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Keywords: Black liquors, Lignin, Depolymerization, Phenol, Catechol.

DIRECT LIGNIN DEPOLYMERIZATION PROCESS FROM SULFUR-FREE BLACK LIQUORS

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Abstract

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Graphical abstract
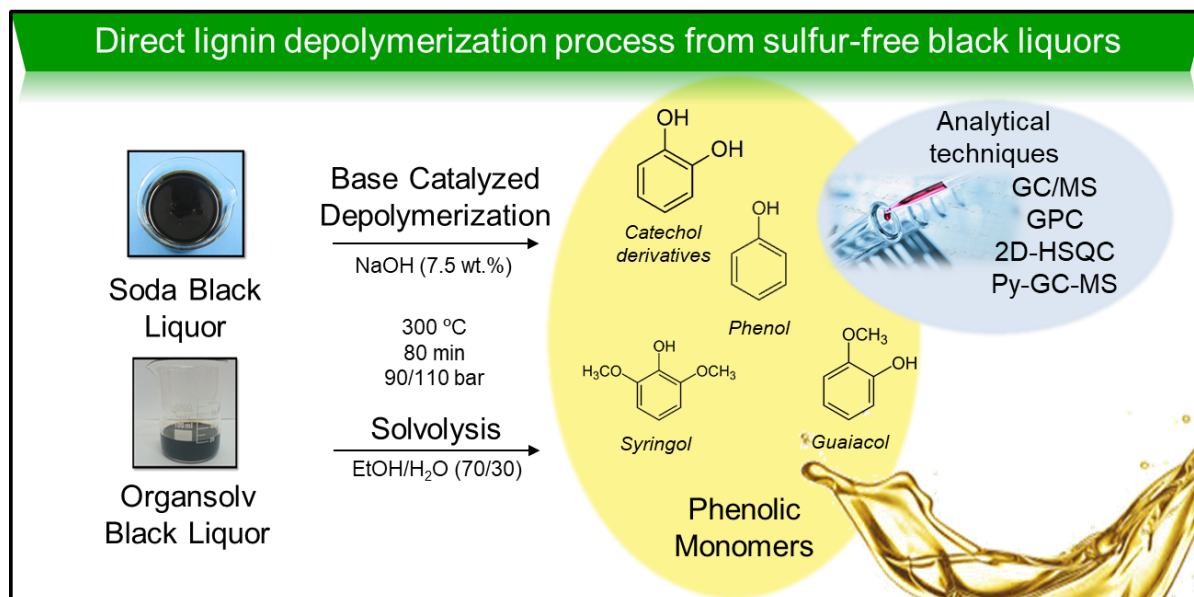
1. INTRODUCTION

Biomass waste valorization processes have also emerged in last years as an important trend in chemical engineering research. The transformation of feedstock initially intended as waste of low value added byproduct has been widely studied to maximize or guarantee the feasibility of the current processes in which they are produced. For instance, the manufacturing of chemical precursors could be a solution to build up high-added value products from these biomass wastes. However the main barriers could arise from the competition of fossil resources, in which production costs are cheaper so far. Therefore, not only the transformations of biomass waste to value-added products are important but also the cost reduction in these processes by their optimization [1].

One clear example of this scenario can be observed in pulp and paper industry, the largest producer of lignin, where lignin is treated as a waste and burned for steam and power generation in most of cases. Lignin is the second most abundant natural polymer made up by the combination of three different phenylpropane monomer units, namely guaiacyl alcohol, *p*-coumaryl alcohol and syringyl alcohol. These phenylpropane units form an amorphous three-dimensional structure and are linked mainly by an aryl-aryl ether linkage [2]. However, the aromatic structure of the lignin, unique in nature, makes it a suitable candidate to be catalytically transformed into low molecular weight phenolic compounds which may substitute petroleum based compounds [3,4].

Lignin can be extracted from lignocellulosic biomass by several methods. Among sulfur-free delignification treatments, alkaline and organosolv processes have received considerable attention as they allow the obtaining of a lignin rich black liquor [5,6]. The production of high-

added value phenolic compounds from black liquor involves the transformation of lignin into much smaller molecules. Alkaline and organosolv lignins have been found to be a suitable raw material for producing low molecular weight compounds like vanillin, simple and hydroxylated aromatics, quinines, aldehydes, aliphatic acids and many others [7]. A number of thermochemical conversion methods have been proposed to depolymerize lignin to low-molecular weight compounds. Among them, base-catalyzed hydrolysis, pyrolysis (lignin to liquid, LtL), hydrogenolysis or oxidation have been deeply studied [8].

In most of the works developed so far, the depolymerization of lignin has been carried out after its precipitation and isolation. Nenkova et al. [9] carried out the alkaline hydrolysis of solid lignin and stated that the best conditions for lignin's depolymerization were 180 ºC, 5% of NaOH, hydromodule of 1:10 and treatment duration of 6 hours. Alkaline lignin degradation in hot-compressed water and ethanol has been accomplished and it was successfully degraded into oligomers with NaOH as catalyst and phenol as capping agent [10]. However, complete suppression of char formation could not been achieved. On the other hand, alkaline hydrolysis of Alcell® lignin using KOH in supercritical methanol or ethanol has also been performed [11]. In this study, it was concluded that the reaction was favored by the used of strong bases and that the combination of bases gave either positive or negative synergistic effects. Furthermore, the analysis of products from model compound reactions revealed that phenyl ether linkages were effectively broken in the base catalyzed depolymerization (BCD) reaction while carbon-carbon linkages were less affected. Roberts et al. [12] concluded that, in alkaline depolymerization of lignin, ether bonds are hydrolyzed at random, most likely from the outside of the oligomer and not in the sequence of their bond strengths, forming first large units and then smaller subunits. In addition, they stated that the formation of monomers is proportional to the concentration of sodium hydroxide in the aqueous medium in the range between 1 and 4 wt.% of NaOH. Furthermore, a mechanism for the NaOH catalyzed breakdown of the ether bonds of lignin is proposed explaining the preferential formation of derivatives of syringol, based on the stabilizing effect that the methoxy groups provide to the transition states of the carbenium ions.

More recently, hydrothermal degradation of an alkali lignin was achieved in sub/supercritical ethanol-water or pure ethanol with and without a catalyst [13]. The most effective solvent combination for lignin degradation into smaller molecules was 50/50 (v/v) water-ethanol co-solvent. In the mentioned work, it was also stated that, at low temperature, there was not sufficient energy to break lignin ether bonds, since no degraded products from lignin were measured after 2 h of reaction at 200 ºC. However, degradation was optimal at 300 ºC for 2 h with 89% yield of degraded lignin, although~~but that~~ high temperatures lead to re-condensation

and char formation. Besides ethanol, other alcoholic solvents have also been used for lignin depolymerization, such as methanol, butanol [14]. High yield of liquid product (75.8%) and phenolic compounds (38.1%) can be obtained from depolymerization of lignin over metal chloride and solvent alcohol. Phenolic monomers have also been produced after the depolymerization process of heavy fraction of bio-oil obtained from biomass pyrolysis [15]. Upgrading of this heavy fraction of bio-oil was carried out in catalytic hydrothermal process with Ru-based catalyst and super/subcritical ethanol obtaining monomeric phenolic and hydrocarbons in a yield above 40%.

In some other studies, lignin has been depolymerized directly from the woody biomass where lignin fractionation and conversion are proceeding simultaneously [16,17]. Van den Bosch et. al. [16] performed simultaneous solvolysis and catalytic hydrogenolysis of birch sawdust obtaining a lignin oil with more than 50% of phenolic monomers (mainly 4-n-propylguaiacol and 4-n-propylsyringol) and about 20% of a set of phenolic dimers. Lignin alkaline aerobic oxidation directly from poplar biomass has also been addressed [17]. At short reaction times, high temperatures, and high NaOH concentrations more than 30 wt% aromatic monomers were achieved from native poplar lignin.

