 4-hydroxybenzaldehyde, acetovanillone, veratrol, 4-hydroxybenzoic acid, 4-hydroxy-3-methoxyphenylacetone, vanillin, vanillic acid, syringaldehyde, 3,5-dimethoxy-4-hydroxyacetophenone, syringic acid and ferulic acid.

3. Results and discussions

3.1. Characterization of solid fractions

The chemical macrocomponents of A and O (cellulose, hemicelluloses, lignin, ashes and extractives) were quantified before and after each stage to assess the selectivity of these methods over the chemical structure of both feedstocks. The results are presented in the Fig. 2.

Initially, in the comparison of the raw materials used in this study, the most remarkable issue is the high content of lignin in A (~50%) while the O presented less than 25%; i.e. more than double

quantity of lignin is available for A than O. On the contrary, cellulose, hemicellulose and extractives content are significantly bigger in percentage in O than in A. Hence, it could be established that A is really interesting to be valorized based on its high lignin content, whereas O could be more attractive in its carbohydrate platform. In any case, both materials were subjected to the whole process to obtain and depolymerize lignin.

In the autohydrolysis pretreatment, the hemicellulose content was reduced for both materials (54% and 71% for A and O respectively), increasing the lignin percentage in the feedstock which was sent to the delignification stage, especially significant for O (70.8%), whereas for A this amount was notably lower (4.52% of increase), which is caused mainly for the initial composition of the raw materials, since A presented lower hemicelluloses content, therefore, much less amount could be removed, and consequently less increase of lignin percentage. In spite of this lower increment, the total amount of lignin per gram of material continues to be higher for A after the pretreatment, concretely 53.2% against 38.1% of the O.

Both pulping processes (organosolv and soda) extracted mainly lignin from the different feedstocks as it was expected. However, depending on the feedstock the selectivity of the pulping process

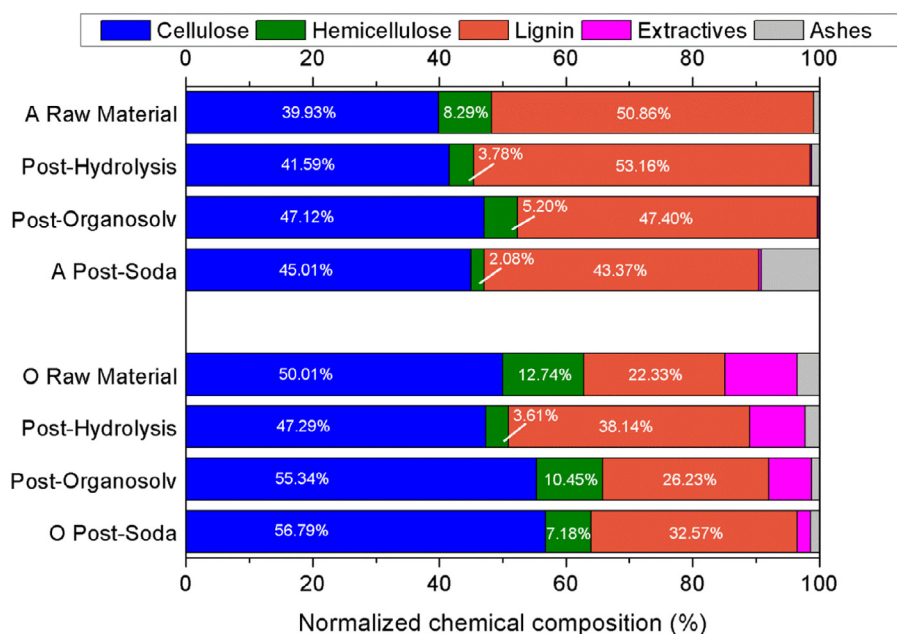


Fig. 2. Chemical characterization of solid fractions after each stage (% on an oven-dry weight basis).

Table 1. Lignin extraction and isolation yield, chemical composition of each purified lignin, and average molecular weight (M_w) and molecular weight distribution (M_w/M_n). AIL: acid insoluble lignin. ASL: acid soluble lignin.

Lignin	Yield (%)	AIL (%)	ASL (%)	Sugars (%)	Ash (%)	M_w (g/mol)	M_w/M_n
AS pH = 2	39.31	85.76 ± 2.72	2.64 ± 0.57	1.11 ± 0.11	7.55	27.32	12.33
AS pH = 4	41.02	91.20 ± 5.34	2.08 ± 0.69	1.54 ± 0.64	7.37	22.74	11.39
AS pH = 6	37.43	94.22 ± 4.51	2.12 ± 0.49	1.92 ± 0.16	9.28	33.19	15.48
AO 1 vol	11.59	98.83 ± 1.03	0.90 ± 0.54	0.23 ± 0.01	3.71	5713	2.98
AO 2 vol	17.18	99.75 ± 1.76	0.64 ± 0.09	0.27 ± 0.07	3.27	4381	3.03
AO 4 vol	19.93	96.12 ± 3.70	1.09 ± 0.27	0.25 ± 0.02	2.44	4166	3.18
OS pH = 2	41.31	88.04 ± 1.21	2.59 ± 0.11	0.18 ± 0.06	4.21	20.41	12.01
OS pH = 4	44.04	93.12 ± 4.60	2.28 ± 0.37	0.20 ± 0.09	4.95	16.28	10.43
OS pH = 6	46.92	92.23 ± 2.41	1.90 ± 0.30	0.17 ± 0.03	8.76	18.15	11.53
OO 1 vol	8.49	99.55 ± 0.83	0.73 ± 0.15	0.19 ± 0.08	3.30	6530	3.94
OO 2 vol	11.16	94.70 ± 2.30	1.20 ± 0.13	0.19 ± 0.04	1.96	5164	3.89
OO 4 vol	8.96	95.24 ± 0.90	1.16 ± 0.20	0.20 ± 0.05	3.31	4725	3.89

