

This is the accept manuscript of the following article that appeared in final form in

Xabier Erdocia, Raquel Prado, M. Ángeles Corcuera, Jalel Labidi, Base catalysed depolymerization of lignin: Influence of organosolv lignin nature, Biomass and Bioenergy, Volume 66, 2014, Pages 379-386, ISSN 0961-9534 <https://doi.org/10.1016/j.biombioe.2014.03.021> .

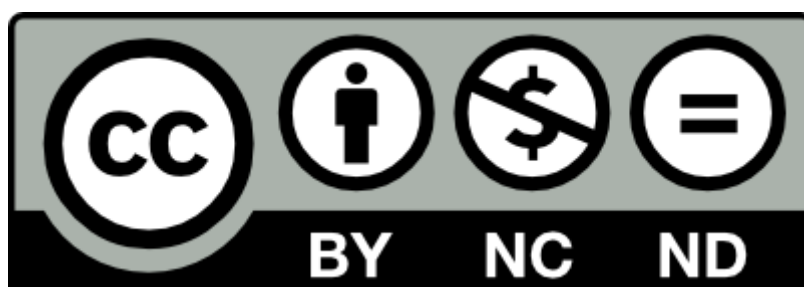
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Xabier Erdocia, Raquel Prado, M. Ángeles Corcuera, Jalel Labidi, Base catalysed depolymerization of lignin: Influence of organosolv lignin nature, Biomass and Bioenergy, Volume 66, 2014, Pages 379-386, ISSN 0961-9534 <https://doi.org/10.1016/j.biombioe.2014.03.021>

(<https://www.sciencedirect.com/science/article/abs/pii/S0961953414001391>)

Abstract: Three different lignins obtained from olive tree pruning by organosolv processes (acetosolv, formosolv and acetosolv/formosolv) were depolymerized by alkaline hydrolysis in a batch reactor to produce high value added compounds. Obtained products (oil, coke, residual lignin and gas) were measured and analyzed determining their composition and yield in order to study the changes of the depolymerization process for different organosolv lignin samples. For this purpose, different analytical methods were used (gas chromatography/mass spectroscopy, high Performance Size Exclusion Chromatography, pyrolysis-GC-MS, Maldi-Tof). Acetosolv lignin and acetosolv/formosolv lignin gave the highest yield of desired product with 18.48 and 16.25% of oil yield respectively. However, formosolv lignin had the highest proportion of monomeric phenolic compounds in the oil (28.19%). Catechol and its derivatives were the main products in all studied cases but it were more abundant in the case of formosolv lignin depolymerization. Otherwise, the residual lignin formed during the repolymerization process was the same in both, yield and nature, for all cases.

Keywords: Lignin; Organosolv; Depolymerization; Phenolic compounds



Base catalyzed depolymerization of lignin: Influence of organosolv lignin nature

Xabier Erdocia, Raquel Prado, M. Ángeles Corcuera, Jalel Labidi

Chemical and Environmental Engineering Department. University of the Basque Country.

Plaza Europa 1, 20018 San Sebastian (Spain)

E-mail: jalel.labidi@ehu.es ; Tel: +34 943017125

Highlights

Different lignins were successfully depolymerized under optimized conditions.

High amounts of catechol and derivative compounds were obtained.

Nature of rough lignin affected oil yield but not its composition.

Obtained residual lignins were very similar regardless the nature of rough lignin.

ABSTRACT

Three different lignins obtained from olive tree pruning by organosolv processes (acetosolv, formosolv and acetosolv/formosolv) were depolymerized by alkaline hydrolysis in a batch reactor to produce high value added compounds. Obtained products (oil, coke, residual lignin and gas) were measured and analyzed determining their composition and yield in order to study the changes of the depolymerization process for different organosolv lignin samples. For this purpose, different analytical methods were used (gas chromatography/mass spectroscopy, high Performance Size Exclusion Chromatography, pyrolysis-GC-MS, Maldi-Tof). Acetosolv lignin and acetosolv/formosolv lignin gave the highest yield of desired product with 18.48 and 16.25% of oil yield respectively. However, formosolv lignin had the highest proportion of monomeric phenolic compounds in the oil (28.19%). Catechol and its derivatives were the main products in all studied cases but it were more abundant in the case of formosolv lignin depolymerization. Otherwise, the residual lignin formed during the repolymerization process was the same in both, yield and nature, for all cases.