However, besides all the works where solid lignin or native lignin from biomass has been depolymerized by alkaline hydrolysis or employing only water and ethanol as hydrolyzing agent, very few studies have been carried out using only the liquors from biomass delignification processes. Organosolv black liquor was submitted to a high temperature and pressure process after its conditioning removing most of the ethanol and concentrating it, obtaining phenolic monomer concentration around 20% of the oily stream, and syringol the most plenty compound [18]. The major compounds obtained were syringol and guaiacol but high quantity of char was undesirably produced. In another work, black liquors from alkaline delignification of biomass employing NaOH and KOH were also treated at high temperatures in order to hydrolyze the lignin [19]. In this case, the black liquors were also concentrated, removing half of the water, prior to their treatment. In this case, the main compound obtained after lignin hydrolysis was catechol in an amount higher than 1.5% concentration in the olily stream, and considerable amounts of phenol and cresols were also reported.

The aim of the present work has been to depolymerize the lignin contained in organosolv and soda black liquors without precipitating it, making the process cheaper and more direct, as the reactants of the delignification of the biomass (NaOH, water and ethanol) are employed for the depolymerization as well. In this sense, the intensification of the lignin valorization process by the removal of some stages was studied. For this purpose, organosolv and soda black liquors from almond shell and olive tree pruning delignification processes carried out in a previous work [20] were subjected to a depolymerization reaction at 300 ºC for 80 min without any

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previous conditioning. The end products (phenolic oil, residual lignin and char) were quantified to identify the product yields of the reactions as well as characterized by different techniques, such as Gas Chromatography-Mass Spectroscopy (GC/MS), Pyrolysis-GC-MS, 2D HSQC NMR and Gel Permeation Chromatography (GPC).

2. MATERIALS AND METHODS

2.1. Black liquors characterization

Black liquors from delignification process of almond shell and olive tree pruning were characterized prior to its transformation. For each raw material two delignification processes were performed: soda and organosolv. The conditions of these two treatments are described in a previous work [20]. Density was determined measuring the weight of the black liquor in a known volume previously weighed. Dry content was determined using a method based on TAPPI T264 cm-97. Inorganic matter was determined after combustion of the sample at 525 $^{\circ}$C using a method based on TAPPI T211 om-93 to determinate the ash content. Organic matter was determined by the difference between dry content and the inorganic matter. Lignin dissolved in the different liquors was calculated by its precipitation at pH = 2 using H_2SO_4 (96 wt.%) as acid agent in case of soda process and adding 2 volumes of acidified water (pH = 2) for organosolv process.

Characterization of lignin extracted by these methods as well as obtained yields were also connected with the evaluation of the energetic efficiency of both processes, using the calculation of the severity factor (R_0), which has been traditionally used in pulp and paper industry to compare reactions when the kinetic of the reaction is considered as pseudo first order reaction [21]. This index is described by Eq. (1), with only time and temperature considered as influential variables.

$$\text{Log}\,(\,R_0\,) = \text{Log}\left(\,t \cdot \exp\left(\frac{T(t)-100}{14.75}\right)\right) \tag{1}$$

The value of 100 corresponds to the reference temperature and 14.75 is the fitted value of the arbitrary constant ω, which is based on the activation energy when assuming pseudo first order kinetic [22]. Despite this constant can be optimized, is commonly used with the value of 14.75 [23]. However, this equation does not take into account that extreme acid or alkaline conditions plays an important role to increase this factor, i. e., affecting to the efficiency of the process. In Eq (2) is included the influence of pH on this factor [24].

$$\log\left(R_0''\right) = \log\,(\,R_0\,) + |\,\text{pH-7}| \tag{2}$$

Although kinetic of reactions during delignification stage has not been demonstrated to follow this order, these parameters were estimated to compare previous processes from which black liquors were obtained.

2.2. Lignin direct depolymerization from black liquors

The black liquors were subjected to two reaction mechanism lignin depolymerization. BCD mechanism was used in the case of soda black liquor and solvolysis for organosolv black liquors. In this way, the media used to extract lignin was also leveraged to its further depolymerization as reagents, simplifying and intensifying the global process for lignin valorization. Both treatments were applied to almond shell and olive tree pruning liquors with the aim of obtaining relevant information about the influence of the raw material in the process and its capacity to process, with similar results, different biomass sources. The reactions were carried out in a batch reactor – 5500 Parr reactor – with a 4848 Reactor controller. The reaction conditions were 300 ºC and 80 minutes with constant stirring and reaching pressure values of 90 bar, in the case of soda liquors and 110 bar, in the case of organosolv liquors. The quantity of liquor introduced in each case was around 20 g. These conditions were kept equal to the prior work where depolymerization was accomplished from isolated lignin by BCD to be capable to establish an evaluation on the different efficiency obtained by the removal of the precipitation and solubilization stages that was approached in this work. Time to reach reaction temperature was really similar among different experiments accomplished, 100 min to reach the temperature and 70 minutes to cooling down before opening the reactor.

2.3. Products separation process

After the reaction, the liquid solution in the batch microreactor was treated in order to separate the products. Firstly, HCl at 37% wt. was added until pH = 2 was reached when soda liquors were used as reaction raw material. In the case of organosolv liquors, 2 volumes of acidified water (pH = 2) were added. Consequently, residual lignin and coke precipitated enabling their separation from the liquid by filtration.

The liquid fraction was subjected to a liquid-liquid extraction process with ethyl acetate. Sodium sulfate anhydrous was added to the organic phase in order to remove the traces of water and then it was filtered. This organic phase was vacuum evaporated in order to remove the ethyl acetate, obtaining an oil which contained the phenolic base products.

The previous solid phase was washed with tetrahydrofuran (THF) and was stirred for 3 hours in a beaker to separate residual lignin (RL) from coke. Then, it was filtered and the undissolved solid (coke) was oven-dried at 50 ºC. The THF solution was vacuum evaporated to fractionate the solvent and the RL (see Fig. 1).
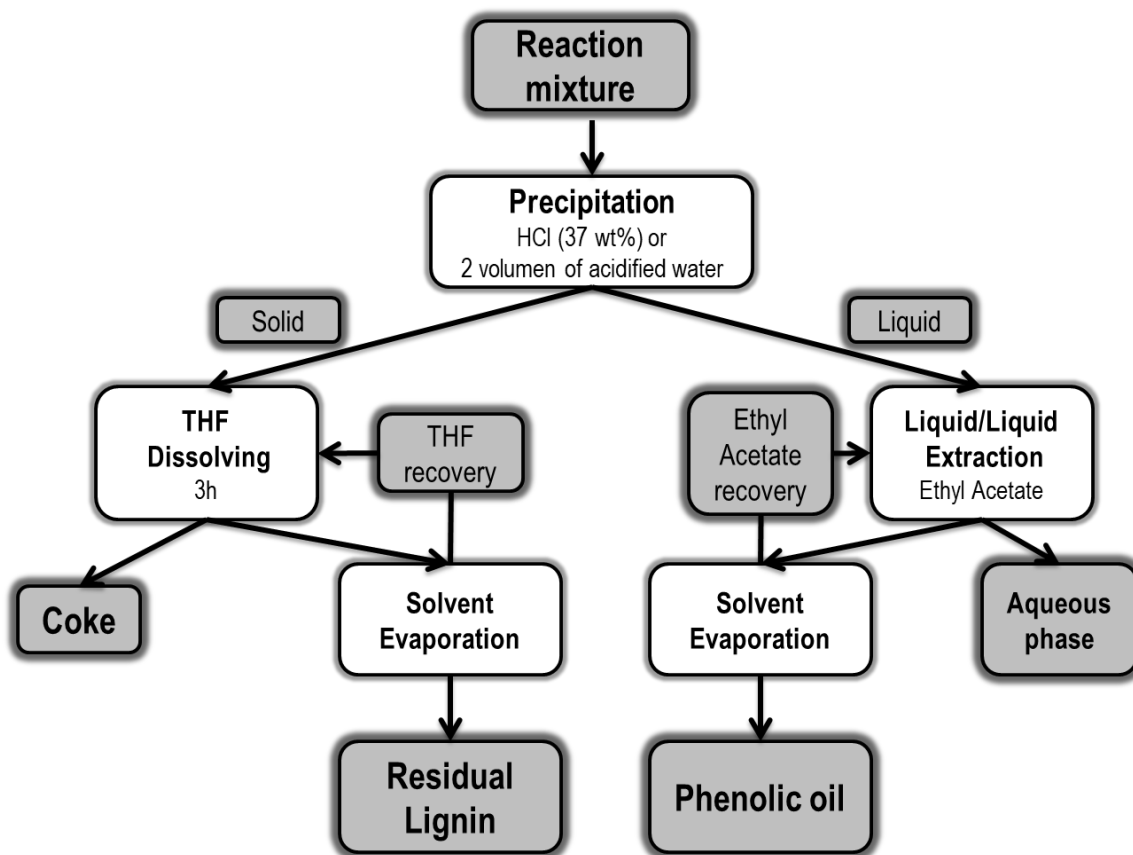
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Fig 1. Separation sequence for product isolation after depolymerization process.