to extract lignin varied. In case of A, soda pulping was more effective with a reduction of 18.4% whereas for organosolv process the reduction in the solid material was only 10.8%. On the other hand, O feedstock, presented higher level of lignin content in the final solid after each pulping process (14.6% for soda and 31.2% for organosolv), this involves a higher selectivity of lignin extraction methods used in this work for O feedstock, without disrupting the most important content of cellulose and hemicellulose; even when the lignin content was lower and the carbohydrates content higher.

After the pulping stage, the isolation of lignin was carried out, determining the yield of the processes to extract lignin from the materials introduced in the pulping processes, neglecting autohydrolysis pretreatment for this calculation. All the lignin samples were also physico-chemically characterized to establish the better pathway to produce lignin with more interesting quality properties. These values, precipitation yield and physico-chemical properties of the different lignin samples are summarized in Table 1.

Lignin extraction yields show that the highest quantities of lignin were obtained with soda treatment (up to 47% for OS pH = 6). Therefore, in spite of soda process was less selective to the lignin extraction, in terms of total volume extracted was higher. On the contrary, the organosolv method showed low yields of lignin extraction and isolation (between 8% and 20%), exhibiting a poorer performance for extract as much lignin as possible. The higher yields from soda process can be explained by the fact that

the dissolution of lignin fragments is facilitated by the action of NaOH, which ionizes aliphatic hydroxyls groups as well as phenolic groups, contributing to the solubility of lignin fragments [33]. The modification of the feedstock does not remark any clear trend. For instance, the same raw material (O) presented the highest isolation yields in soda process in comparison with the rest of samples, but also the lowest yields were obtained from O as lignocellulosic source after organosolv pulping in this case. This involves that the feedstock is not the determining variable to extract more lignin.

The purity of the lignin was measured considering the sum of AIL and ASL. The values for all obtained samples showed a minimum purity of 88%, a really high value, demonstrating the importance of the pretreatment stage which was the main difference in comparison with previous studies [34,35], lignin samples and, in general, the lignin amount precipitated with less volumes since in this pretreatment one of the main component that could be considered as impurity in the lignin samples (the sugar content) was notably reduced leading to a lignin samples with absolutely low sugar impurities. The best results were obtained for organosolv of acidified water presented almost a 100% of purity. The isolated lignin samples from the soda liquors presented lower purity contents, with values between 88% and 95%, being higher the content in for samples extracted with greater pH level of precipitation, since with more addition of acid more species (mainly inorganic salts) could have precipitated contaminating the

precipitated lignin samples. Despite of the lower purity of the soda lignin samples, the purity of these samples is certainly high, fact that makes the soda process an attractive method to extract lignin with high performance keeping a quite elevated level of purity of the final lignin samples.

The lignin impurities present in the samples were mainly composed by sugars and ashes. The small impurities of hemicellulosic monomers were more noticeable in lignin samples obtained from A than in the ones obtained from O. On the other hand, soda lignin samples presented the highest amounts of total sugars content, since the organosolv process is more selective for lignin extraction as it was showed below, interacting in less degree with sugars from hemicelluloses. The lowest sugar concentration results were achieved with the lowest pH level of precipitation due to the linkages between lignin and attached sugars could be damaged at these acid conditions. This fact justifies the use of the pretreatment stage, as the major monomer sugar presented in the precipitated lignin samples came from the hemicelluloses. Hence, the fewer amounts of hemicelluloses in the feedstock, the less sugar impurities over the lignin were obtained.

Respect to the ash content, as it was expected, less content was found in the lignin samples obtained from the organosolv process, whereas the soda treatment produced samples with more impurities based on the inorganic chemicals used in the white liquor as well as in the precipitation method. Lignin obtained after organosolv treatment presented similar results at different conditions and for both raw materials (between 1.96% and 3.71%). In the soda process, the lignin samples obtained at pH = 6 presented the highest quantity of ashes (9.28% and 8.76%).

Regarding the molecular weights and molecular weight distributions, the lignin samples obtained from AO and OO, presented very low M_w (4166 g/mol for AO 4 vol as minimum value) and polydispersity index (2.98 for AO 1 vol), in agreement with values published by other authors that used the organosolv method to isolate lignin from lignocellulosic biomass [36]. Nonetheless, AS and AO lignin samples presented the highest M_w and polydispersity index (up to 33,190 g/mol and 15.48 respectively, for AS pH 2). This fact could be justified because higher temperatures and longer reaction times were used in organosolv treatment in comparison to the soda method ones. According to Zhang et al. [37], using harsh reaction conditions could lead to the obtaining of lower size lignin samples, owing to the fact that the degree of cleavage of the ether bonds in the lignin molecule can increase. In addition, in organosolv pulping the extraction of lignin is carried out by its solubilization in the solvent media. In this process, the lower molecular weight of lignin molecules, the easier are extracted due to the steric impediment to the solvent to dissolve lignin tends to be increased when molecules are bigger [38]. Hence, as the yield of lignin extraction from organosolv process is quite lower than soda one, lignin fractions with higher molecular weight are more difficult to be extracted by this method. In case of soda lignin samples, repolymerization reactions can occur under high alkaline conditions, since some α -hydroxyl groups form quinone methide intermediates that react easily with other lignin fragments lead to alkali-stable methylene linkages than affect considerably to the M_w of extracted lignin [39].

In the case of organosolv lignin samples, OA and OO showed higher M_w adding less volumes of acidified water. This behavior could be explained due to the fact that at higher M_w lignin fractions are less soluble than the lower fractions ones, precipitating faster with less solvent alteration, i.e., with lower water addition. On the contrary, lower M_w lignin fractions needed larger quantity of water to achieve precipitation. However, in the soda lignin samples, the highest M_w values were obtained by precipitating at pH 2 instead of pH 6. In general, the use of higher amounts of acid to precipitate generates lignin samples with smaller M_w , whereas the

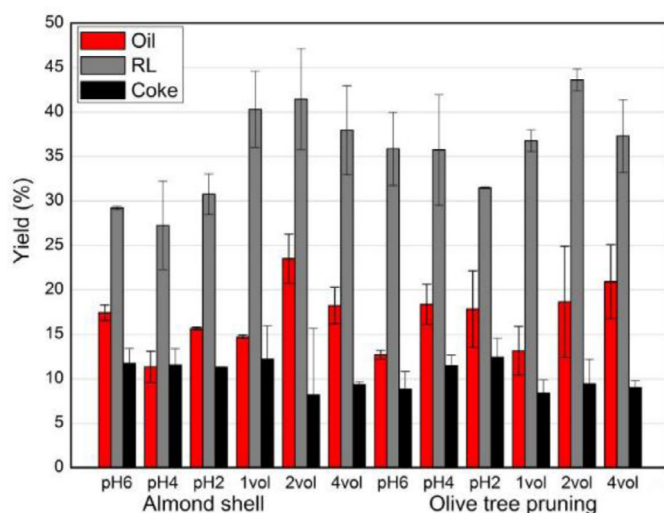


Fig. 3. Product yields from the lignin depolymerization of the three main streams: phenolic oil, residual lignin (RL) and coke.

use of lower acid quantities results in lignin samples with higher M_w . Furthermore, the high polydispersity index presented by the samples indicated the presence of very different molecular weights fractions in the lignin.

Once all the lignin samples were completely characterized, they were used as raw materials for the phenolic monomers production by their depolymerization reaction.

3.2. Depolymerization product yields

As a result of the depolymerization reactions, three main products were obtained through the above described method: oil, enriched in small phenolic molecules, residual lignin and coke. An aqueous stream was also produced, which was characterized using a HPLC equipment. Only small quantities of acetic acid, formed by the degradation of sugars, were found (concentration lower than 0.1%), and hence this stream was neglected. This fact was expected due to the low amount of sugars in the precipitated lignin samples, main precursors of these components. The yields of the rest of streams are shown in the Fig. 3.

Regarding oil production, the target product of the reaction, the variation of the yields did not follow a clear trend. However, it can be established that the highest yields of oil (from 18.23% up to 23.5%) were obtained from the organosolv lignin samples, except those ones that had been precipitated using 1 volume of acidified water, whose yields were much lower (14.72% and 13.16%), caused by this higher M_w . Hence, the property of the M_w can be considered as one of the main key factor to obtain high yield for the oil production, since the low M_w presents the lignin sample, the highest yield is reached. In the case of the soda lignin samples, the trend was more complex, pointing the independency of the lignin precipitation pH value and the lignin source (almond shell or olive tree pruning).

The most abundant product was the residual lignin, regardless the lignin source, being around the double of the oil yield. This high amount indicates that the repolymerization of lignin is happening in parallel during the reaction, as it was described by Yuan et al. [40]. In terms of yield, the reactions carried out using organosolv lignin samples generated also higher quantities of residual lignin. This fact could be justified by the greater amount of salts that soda lignin samples contained, which could reduce the repolymerization reaction of the lignin. Hence, the lower salts content of the organosolv lignin samples was found to be a drawback for reducing the undesirable repolymerization reaction of the lignin. This