The product yields were calculated on a weight basis using the following equations:

$$\text{Yield}_{\text{oil}} = \frac{\text{mass}_{\text{oil}}}{\text{mass}_{\text{organic content}}} \times 100 \tag{3}$$

$$\text{Yield}_{\text{residual lignin}} = \frac{\text{mass}_{\text{residual lignin}}}{\text{mass}_{\text{organic content}}} \times 100 \tag{4}$$

$$\text{Yield}_{\text{coke}} = \frac{\text{mass}_{\text{coke}}}{\text{mass}_{\text{organic content}}} \times 100 \tag{5}$$

2.4. Analysis of reaction products

The different black liquors studied in this work were characterized prior to its treatment at high temperature and pressures. Density was determined measuring the weight of the black liquor in a known volume previously weighed. Total dissolved solids (TDS) were determined using a method based on TAPPI T264 cm-97 to determinate the moisture content. Inorganic matter was determined after combustion of the sample at 525 ºC using a method based on TAPPI

T211 om-93 to calculate ash content. Organic matter was determined by the difference between total dissolved solids and inorganic matter. Lignin content was estimated by its precipitation, considering that all lignin is isolated. To this, a precipitation with H_2SO_4 (pH = 2) was carried out and then filtered through a 0.45 mm nylon filter. Finally the precipitated lignin was washed twice with acidified water (pH = 2) and then dried at 50 ºC. Lignin content was gravimetrically calculated.

Lignin isolated from black liquors as well as residual lignin recovered after the liquor treatment were subjected to Gel Permeation Chromatography (GPC) to evaluate their average molecular weight (Mw), number-average molecular weight (Mn) and to see the molecular weight distribution (MWD) using a JASCO instrument equipped with an interface (LC-NetII/ADC) and a refractive index detector (RI-2031Plus). Two PolarGel-M columns (300 mm x 7.5 mm) and PolarGel-M guard (50 mm x 7.5 mm) were employed. The flow rate was 700 $mm^3 \cdot min^{-1}$ at 40 °C and N,N-dimethylformamide (DMF) was used as mobile phase. Calibration was made using polystyrene standards (Sigma-Aldrich) ranging from 70,000 to 266 g/mol.

Precipitated lignin samples were also characterized by Py-GC-MS using a 5150 Pyroprobe pyrolyzer (CDS Analytical Inc., Oxford, PA). The identification of the pyrolysis products was accomplished using a GC-MS instrument (Agilent Techs. Inc. 6890 GC/5973 MSD). The Py-GC-MS was carried out following the method described by Herrera and co-workers [25]. A quantity between 400-800 mg was pyrolyzed in a quartz boat at 600 ºC for 15 s with a heating rate of 20 ºC/ms (ramp-off) with the interface kept at 260 ºC. The pyrolyzates were purged from the pyrolysis interface into the GC injector under inert conditions using helium gas. The fused-silica capillary column used was an Equity-1701(30 m x 0.20 mm x 0.25 µm). The GC oven program started at 50 ºC and was held for 2 min. Then it was raised to 120 ºC at 10 ºC/min and was held for 5 min after that raised to 280 ºC at 10 ºC/min. was held for 8 min and finally raised to 300 ºC at 10 C/min and was held for 10 min. The compounds were identified by comparing their mass spectra with the National Institute of Standards Library (NIST) and with compounds reported in the literature [26–30]

For the 2D HSQC NMR, around 50 mg of lignin was dissolved in 0.5 mL of DMSO-d_6. 2D HSQC NMR spectra were recorded at 25 ºC in a Bruker AVANCE 500 MHz equipped with a z-gradient double resonance probe. The spectral widths for the HSQC were 5000 and 12300 Hz for the ^1H and ^{13}C dimensions, respectively. The number of collected complex points was 1024 for the ^1H dimension with a recycle delay of 1.5 s. The number of transients was 64, and 256 time increments were always recorded in the ^{13}C dimension. The 1JCH used was 145 Hz. Prior to Fourier transformation, the data matrices were zero filled to 2048 points in the ^{13}C dimension. Data processing was performed using MestReNova software. The central solvent (DMSO) peak was used as an internal chemical shift reference point (δC/δH 39.5/2.49).

Phenolic oil was characterized based on the monomeric phenolic compounds that constituted this stream. 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 equipped with a capillary column HP-5MS ((5%-Phenyl)-methylpolysiloxane, 30 m x 0.25 mm). The temperature program started at 50 ºC; then, the temperature was raised to 120 ºC at 10 K·min^{-1}, held at this temperature for 5 min, raised to 280 ºC at 10 K·min^{-1}, held 8 at this temperature for min, raised to 300 ºC at 10 K·min^{-1} and held at this temperature for 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 and syringic acid. The yield of each phenolic monomer was calculated as follows:

$$\text{Yield}_{\text{phenolic monomer}} = \frac{\text{mass}_{\text{phenolic monomer}}}{\text{mass}_{\text{lignin from the liquor}}} \times 100 \qquad (6)$$

3. RESULTS AND DISCUSSION

3.1. Black liquors characterization

The results of the characterization of the black liquors from soda and organosolv processes of almond shells and olive tree pruning are shown in Table 1.

Table 1.

Physico-chemical characterization of black liquors used in this work (AOL: Almond Organosolv Liquor; ASL: Almond Soda Liquor; OOL: Olive Organosolv Liquor; OSL: Olive Soda Liquor).

	AOL	ASL	OOL	OSL
Density (%)	0.85 ± 0.01	1.07 ± 0.00	0.86 ± 0.00	1.08 ± 0.01
pH	4.11 ± 0.01	13.89 ± 0.02	4.02 ± 0.03	13.77 ± 0.02
Dry content (%)	4.90 ± 0.06	14.99 ± 0.07	5.06 ± 0.11	15.29 ± 0.08
Organic matter (%)	4.86 ± 0.06	5.39 ± 0.07	5.01 ± 0.11	5.67 ± 0.05
Inorganic matter (%)	0.04 ± 0.00	9.60 ± 0.01	0.04 ± 0.01	9.61 ± 0.04
Lignin content (%)	4.70	4.57	4.79	4.73

As it was expected soda liquors presented a much higher inorganic matter content than organosolv liquors. This high percentage was due to the moderate quantity of sodium hydroxide introduced in the soda process while in the organosolv process none inorganic

compound was used as reagent. The organic matter content was also higher in the case of the soda processes. This fact was associated to the higher potential of the soda process to increase the yield of the delignification stage because, besides lignin, it also solubilizes hemicelluloses as well as some parts of the cellulose. On the contrary, the organosolv process is more selective to dissolve lignin uniquely. The other parameters of the black liquors were inherent to the biomass used as feedstock. The density was higher in soda liquors as it was a mixture of water and sodium hydroxide while organosolv black liquors had lower density as they were a mixture of water and ethanol. The measured pH were almost 14 in the case of soda black liquors because of the sodium hydroxide dissolved in the medium, and around 4 for organosolv black liquors. This acid character of these liquors was principally associated to the acetic and formic acid formed in the delignification process from the degradation of the hemicelluloses.

Before describing the lignin content in the liquors, it is necessary to include the information about the severity factors calculated following the Eq. 1 and Eq. 2. Hence, in Table 2 are detailed the severity factor, with and without considering the effect of pH on the calculations.

Table 2.

Severity factor estimations for delignification methods.

	Delignification stage	
	$Log\ R_0$	$Log\ R^{"}_0$
Organosolv	16.4	19.4
Soda	4.85	11.7

At first point, it has to be mentioned that the pH values were considered constant during all the reactions, using values collected from Table 1 to make the calculations. Now, regarding the lignin content extracted from black liquors, once again the raw material did not have huge influence on the lignin concentration in the final liquor. It was surprising in a certain degree the similar values for lignin concentration on the liquor for both process. Although in the previous work it was already mentioned that the total extraction yield for soda process was higher, the concentration is very similar in both liquors. The catalyst effect of extremely alkaline medium to solubilize lignin in soda process was balanced by the greater severity factor applied in organosolv process, where the higher temperature applied during the delignification reaction (200 ºC against 121 ºC for soda process) had a big influence to reduce the typical difference that exists among both methods in terms of lignin extraction yields. In fact, higher selectivity of organosolv method to solubilize only lignin and not the carbohydrates from hemicelluloses mainly as in case of soda process, led to bigger percentage of lignin with regard to the total

organic matter extracted in comparison with soda process. In the case of soda liquors, around 84% of the total organic content was lignin whereas in the case of organosolv liquors this amount rose up to 95%.

Additionally to the lignin content, the molecular weight distribution is also an important parameter in further depolymerization reactions. In this line, the molecular weight and the polydispersity index of the lignin samples collected from each of the liquors were analyzed and presented in Table 3.

Table 3.

Average molecular weight (Mw), number-average molecular weight (Mn) and polydispersity index (PI) of lignin dissolved in the black liquors.

Sample	Mw (g/mol)	Mn (g/mol)	PI
AO	4381	1446	3.03
AS	22,743	1995	11.4
OO	5164	1328	3.89
OS	16,282	1566	10.4

It is clearly noticeable the big difference between organosolv lignin and soda samples in these parameters. Oganosolv lignin samples presented Mw and PI values between 3 or 4 times lower than soda samples regardless the raw material. In organosolv pulping, the extraction of lignin is carried out by its solubilization in the solvent media. Whereas lignin from soda process could suffer repolymerization reactions that take place under the high alkaline conditions of this treatment. When hydroxyl groups form quinone methide intermediates react with other lignin fragments, alkali-stable methylene linkages can appear, affecting considerably the Mw of the final extracted lignin [31].

Analytical pyrolysis at 600 ºC was carried out in order to analyze the monomeric composition of lignin samples and determine the syringyl/guaiacyl ratio (S/G). In a previous work it was demonstrated that 600 ºC is the temperature which achieved the maximum yield of phenolic compounds [29]. The identified phenolic products from pyrolysis were classified into four categories according to their aromatic structure: phenol-type compounds (H), guaiacyl-type compounds (G), syringol-type compounds (S), and catechol-type compounds (Ca). Catechol derivatives were considered as S-type compounds according to other studies, where it was proved that these phenolic products come from the degradation of syringyl compounds when the pyrolysis is performed at elevated temperatures [32–34]. Consequently, the

syringyl/guaiacyl ratio (S/G) was calculated by dividing the sum of peak areas from syringyl units (including catechol derivatives) by the sum from the peak areas of guaiacyl derivatives. The results are listed in the Table 4.

Table 4.

Identification of the pyrolysis products from four lignin samples their mass fragments (AO: Almond Organosolv; AS: Almond soda; OO: Olive Organosolv; OS: Olive Soda).

Compound	Origin*	Area percentage (%)				Mass fragments
		AO	AS	OO	OS	
Phenol	H	0.75	0.59	0.79	0.74	94/66/65
p-cresol	H	0.72	0.49	0.65	0.70	107/108/77/79/51
o-cresol	H	0.43	0.37	0.18	0.28	108/107/79/77/90
4-Etylphenol	H	0.43	0.45	0.27	0.36	107/122/121/77
Total		*2.33*	*1.90*	*1.89*	*2.08*	
Catechol	Ca	---	1.32	0.78	1.57	110/81/64
3-Methoxycatechol	Ca	5.94	4.54	7.45	6.45	140/125/97
4-Methylcathechol	Ca	1.49	---	0.87	---	124/123/78
Total		*7.43*	*5.86*	*9.10*	*8.02*	
Guaiacol	G	6.24	14.79	5.34	9.66	109/124/81/53
3-Methylguaiacol	G	0.64	0.93	---	---	123/138/77/95/67
4-Methylguaiacol	G	13.46	4.05	6.77	4.40	138/123/95
5-Methylguaiacol	G	---	0.21	---	---	123/138/95
4-Vinylguaiacol	G	4.09	5.05	2.74	3.41	150/135/107/77
4-Ethylguaiacol	G	2.82	2.23	2.33	1.99	137/152
Isoeugenol	G	0.23	---	---	---	164/77/149
Vanillin	G	4.79	3.17	2.42	1.45	151/152/109/81
Acetoguaiacone	G	1.01	1.17	0.75	0.49	151/166/123
Guaiacyl acetone	G	0.99	0.77	0.50	0.43	137/180/122
4-Propylguaiacol	G	0.85	0.20	0.63	---	137/166/122
Propenylguaiacol	G	0.27	0.26	---	---	162/147/91
3.4-dimetoxytoluene	G	0.11	0.42	0.14	0.28	152/109/137
Total		*35.49*	*33.24*	*21.61*	*22.11*	
Syringol	S	8.05	25.53	15.48	28.59	154/139/111/96

3.4-dimethoxyphenol	S	2.26	0.64	2.58	1.22	154/139/111
4-Methylsyringol	S	18.31	10.07	20.31	12.39	168/153/125
Acetosyringone	S	1.03	0.86	0.45	0.46	181/196
4-Vynilsyringol	S	4.44	4.77	6.21	5.74	180/165/137
4-Ethylsyringol	S	2.55	2.43	4.57	4.07	167/182/168/77
4-Propylsyringol	S	0.64	0.91	1.07	0.78	167/196/168/123
4-Propenylsyringol	S	0.44	0.31	0.34	0.27	194/91/151
Syringaldehyde	S	1.40	1.13	0.80	---	182/181/111
4-Allylsyringol	S	9.54	5.62	10.82	7.69	194/91/179/119
Syringilacetone	S	---	0.65	---	0.39	167/210
Total		*48.66*	*52.93*	*62.63*	*61.59*	
Fatty acids		2.12	1.61	2.02	0.82	
Esters		0.67	0.67	0.41	0.08	
Furan derivatives	C	0.29	0.30	0.27	0.11	
S/G ratio		**1.6**	**1.8**	**3.3**	**3.1**	

[*]H: Phenol; G: 2-methoxyphenol (guaiacyl); S: 2.6-dimethoxyphenol (syringyl); Ca: 1.2-benzediol (catechol); C: carbohydrate

31 phenolic compounds, which represents 93-96 % of the lignin samples, were identified. Moreover, small amount of fatty acids (0.8-2.1 %), fatty acids derivatives (esters) (0-0.7 %) and furan derivatives (0.1-0.3 %) were detected in the pyrogram. Other studies assert that furanic compounds are commonly originated from the pyrolysis of residual carbohydrates and the presence of fatty acids is usually attributed to their resistance to thermochemical extraction processes such as organosolv and alkali treatments [35,36]. In terms of monomeric composition, several structural differences were found between lignins from almonds shells and olive tree pruning. The chemical structure of lignins isolated from almond shells by organosolv and alkali treatments were based on 33-36% of guaiacyl and 55-58% of syringyl (S/G: 1.6-1.8). However, lignins from olive tree pruning presented higher syringyl content (69-71%) and around 21-23% of guaiacyl units in their structural composition (S/G: 3.1-3.3). Hence, significant variations between lignin samples from the same raw material were not detected, evidencing that the monomeric composition was totally dependent on the origin and not on the extraction processes.