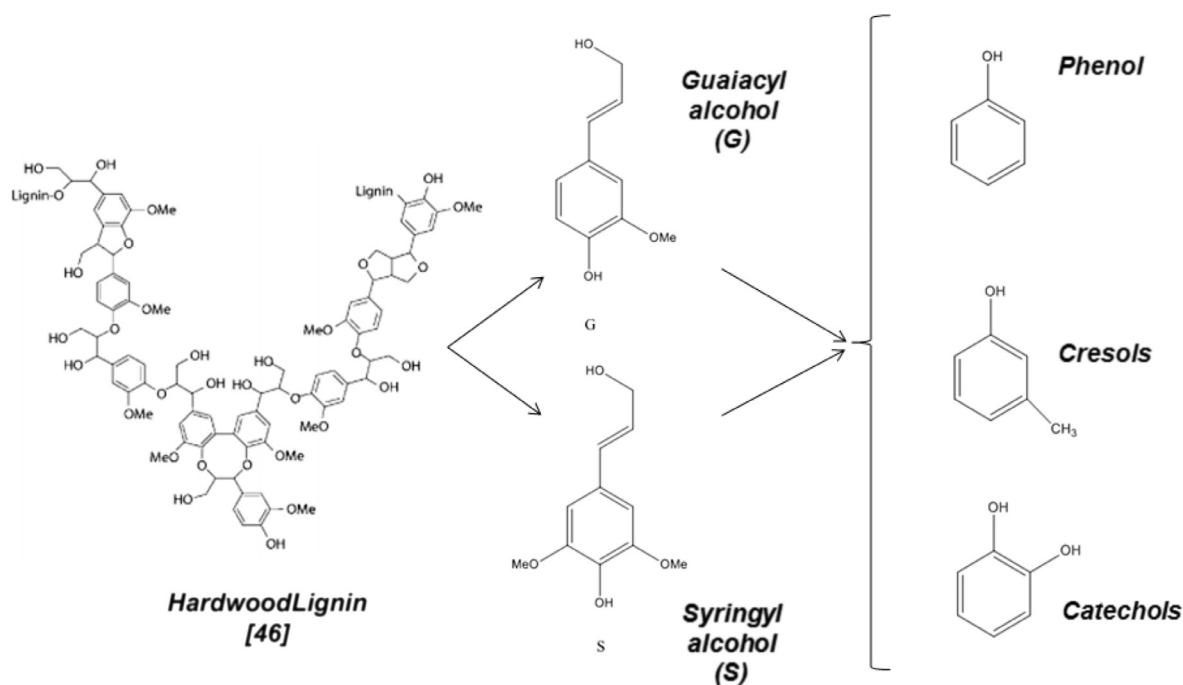


Fig. 4. Schematic mechanism of the undergone lignin depolymerization [46].

is countersigned by the highest value of residual lignin (43.62%), which was achieved from the lignin with lowest ash content (OO 2 vol).

In spite of residual lignin is not the most desirable product of the reaction, would allow its recirculation in the case of a continuous process or its valorization as a modified lignin, as it was published by Mahmood et al. [41], who proposed to use residual lignin as feedstock for polyurethane production since this residual lignin contained more hydroxyls groups than the initial one. Therefore, residual lignin can be considered as a byproduct of the reaction and not a waste product.

Coke is considered the most undesirable product of this reaction, as its potential for further valorization is more limited than the rest of the products. In this case, it was the fraction produced in less amount, although mitigate the generation of this component should be a goal in future works. Unfortunately, it was not possible to characterize this product due to the lower amount recovered after the reaction. In any case, coke is considered the most insoluble fraction that appears during the repolymerization, condensation and dehydration of small phenolic fractions as it was demonstrated by Long et al. [42] since the ratio of oxygen per carbon atom is lower than the initial lignin. As consequence, the solubility of this component is quite low due to its high condensed structure, making it a recalcitrant species. The yield values were around 8.20–12.45%, being lower for the lignin samples obtained from the organosolv process than the ones obtained by soda pulping. In contrast to the highest amount of residual lignin produced from organosolv lignin samples, the coke yield was reduced. Therefore, the pulping process should be decided in consonance with the undesirable product that would interest to produce in the lowest amount, however on the basis of considering less desirable the production of coke, in addition with the higher phenolic oil yield, lignin samples from organosolv process are more suitable to be depolymerized than soda ones. On the other hand, the independency of the precipitation process was remarkable, with coke yield values very similar for the lignin samples that were precipitated with different methods, without observing a clear tendency that would help to determine the best conditions for this stage.

3.2.1. Products characterization

In this work, not only the product yields were studied, the characterization of these products was also accomplished in order to know, besides the efficiency of the process, the quality and properties of the different resulting streams. Thus, the characterization of the three main components evaluated above will be developed thereupon.

3.2.1.1. Phenolic oil. As it was mentioned before, lignin is composed by three main monomer units. However, lignin from hardwood species, as it is the case of the species used in this work (*P. amygdalus* and *O. europaea*); present only two of these monomers: guaiacyl alcohol (G) and syringyl alcohol (S). Despite lignin presents a wide variety of linkages, the most abundant (β -O-4 ether bond), which conforms around the 60% of the existent linkages, can be cleaved during the hydrothermal degradation of lignin [43]. Therefore, the results of the depolymerization reaction of the lignin lead to the formation of these monomers after the ether bond cleavage, as it was demonstrated by several studies [44]. However, if the lignin depolymerization reaction can be carried out under extremely harsh conditions and helped by a suitable catalyst, G and S can be converted into other simpler products, such as catechols, cresols and phenol [22]. Fig. 4 presents the mechanism of this reaction. These final products are well considered because of the wide applications as value-added building blocks which they can be used in, e. g., pharmaceutical, medical or polymers industries [45].