Conversely, 2D-HSQC analysis revealed several differences concerning the main inter-unit linkages between the elemental units of lignin samples. In Fig. 2 it was shown the main substructures found in lignin samples, whereas Table 5 summarized the ^{13}C-^{1}H cross signals, which were assigned according to previous reported data [37–39]. These signals were divided

into side-chain region (δ_C/δ_H 50-90/2.6-6) and aromatic region (δ_C/δ_H 100-150/5.5-8). With regard to aromatic region, presence of S-unit and G-unit was observed and detailed in Table 5 for all lignin samples.
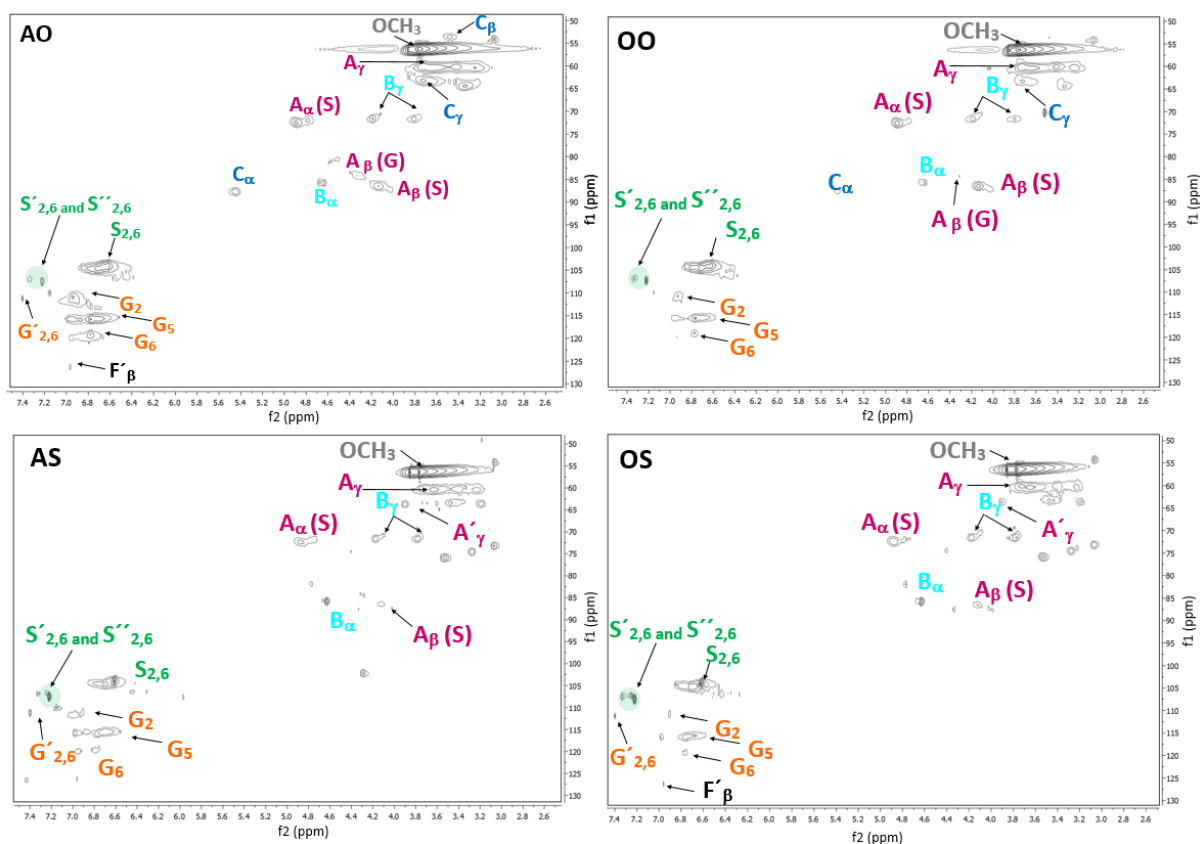

Fig. 2. Main structures present in lignin samples found in the black liquors.

Table 5.

Assignments of ^{13}C-^{1}H cross signals in the HSQC spectra and their presence in lignin samples isolated from the studied black liquors.

δ_C/δ_H (ppm)	Assignments	AO	AS	OO	OS
126.3/6.96	C_β–H_β of cynnamyl acetate end-groups (F′$_\beta$)	✓	✗	✗	✓
119.2/6.80	C_6-H_6 in guaiacyl units (G_6)	✓	✓	✓	✓
115.8/6.77	C_5-H_5 in guaiacyl units (G_5)	✓	✓	✓	✓
111.2/7.40	$C_{2,6}$-$H_{2,6}$ in oxidized ($C\alpha$=O) guaiacyl unit (G′$_{2,6}$)	✓	✓	✗	✓
110.8/6.93	C_2-H_2 in guaiacyl units (G_2)	✓	✓	✓	✓
107.5/7.33 and 7.22	$C_{2,6}$-$H_{2,6}$ in oxidized ($C\alpha$=O) syringyl unit (S′$_{2,6}$ and S′′$_{2,6}$)	✓	✓	✓	✓
104.3/6.70	$C_{2,6}$-$H_{2,6}$ in syringyl unit ($S_{2,6}$)	✓	✓	✓	✓
87.7/5.45	C_α–H_α in β-5′ (phenylcoumaran) substructures (C_α)	✓	✗	✓	✗
86.5/4.12	C_β–H_β in β-O-4 substructures linked to S unit (A_β (S))	✓	✓	✓	✓
85.8/4.63	C_α–H_α in β-β′ (resinol) substructures (B_α)	✓	✓	✓	✓

15

84.2/4.32	C_β–H_β in β-O-4 substructures linked to G unit (A$_\beta$ (G))	✓	✗	✓	✗
72.4//4.90	C_α–H_α in β-O-4 substructures linked to S unit (A$_\alpha$ (S))	✓	✓	✓	✓
71.6/3.81 and 4.18	C_γ–H_γ in β-β´ (resinol) substructures (B$_\gamma$)	✓	✓	✓	✓
63.7/3.90	C_γ–H_γ in γ-acetylated β-O-4 (A´$_\gamma$)	✗	✓	✗	✓
63.2/3.73	C_γ–H_γ in β-5´ (phenylcoumaran) substructures (C$_\gamma$)	✓	✗	✓	✗
60.3/3.68	C_γ–H_γ in β-O-4 substructures (A$_\gamma$)	✓	✓	✓	✓
53.6/3.48	C_β–H_β in β-5´ (phenylcoumaran) substructures (C$_\beta$)	✓	✗	✗	✗
56.3/3.76	C-H in methoxyl groups (OCH$_3$)	✓	✓	✓	✓

The quantification of inter-unit linkages of lignin polymer was carried out following the quantitative strategy proposed by Wen et al. [40]. Table 6 represents the abundance of lignin inter-unit linkages per aromatic unit. The most meaningful results were provided by the side-chain region, which demonstrated that the extraction processes had an important influence on the inter-unit linkages between the phenylpropane units of lignins from the same origin.

Table 6

Abundance of lignin inter-unit linkages expressed as linkage per aromatic units and S/G ratio from integration of ^{13}C-^{1}H correlation peaks in the HSQC spectra.

	AO	AS	OO	OS
β-O-4	1.69 (63.5%)	1.56 (63.4%)	1.75 (74.4%)	1.02 (67.8%)
β-β´	0.38 (14.3%)	0.9 (36.6%)	0.40 (16.9 %)	0.48 (32.2%)
β-5´	0.59 (22.2%)	nd	0.20 (8.7%)	nd
S/G*	1.3	1.5	2.9	2.6

S/G ratio calculated according to previous works [36,38]

As it can be observed, β-aryl-ether linkage (β-O-4) was the most abundant bond in all studied lignins. However, the use of organosolv process for lignin extraction generated lignin samples with higher β-O-4 linkages in their chemical structure than using soda delignification process. This difference was particularly detected in the case of lignin isolated from olive tree. Moreover, soda lignins presented the highest content of β-β´ bonds in resinol substructures. Additionally, β-5´ linkage in phenylcoumaran substructures was only found in organosolv lignins, being significantly more abundant in organosolv almond lignin. The higher amount of this type of inter-unit linkage in AO could be due to the lowest S/G ratio. The presence of higher content of guaiacyl units in its chemical structure, which contains reactive positions (C_5 positions) in the aromatic ring, allows the formation of condensed bonds like β-5´ [42]. The S/G ratio

calculated from HSQC spectra follow the same trend than as those were obtained from pyrolysis technique.

3.2. Black liquors depolymerization process

Black liquors were treated in a batch microreactor in order to depolymerize the lignin contained in them. After the lignin depolymerization from the liquors and the downstream separation processes, three different products were isolated: oil, residual lignin and char.

3.2.1. Reaction products yield

The yields of the three identified products are shown in Fig. 3. These yields were calculated using the organic matter contained in the black liquors as the basis.
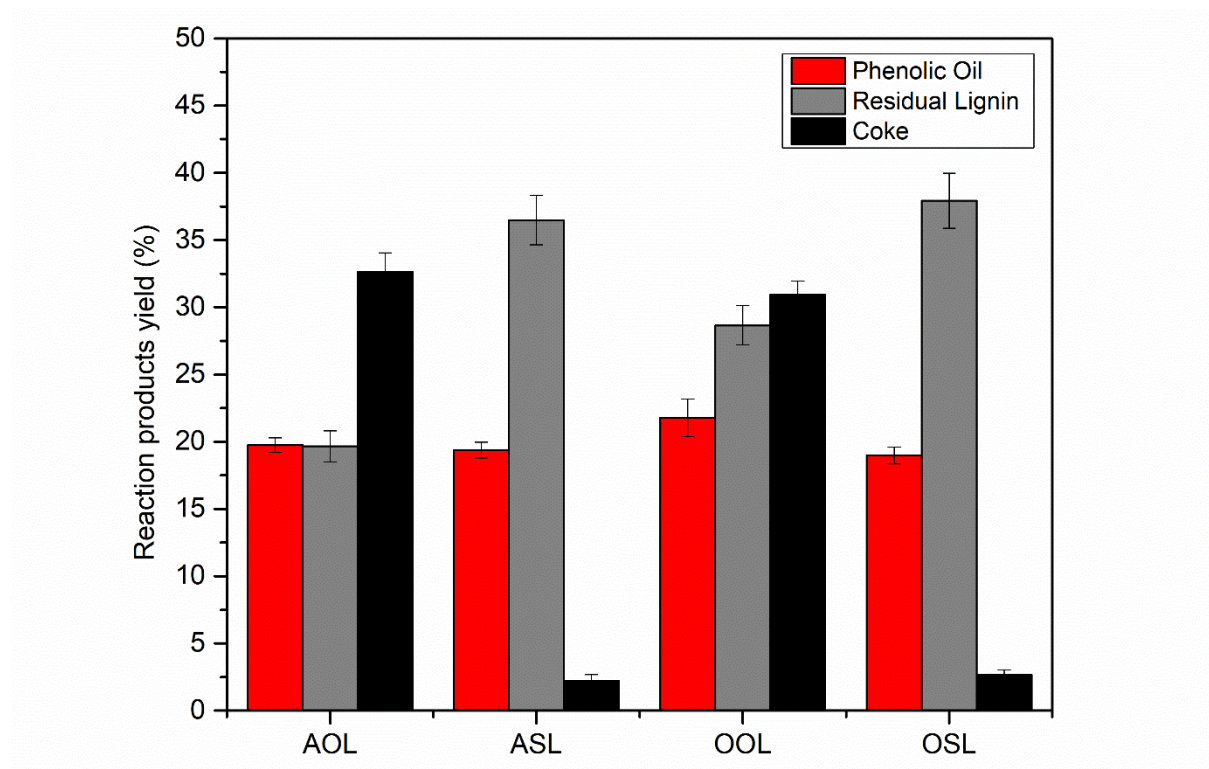

Fig. 3. Yield of the products recovered after depolymerization processes, referred to the organic matter of each black liquor (wt.%).

It can be observed that the yield of phenolic oil, the most desirable product of the reaction, was practically the same in all cases, around 20%, with regard to the organic matter contained in the liquor (from 18.98% to 21.78%). These values are really close to those obtained when solid lignin was depolymerized in alkaline solutions and same operation conditions [20,43,44]. However, it has to be borne in mind that these yields were referred to the total organic content matter, which includes not only lignin but also other components originated from hemicelluloses and cellulose platform. Therefore, it could be said that the obtained reaction

yields were even higher that the ones obtained from precipitated lignin if we could have separated the exact amount of lignin at the initial black liquors, what was impossible to achieve without create errors. As it was pointed out before, the lignin content in the liquors was almost the same and the treatments of these liquors lead to very similar quantity of phenolic oil, remarking the independency of the raw material and used catalytic agent when a reaction is carried out in such harsh conditions.

However, a huge influence of the different solvent was observed on the undesirable product yields. Regarding the residual lignin, when soda liquor was used, the generation of this byproduct were significantly higher than in the case of the organosolv processes (from 35-40% for soda samples to 20-28% for organosolv ones), whereas the char production performed the other way around, with higher percentages for organosolv samples (around 30-35%), while soda samples presented a really small production of char (lower than 3%).

This behavior could be explained due to the activity of the NaOH, which acts as a catalyst but also inhibits the formation of char [43]. The OH$^-$ ions of the sodium hydroxide neutralize the molecules which cause the polymerization for char formation, as for example the carboxylic acids, which are prone to react with hydroxyl groups to form ester bonds responsible of the char formation [45]. The lower yield was followed by an increase in residual lignin formation what leads to the conclusion that residual lignin was created by polymerization reaction and char formation is one step forward in such polymerization reaction, where highly condensed structure are created, which are not possible to be solubilize even in organic solvents such as THF. Therefore, because of the lack of these OH$^-$ ions presented in organosolv liquors an increase in char formation was undergone.

3.2.2. Oil characterization

The obtained phenolic oil was composed by a wide range of products due to the heterogeneity of lignin. In addition, the depolymerization was not completely conducted since the cleavage of C-C linkages was not totally achieved despite these harsh conditions. However, only the monomeric phenolic compounds were characterized by GC-MS technique. The most important compounds quantified in the phenolic oils are shown in Table 7. Phenolic monomer yields were referred to phenolic oil fraction obtained in each reaction.

Table 7

Phenolic monomer yields (%wt. of the phenolic oil) of the different samples subjected to the depolymerization reaction.

Compound (%)	AOL	ASL	OOL	OSL
Phenol	0.28 ± 0.02	0.66 ± 0.07	0.33 ± 0.02	1.01 ± 0.13
Cresols	0.15 ± 0.02	0.30 ± 0.01	0.27 ± 0.08	0.42 ± 0.00
Guaiacol	5.44 ± 0.34	0.03 ± 0.00	3.90 ± 0.34	0.05 ± 0.01
Catechol	0.77 ± 0.06	1.63 ± 0.13	0.45 ± 0.05	1.50 ± 0.02
3-methylcatechol	0.11 ± 0.00	0.90 ± 0.03	---	0.91 ± 0.02
3-methoxycatechol	2.64 ± 0.24	---	2.10 ± 0.25	---
4-methylcatechol	0.16 ± 0.02	1.85 ± 0.02	---	1.81 ± 0.11
Syringol	11.30 ± 0.56	----	10.25 ± 0.23	----
4-ethylcatechol	0.14 ± 0.00	0.89 ± 0.08	---	0.97 ± 0.05
Acetovanillone	0.32 ± 0.08	----	0.09 ± 0.03	---
Guaiacylacetone	0.73 ± 0.16	----	0.32 ± 0.04	----
Acetosyringone	0.19 ± 0.03	---	0.13 ± 0.04	----
Monomers yield (%)	22.23 ± 0.9	6.26 ± 0.4	17.51 ± 1.10	6.67 ± 0.30