The amount of the phenolic monomers obtained during the reaction, which were measured by GC–MS analysis, are detailed in the Table 2.

The results confirm the harsh conditions of the reaction, since the major components were catechol and its derivatives (3-methylcatechol, 3-methoxycatechol, 4-methylcatechol, 4-ethylcatechol), followed by phenol and cresols (*o-m-p*-cresol) respectively. Finally, the measured quantity of G and S in the oils can be considered negligible, demonstrating that the monomers of lignin were converted into smaller products as it was aimed. Concretely, the great amount of catechol compounds made these

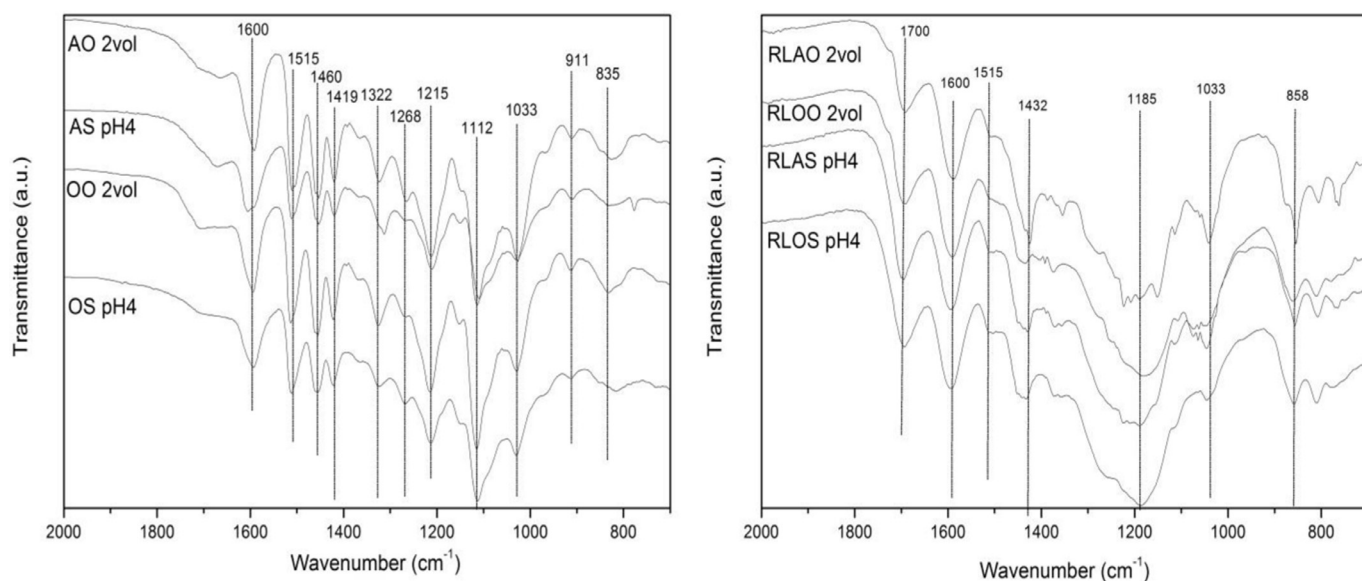


Fig. 5. FT-IR spectra of raw lignins (right side) and their corresponding residual lignins after the depolymerization process (left side).

Table 2. Monomeric phenolic compounds measured in the oil fraction after the reaction.

Lignin sample	Yield (% w/w)	Catechols (%)	Phenol (%)	Cresols (%)	Guaiacol (%)	Syringol (%)
AS pH = 6	6.20 ± 0.49	5.80 ± 0.55	0.25 ± 0.05	0.13 ± 0.01	0.02 ± 0.01	–
AS pH = 4	3.16 ± 0.74	2.85 ± 0.60	0.18 ± 0.06	0.11 ± 0.06	0.02 ± 0.01	–
AS pH = 2	6.32 ± 2.22	5.97 ± 2.14	0.23 ± 0.05	0.11 ± 0.02	0.02 ± 0.01	–
AO 1 vol	6.44 ± 0.63	6.01 ± 0.45	0.25 ± 0.09	0.12 ± 0.04	0.04 ± 0.04	–
AO 2 vol	8.27 ± 0.62	7.78 ± 0.47	0.31 ± 0.09	0.15 ± 0.04	0.02 ± 0.01	–
AO 4 vol	6.62 ± 0.84	6.24 ± 0.73	0.24 ± 0.06	0.12 ± 0.04	0.01 ± 0.00	–
OS pH = 6	3.11 ± 0.21	2.82 ± 0.17	0.16 ± 0.01	0.12 ± 0.03	0.01 ± 0.00	0.01 ± 0.00
OS pH = 4	4.56 ± 0.38	4.22 ± 0.34	0.19 ± 0.01	0.12 ± 0.01	0.02 ± 0.00	0.01 ± 0.00
OA pH = 2	4.91 ± 0.06	4.59 ± 0.05	0.19 ± 0.01	0.12 ± 0.01	0.02 ± 0.00	–
OO 1 vol	3.84 ± 1.29	3.65 ± 1.16	0.11 ± 0.09	0.07 ± 0.04	0.01 ± 0.00	–
OO 2 vol	3.91 ± 0.39	3.61 ± 0.34	0.18 ± 0.02	0.11 ± 0.03	0.01 ± 0.00	–
OO 4 vol	6.41 ± 0.63	6.06 ± 0.65	0.22 ± 0.01	0.13 ± 0.02	0.02 ± 0.00	–

Table 3. Molecular weight distribution of the initial lignin samples and those ones obtained as residual lignin after the depolymerization reaction.

Residual lignin sample	M_w (g/mol)	M_w/M_n	Residual lignin sample	M_w (g/mol)	M_w/M_n
RLAS pH = 6	6253	7.14	RLOS pH = 6	5103	6.89
RLAS pH = 4	7892	7.54	RLOS pH = 4	4844	6.64
RLAS pH = 2	5031	6.07	RLOS pH = 2	4819	6.85
RLAO 1 vol	7311	8.15	RLOO 1 vol	6804	8.71
RLAO 2 vol	7004	7.73	RLOO 2 vol	5910	7.44
RLAO 4 vol	6535	7.34	RLOO 4 vol	5281	7.03

results very interesting as a pathway to obtain high value-added products from lignin with its further utilization.

Amongst the yields reached by each lignin samples used in the study, the almond shell lignin samples presented the highest yield values, over 6% in all the cases except for “AS pH 4”. For olive tree pruning lignin samples, the total yield values were always lower than 6%, with the exception of “OO 4 vol”. Regarding the difference between the pulping processes used for the lignin extraction, a clear trend was not found in the results. In the case of almond shell lignin samples, a slight increase in the yield for the organosolv lignin samples could be observed. Nevertheless, for the O, the variation of the yield was not associated to a clear influence. Finally, once again, it could not be found a clear trend for the variation on the obtained yields according to the precipitation methods used for the lignin isolation.

3.2.1.2. Residual lignin. The results of the molecular weight and the polydispersity index of the residual lignin samples produced after the initial lignin depolymerization are shown in Table 3.

Considering the M_w and M_w/M_n characterization of the initial lignin samples used for the survey of the depolymerization, whose values were represented in Table 1, there was a clear difference among the initial lignin samples obtained by means of the soda process, which presented significant higher values (more than 10,000 g/mol), with regard to those ones obtained by the organosolv process (around 4000–6000 g/mol). However, this difference was reduced for the residual lignin obtained after the reaction, presenting all the residual lignin samples a similar size and polydispersity values. This fact indicated that the mechanism of the undesirable repolymerization reaction through which residual lignin is produced, is similar regardless of the species of lignin used as raw material, due to the phenolate carbanions formed mainly from catechols and phenols in such alkaline conditions are not being blocked by an extra capping or blocking agent. As consequence, there is not a big difference in the yields of residual lignin and coke with regard to the lignin source neither in the nature of this fraction. The structure of this residual lignin is also analyzed by FT-IR spectrums and compared with initial raw lignin.

In Fig. 5 only the spectra of representative samples, both raw and residual lignins are shown. To include the spectra from all the samples would make more complex the understanding of the figure. Additionally, it was found that differences among sample from same raw material and pulping method, only with different isolation method, were not noticeable. Some similarities were observed between the raw and residual lignins but there are many changes which confirm that their structure is not the same. The peak at 1700 cm^{-1} characteristic stretching frequency of carbonyl group [42] is much more intense in the case of residual lignins. This could be due to the cleavage of β -O-4 ether bonds of the raw lignin during the depolymerization reactions that lead to an unstable fragments which in order to stabilize themselves, form a double bond between the carbon and oxygen creating the carbonyl group in the residual lignins. The peaks at 1515 and 1460 cm^{-1} related to benzene structural lignin absorbance almost disappeared in residual lignins spectra which suggests that these lignins have lower aromatic nature than the raw lignin. Otherwise, the C=O stretching in syringyl unit which appears at 1322 cm^{-1} is not detected in the residual lignins. In addition, the peak at 1215 cm^{-1} which is assigned to ring breathing with C–O stretching of both the syringyl and guaiacyl structures [47]; is only visible in raw lignin samples. Finally, the peaks at 911 and 835 cm^{-1} that only appeared in raw lignins spectra are attributed to C–H out of plane aromatic ring deformation and C–H out of plane in positions 2 and 6 of syringyl units [48]. All this indicates that the so-called residual lignin fractions have lower quantity of syringyl and guaiacyl units which have reacted during the depolymerization reactions and been transferred to the phenolic oil fraction. Hence, as the residual lignin presents a difference structure in comparison with the initial one, it can be established that the conversion of all raw lignin samples is total, generating the three main products described ahead.

4. Conclusions

The present research was focused on the development of a tailor made process for lignin extraction and its depolymerization to small phenolic compounds. The influence of the raw materials, the pulping process and the lignin precipitation stage on the structure and characteristics of the obtained lignin samples was studied in order to establish the best conditions for the obtaining of high purity lignin samples, enabling its further valorization.