There was an appreciable difference between the compounds in the oil from soda liquors and organosolv liquors. In the organosolv liquors, the main obtained compounds were guaiacol and syringol while these two compounds almost did not appear in the oil from soda liquors. This fact reinforces the statement that, in soda liquors, the NaOH catalyzes the depolymerization reactions and, apart from hydrolysis of ether bonds which lead to syringol and guaiacol, demethoxylation, demethylation and dealkylation reactions also occurred. The mechanism of this reaction can be seen in Fig. 4. In this way, catechol, 3-methylcatechol, 4-methylcatechol and 4-ethylcatechol were identified in soda liquors oils. In alkaline conditions, the hydroxyl groups in the phenolic ring reacts with NaOH to form a phenolate anion. After several electron migration steps, a phenolate side chain was eliminated by hydrolytic cleavage of an ether bond to form a quinone intermediate [9]. As a consequence, phenol, cresol or catechols are produced. On the other hand, in the case of organosolv black liquors, the β-O-4 ether bonds of the lignin were broken down due to the solvolysis of the reaction mixture

(water/ethanol), where the hydrogen-donating medium created a lower oxidant medium that did not lead to demethoxylation, demethylation and dealkylation reactions as in case of extreme alkaline medium. The cleavage of these bonds, which are the major bonds in lignin macromolecule, lead to the formation of syringol and guaiacol but did not go on to form other monomeric phenols.
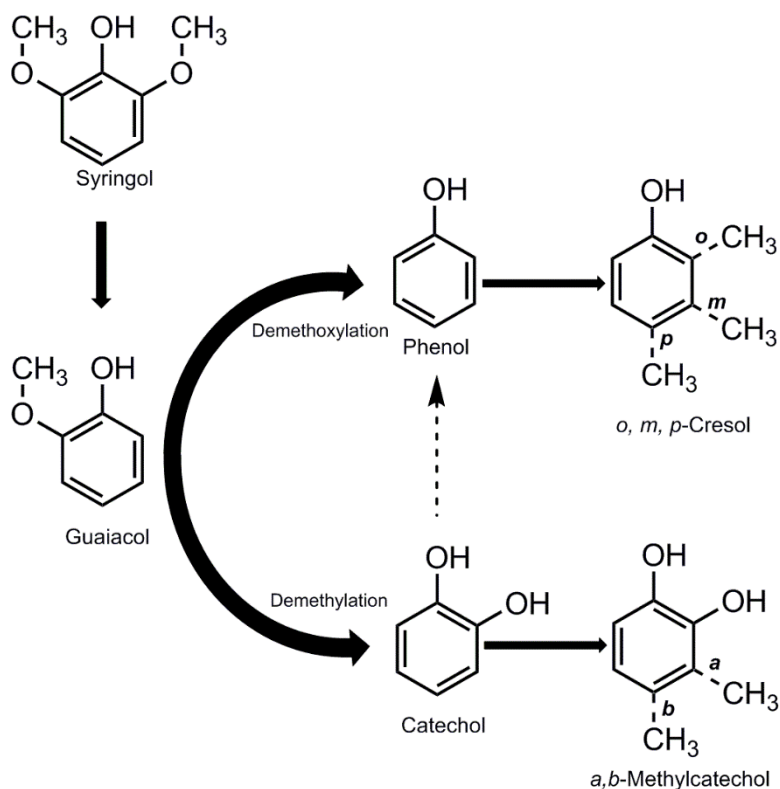

Fig. 4. Schematic representation of the demethoxylation and demethylation reactions undergone in BCD [46].

It has to be mentioned as well that the methoxy functional groups were the most sensitive ones to be cleaved by the action of NaOH. All the monomers identified in the case of soda black liquors treatment have no methoxy groups whereas in the case of organosolv black liquors besides guaiacol (1 methoxy group) and syringol (2 methoxy group) high quantity of 3-methocycatechol was recovered. In addition, acetovanillone, guaiacylacetone and acetosyringone, all of which have a mehoxy group, did not appear in the soda black liquor.

Comparing the yield of the monomers production, big difference between organosolv and soda methods was observed. The former presented a higher purity of this oil in phenolic monomers compounds, as it was intended (around 20% for both feedstock). On the contrary, barely 6-7% of the oil was formed by monomers using soda liquors. Therefore, soda as solvent allowed the achievement of complete reactions of demethoxylation, demethylation and dealkylation, but the total yield of monomers were found to be around three times lower than in organosolv black

liquors. The reason of this difference can be linked to the properties of the lignin feed to the reaction. Lignin cleavage in its monomeric structure is clearly connected with the linkages of initial lignin molecules as it has been proposed in several works [47,48]. As it was shown in Table 6 the density of ether linkages (β-O-4) was much higher for organosolv lignin samples than soda ones regardless the feedstock used in the process. As the energy required to break these ether bonds is lower than in case of C-C linkages, the phenolic monomers yield was expected to be higher as it was furtherly experimented according to the results presented in Table 7. However, among organosolv processes the greatest monomer yield was reached by AO instead OO as it was expected according to their difference in ether linkages density. The results suggest that, despite the main influential parameter to obtain higher phenolic monomers compounds were the density of ether linkages, there are other parameters that plays an important role, such as the lignin condensation degree which can be estimated from S/G ratio obtained from Py-GC-MS. The bigger S/G ratio, the more trend to create more recalcitrant lignin samples with difficulties to be processed in further valorization processes[49]. Therefore, since the S/G ratio was bigger for olive lignin samples, it can be suggested that this fact was an inhibition to produce as good yields as in case of organosolv lignin from almond shells. In addition, the difference of reaction mechanism (base catalyst depolymerization or solvolysis) did not influenced on the monomer yields, but in the final obtained species instead.

In addition, to facilitate the comparison of phenolic monomer yields obtained by the direct depolymerization of lignin contained in black liquors against the yields reached when precipitated lignin was submitted to the depolymerization reaction [50], a brief summary of the detected compounds is detailed in Table 8. Total phenolic monomers yield for black liquors were expressed using lignin contained in black liquors, whose amount were already shown in Table 1, as basis. In this case the error was assumable to compare both works to the same basis to compare both works. Phenolic monomer composition was expressed by monomer groups to facilitate the understanding. Catechols group was formed by catechol, 3-methylcatechol, 3-methoxycatechol, 4-methylcatechol, and 4-ethylcatechol; cresols group by *o*-, *m*-, and *p*-cresol; guaiacol groups by guaiacol, vanillin, acetovanillone, and 4-hydroxy-3-methoxy-phenylacetone; and finally syringol group by syringol, syringaldehyde, and acetosyringone.

Table 8

Total phenolic monomer yields from solid samples [46] and lignin from black liquors.

Lignin Sample	Yield (%)	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	-
AOL	4.57 ± 0.05	0.781 ± 0.05	0.057 ± 0.01	0.030 ± 0.01	1.35 ± 0.05	2.36 ± 0.06
ASL	1.44 ± 0.04	1.20 ± 0.01	0.151 ± 0.01	0.068 ± 0.01	0.007 ± 0.01	0.012 ± 0.01
OOL	4.01 ± 0.10	0.572 ± 0.06	0.075 ± 0.01	0.060 ± 0.02	0.967 ± 0.06	2.37 ± 0.08
OSL	1.52 ± 0.01	1.182 ± 0.01	0.228 ± 0.03	0.095 ± 0.02	0.011 ± 0.02	0.00 ± 0.00

Phenolic monomer yields from organosolv black liquors reached similar values than worse yields obtained by solid lignin depolymerization, even in some cases were even higher. Thus, taking into account these performances together with total phenolic oil yield which were also

high, it can be established that solvolysis of direct black liquor depolymerization was an acceptable approach to obtain small phenolic compounds from lignin. In case of direct soda black liquors, despite the high total phenolic oil yields (above 20%), monomers yields were the lowest of all tested strategies. Hence, the influence of the higher impurities quantity contained in soda liquor, both organic but overall inorganic substances, were playing a negative role on maximizing the achievement of great phenolic monomer yields. It was also demonstrated that the BCD mechanism was very similar in terms of monomeric compound generation regardless the feedstock used: precipitated lignin or direct soda black liquors. While depolymerization of lignin from organosolv black liquors led to get guaiacol and syringol compounds as main products.

In comparison with similar works developed previously in this research group [18,19], phenolic monomer yields were even higher. Nevertheless, in comparison with other processes were harsher conditions, selective catalytic agents or other solvents were used [15–17], the values presented in this work were lower.

3.2.3. Residual lignin

The molecular size and the polydispersivity of the residual lignins were assessed by GPC analysis and compared to the ones of the lignin samples from the black liquors. The results are presented in Table 9.

Table 9

Average molecular weight (Mw), number-average molecular weight (Mn) and polydispersity index (PI) of the residual lignin isolated after depolymerization reaction.

Sample	Mw (g/mol)	Mn (g/mol)	PI
RL organosolv almond	2433	541	4.50
RL soda almond	2177	456	4.77
RL organosolv olive	3426	802	4.27
RL soda olive	2465	509	4.84

The Mw of all residual lignin samples were lower than its respective raw lignin present in the liquor, as it was depicted in Table 2. This descend was very significant in the case of soda lignin samples proving that lignin depolymerization was successfully achieved in these cases, in good agreement with previous results [20]. In organosolv lignins, this descend was not so pronounced, as the organoslv raw lignin samples already presented a low molecular weight.

In addition, the polydispersity index of the residual lignin samples was higher than their respective raw lignin samples, proving that some fractions of different Mw were formed during the organosolv black liquors treatments. It is remarkable the big similarity of the residual lignin in both Mw as well PI regardless the used process. This fact indicates an analogous mechanism of the repolymerization reaction of lignin, which favored the formation of this byproduct regardless the source and catalytic agent used in the reaction. Therefore, the influence of the solvent used was noticeable on the yield of the depolymerization reaction, but not in the mechanism of the reaction.

Fig. 5 presents the spectrum curves from the GPC analysis of almond shell samples, selected as reference to facilitate the visual interpretation. Additionally, the curves of the phenolic oil were also included to qualitatively compare them with rest of samples.
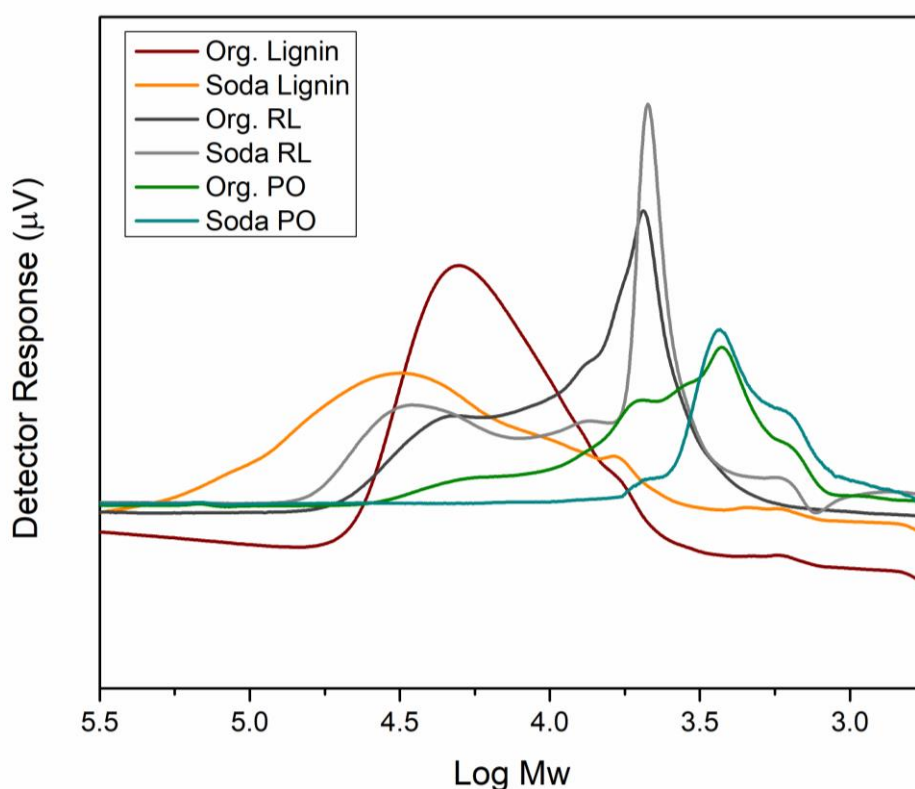

Fig. 5. Spectrum curves of the GPC analysis (Org. Lingin: Initial lignin sample from organosolv process. Soda Lignin: Initial lignin sample from soda process. Org. RL: Residual lignin obtained from the depolymerization of initial organosolv lignin. Soda RL: Residual lignin from the depolymerization of initial soda lignin. Org. PO: Phenolic Oil from the depolymerization of organosolv lignin. Soda PO: Phenolic Oil from the depolymerization of soda lignin.

Different shapes and peak locations between samples can be observed. Initial soda lignin was the sample whose main peak was most displaced to the bigger Mw size part of the graphic. This peak was found to be really wide, remarking both the big average size of the sample as well as its high polydispersity. The organosolv initial sample showed a narrower peak in comparison with other samples as the polydispersity values indicated before (3.03). The residual lignin spectrum curves were very similar among then, with two main peaks that led to a higher polydispersity than the organosolv sample one. This similarity between curves highlighted that this component was obtained by the same mechanism during the reaction despite the used initial lignin and solvent. The shape of the two peaks of the curve indicated that not all the fraction of the repolymerized lignin was able to reach such big structure and also that some the most recalcitrant part of the original lignin may form the structure of this residual lignin. Finally, it was remarkable the difference of the curves corresponding to the phenolic oils, with a clear displacement to the lower Mw section. Additionally, the difference among the phenolic oils was also noticeable, since the phenolic oil from the organosolv lignin presented a displaced curve to the lower Mw part, what it is in consonance with the higher percentage of monomeric compounds measured by GC/MS for such phenolic oil.

4. CONCLUSIONS

Two different black liquors obtained from two different raw materials were treated in this study in order to produce phenolic monomers. A depolymerization reaction was carried out directly over the liquors using their subsequent solvent as reaction medium. Therefore, solvolysis of lignin was conducted when organosolv liquor was used and base catalyzed depolymerization for soda liquors.

Prior to the reaction, a characterization of the different liquors was accomplished to establish the starting point of this survey. Despite the differences in inorganic and organic content of the liquors, the estimation of lignin content was similar for all the liquors. The main observed difference was the Mw and PI parameters between organosolv and soda sample regardless the raw material used, being much lower the Mw and PI values for organsolv samples and the percentages of ether linkages, which were higher for organosolv samples. Whereas S/G ratio of lignin samples were more dependent on the feedstock than the delignification process.

The reaction product quantification pointed out that the phenolic oil streams were very similar in yield for all the reaction assessed (around 20%). The main difference was noticed in the byproduct quantities obtained during the reaction. The organosolv liquors produced much more coke (more than 30%) but lower residual lignin (20-30%), whereas soda liquors produced more residual lignin (35-40%) and much lower amount of coke (2-3%), almost negligible.

Regarding the phenolic monomers composition, base catalyzed reactions led to complete reactions of demethoxylation, demethylation and dealkylation, since the monomers obtained were more elementary in terms of their molecular structure. However, the total yield of monomers generation was found to be around three times lower than the one provided by lignin solvolysis, which allowed to reach significant high yields. As main conclusion, it can be established that the most important parameter to obtain higher phenolic monomer yields were the abundancy of β-O-4 bonds, although S/G ratios had also an influence, and the reaction mechanism presented its influence more on the final species obtained than on the products yields.

Residual lignin was demonstrated to be different from the initial lignin according to the GPC analysis, where the fractions involved in the reaction were analyzed. The similar characteristics of residual lignin despite the method they were obtained from, pointed out the same generation mechanism during the reaction.

The same products were obtained regardless the used raw material. This fact is considered as an important achievement since it allow using several biomass wastes that could reduce one of the most important drawbacks of the process where lignocellulosic wastes are used, that is the seasonality of such streams.

As summary, it has been demonstrated that phenolic monomers production by direct treatment of delignification black liquors was acceptable so that lignin precipitation stage could be avoided. In terms of phenolic monomers yield organosolv black liquor presented the best results with more than 22% of total phenolic oil recovered in the organic phase. However, the total monomers yield from liquors is not has high as from precipitated lignin. In further studies, optimization of liquor treatment conditions should carried out to improve lignin valorization process from this faster and simpler way.

ACKNOWLEDGEMENTS

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