The inclusion of an autohydrolysis pretreatment provided purer lignin samples (more than 88% for all the samples) since a considerable amount of hemicelluloses had been already removed prior to the delignification processes, reducing significantly the sugar impurities in the isolated lignin.

High lignin yields were achieved by the soda process, especially from olive tree pruning. Although the purity of these lignin samples was lower than organosolv lignin samples, soda lignin ones were found to be quite pure, with lignin percentages higher than 95% of the total sample composition in some of the cases. Hence, soda process was found to be the most suitable process in terms of lignin production and purity.

Considerable differences were observed in the molecular size distribution. Organosolv lignin samples presented lower values ($M_w < 7000\text{ g/mol}$, in all cases) than soda process ones ($M_w > 16,000\text{ g/mol}$). These small values for organosolv lignin samples enabled their depolymerization, since the smaller the initial molecule is, the highest yield of depolymerized products was achieved, remarking the importance of this property for lignin depolymerization. The polydispersity index followed this trend as well, with smaller values for organosolv samples (lower 4), than soda lignin (bigger than 10 for all the samples).

After their extraction and characterization, these lignin samples were subjected to a depolymerization reaction, producing three main streams: phenolic enriched oil, residual lignin and coke. Organosolv lignin samples presented higher yield values for phenolic oil (from 18.23% to 23.5%) in comparison with soda lignin samples. However, more residual lignin yield values (around 35%–45%) were achieved from organosolv ones, although the yield of coke was lower than in the soda ones. The undesirable repolymerization occurs following the same mechanism regardless the lignin sample used, since it was observed that the chemical composition of all residual lignin presented similar size and yield.

Focusing on the composition of the phenolic oil, the most abundant monomer types found in the oil were the catechols derivatives demonstrating that the guaiacol and syringol, main products of the lignin depolymerization, had been degraded into more elemental products due to the harsh conditions of the reaction. Almond shell samples presented higher yields than olive tree pruning ones; however regarding the different pulping processes and isolation methods, no clear influence was observed.

As summary, the main differences were found in the delignification process, being the soda treatment the most profitable, in terms of quantity, whereas organosolv process generated the highest purity lignin samples with lower M_w sizes, fact which could lead to the highest yields and better quality of the most desirable depolymerization product (phenolic oil). Hence, a compromise between the quantity, represented by the soda treatment, and the quality, reached in higher degree with the organosolv method should be defined for the design of the global process.

Acknowledgments

Authors would like to thank the Spanish Ministry of Economy and Competitiveness (CTQ2013-41246-R), the Department of Education of the Basque Government (project IT1008-16) and the University of the Basque Country (postdoctoral fellowship no. ESPDOC15/044) for financially supporting this work.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jechem.2017.02.007.

References

- [1] D. Savy, P. Mazzei, R. Roque, A. Nuzzo, S. Bowra, R. Santos, *Fuel Process. Technol.* 138 (2015) 637–644.
- [2] J. Pérez, J. Muñoz-Dorado, T.D.L.R. de la Rubia, J. Martínez, *Int. Microbiol.* 5 (2) (2002) 53–63.
- [3] J.X.W. Hay, T.Y. Wu, J.C. Juan, J.M. Jahim, *Energy Convers. Manage.* 106 (2015) 576–583.
- [4] J. Zakzeski, P.C. Bruijninx, A.L. Jongerius, B.M. Weckhuysen, *Chem. Rev.* 110 (6) (2010) 3552–3599.
- [5] R.J. Gosselink, J.E. van Dam, E. de Jong, E.L. Scott, J.P. Sanders, J. Li, G. Gellerstedt, *Holzforchung* 64 (2) (2010) 193–200.
- [6] N. Smolarski, Frost & Sullivan, 2012.
- [7] J. Lora, *Monomers, Polymers and Composites from Renewable Resources* Elsevier, Oxford, UK, 2008, pp. 225–241.
- [8] A. Van Heiningen, *Pulp Pap. Can.* 107 (6) (2006) 38–43.
- [9] S. Laurichesse, L. Avérous, *Prog. Polym. Sci.* 39 (7) (2014) 1266–1290.
- [10] A.G. Vishtal, A. Kraslawski, *BioResour* 6 (3) (2011) 3547–3568.
- [11] W. Qiao, S. Li, *J. Ind. Eng. Chem.* 21 (2015) 1417–1422.
- [12] S.M. Yáñez, B. Matsuiro, C. Nuñez, S. Pan, C.A. Hubbell, P. Sannigrahi, A.J. Ragauskas, *Polym. Degrad. Stabil.* 110 (2014) 184–194.
- [13] D. Stewart, *Ind. Crops Prod.* 27 (2) (2008) 202–207.
- [14] M. Nagy, M. Kosa, H. Theliander, A.J. Ragauskas, *Green Chem* 12 (1) (2010) 31–34.

- [15] T.Q. Yuan, J. He, F. Xu, R.C. Sun, *Polym. Degrad. Stabil.* 94 (7) (2009) 1142–1150.
- [16] W.J. Huijgen, J.H. Reith, H. den Uil, *Ind. Eng. Chem. Res.* 49 (20) (2010) 10132–10140.
- [17] T. Aysu, M. Masuk Küçük, *Energy* 64 (2014) 1002–1025.
- [18] A.J. Ragauskas, G.T. Beckham, M.J. Biddy, R. Chandra, F. Chen, M.F. Davis, B.H. Davison, R.A. Dixon, P. Gilna, M. Keller, P. Langan, A.K. Naskar, J.N. Saddler, T.J. Tschaplinsky, G.A. Tuskan, C.E. Wyman, *Science* 344 (6185) (2014) 1246843.
- [19] J.Y. Kim, J. Park, H. Hwang, J.K. Kim, I.K. Song, J.W. Choi, *J. Anal. Appl. Pyrol.* 113 (2014) 99–106.
- [20] C. Xu, R.A.D. Arancon, J. Labidi, R. Luque, *Chem. Soc. Rev.* 43 (22) (2014) 7485–7500.
- [21] P. Azadi, O.R. Inderwildi, R. Farnood, D.A. King, *Renew. Sustainable Energy Rev.* 21 (2013) 506–523.
- [22] X. Erdocia, R. Prado, M.A. Corcuera, J. Labidi, *Biomass Bioenergy* 66 (2014) 379–386.
- [23] V. Roberts, V. Stein, T. Reiner, A. Lemonidou, X. Li, J.A. Lercher, *Chem. Eur. J.* 17 (21) (2011) 5939–5948.
- [24] T.J. McDonough, *Tappi J* 76 (1993) 186–193.
- [25] C. Sánchez, L. Serrano, M.A. Andres, J. Labidi, *Ind. Crop Prod.* 42 (2013) 513–519.
- [26] A. Toledano, L. Serrano, J. Labidi, *Ind. Eng. Chem. Res.* 50 (2011) 6573–6579.
- [27] I. Urruzola, E. Robles, L. Serrano, J. Labidi, *Cellulose* 21 (3) (2014) 1619–1629.
- [28] X. Erdocia, R. Prado, M. Corcuera, J. Labidi, *Front. Energy Res.* 2 (13) (2014) 1–7.
- [29] A. Toledano, L. Serrano, J. Labidi, *Fuel* 116 (2014) 617–624.
- [30] TAPPI Standards. TAPPI Test Methods, Atlanta; 2007.
- [31] L.E. Wise, M. Murphy, A.A. D'Adieco, *Paper Trade J.* 22 (1946) 34–44.
- [32] R.M. Rowell, American Chemical Society, Washington DC 84 (1984).
- [33] D. Dimmel, G. Gellerstedt, in: C. Heitner, D. Dimmel, J.A. Schmidt (Eds.), *Lignin and Lignals: Advances in Chemistry*, CRC Press, Boca Raton, USA, 2010, pp. 349–392.
- [34] O. Gordobil, I. Egüés, R. Llano-Ponte, J. Labidi, *Polym. Degrad. Stabil.* 108 (2014) 330–338.
- [35] A. Sequeiros, D.A. Gatto, J. Labidi, L. Serrano, *J. Biobased Mater. Bioenergy* 8 (3) (2014) 370–376.
- [36] A. Toledano, I. Alegría, J. Labidi, *Biomass Bioenergy* 59 (2013) 503–511.
- [37] J. Zhang, H. Deng, L. Lin, Y. Sun, C. Pan, S. Liu, *Bioresour. Technol.* 101 (2010) 2311–2316.
- [38] B. El Khaldi-Hansen, M. Schulze, B. Kamm, in: S. Vaz (Ed.), *Analytical techniques and methods for biomass*. Springer International Publishing, Cham, Switzerland, 2016, pp. 15–44.
- [39] G.H. Van der Klashorst, *Wood Adhes. Chem. Technol.* 2 (1989) 155–187.
- [40] Z. Yuan, S. Cheng, M. Leitch, C. Xu, *Bioresour. Technol.* 101 (2010) 9308–9313.
- [41] N. Mahmood, Z. Yuan, J. Schmidt, C.C. Xu, *Eur. Polym. J.* 68 (2015) 1–9.
- [42] J. Long, Y. Xu, T. Wang, Z. Yuan, R. Shu, Q. Zhang, L. Ma, *Appl. Energy* 141 (2015) 70–79.
- [43] J. Li, G. Henriksson, G. Gellerstedt, *Bioresour. Technol.* 98 (16) (2007) 3061–3068.
- [44] M.O. Bengoechea, A. Hertzberg, N. Miletić, P.L. Arias, T. Barth, *J. Anal. Appl. Pyrol.* 113 (2015) 713–722.
- [45] S. Cohen, P.A. Belinky, Y. Hadar, C.G. Dosoretz, *Bioresour. Technol.* 100 (7) (2009) 2247–2253.
- [46] Y. Gizaw, B.A.J. Hubesch, J.S. Dupont, X.J. Wang, L.A. Zannoni, U.S. Patent No. 8,075,637. Washington, DC: U.S. Patent and Trademark Office. 2011.
- [47] J. Long, Q. Zhang, T. Wang, X. Zhang, Y. Xu, L. Ma, *Bioresour. Technol.* 154 (2014) 10–17.
- [48] L. Chen, X. Wang, H. Yang, Q. Lu, D. Li, Q. Yang, H. Chen, *J. Anal. Appl. Pyrol.* 113 (2015) 499–507.