Keywords

Lignin; Organosolv; Depolymerization; Phenolic compounds

1. INTRODUCTION

Lignin is the second most abundant naturally synthesized compound with 25–30% in dry wood. Lignin is an amorphous, polyphenolic material arising from the copolymerization of three phenylpropanoid monomers: coniferyl, sinapyl, and p-coumarylalcohol. These monomers are connected by ether and carbon-carbon bonds [1,2] forming a randomized structure in a three-dimensional network inside the cell wall [3]. In plant cell walls, lignin fills the spaces between cellulose and hemicellulose, and it acts like a resin that holds the lignocellulose matrix together.

Biomass pretreatment is an essential key for lignin valorization. There are several different treatments where lignin is produced as product or by-product. This lignin could be a by-product from pretreatments in the pulp and paper industries (i.e., kraft or lignosulfonate) or it can be specifically produced in treatments of the new biorefinery scheme (i.e., organosolv). Under organosolv treatments different organic solvents, like organic acids, can be used [4-6]. All the various lignin pretreatments use different conditions and degradation techniques, including temperatures, pressures, solvents, and pH ranges, that alter the chemical structure and linkages of the lignin.

Several studies have been done to convert lignin to more value-added products. Organosolv lignins have been found to be an appropriate raw material for producing low molecular weight (LMW) compounds. Among many thermochemical methods, base catalyzed depolymerization (BCD) has been borne out to produce phenolic monomeric compounds [7-9]. Miller et al. [7] performed alkaline hydrolysis of Alcell lignin using KOH in supercritical methanol or ethanol. In this study they concluded that the reaction was favored by strong bases and that 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 BCD reaction while carbon-carbon linkages were less affected. Several years later, Miller et al. [10] studied alkali depolymerization of lignin but using water as solvent. They

found that the most important factor leading lignin depolymerization was base concentration. Moreover, they observed that molar excess of a strong base gave better results on lignin depolymerization. In addition, a little amount of a strong base (NaOH) together with a larger amount of less expensive base (CaO) produced good results. Most recently, Karagoz et al., [11] carried out catalytic hydrothermal treatment of wood biomass employing Rb and Cs carbonates to produce mainly phenolic compounds.

In other works alkaline depolymerization of lignin has also been studied. Nenkova et al., [12] found that lignin could be depolymerized in an aqueous alkaline solution (NaOH) at 180 °C for 6 h employing anthraquinone as a catalyst (0.5 wt%). Otherwise, Roberts et al., [8] 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 directly proportional to the concentration of sodium hydroxide in the aqueous medium. 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 provides to the transition states of the carbenium ions. They also concluded that the production of monomers is limited by the oligomerization and polymerization reactions of the products formed.

The aim of this study was to evaluate the influence of organosolv lignin nature on its depolymerization process. For this purpose, three different liginins, obtained from acidic organosolv pulping, were subjected to high temperatures and pressures with sodium hydroxide as catalyst in an aqueous medium. The resulted products (oil, residual lignin, coke and gas) were measured and analyzed by different techniques in order to determine their composition and yield.

2. MATERIALS AND METHODS

2.1. Lignin

Lignin employed in this study was obtained from organosolv pulping of olive tree pruning. Three different lignins were used: Lignin from acetosolv pulping (AL), lignin from formosolv pulping (FL) and lignin from acetosolv/formosolv pulping (AFL). All the reaction conditions for olive tree pruning delignification were described in a previous work [13].

2.2. Base catalyzed depolymerization

The reactions were conducted in a batch reactor – 5500 Parr reactor – with a 4848 Reactor controller. The reaction conditions were 300 °C and 80 minutes with constant stirring, reaching pressures about 9 MPa. Lignin : solvent (water) mass ratio was 1 : 20 and the catalyst (NaOH) concentration was set at 4% wt. respect to all reaction system (water+lignin) (Previous optimized conditions).

2.3. Products separation process

After the reaction time the gas phase was recovered and measured in a latex rubber inflatable device. The liquid solution in the batch microreactor was treated in order to separate the products. Firstly, HCl at 37% wt. was added until pH 1 was reached. This way, residual lignin and coke precipitated and were separated from the liquid by filtration and washed with acidified water to remove residual liquid.

This liquid fraction was subjected to a liquid-liquid extraction process with ethyl acetate. Sodium sulphate anhydrous was added to the obtained organic phase in order to remove the traces of water and then it was filtrated. This organic phase was vacuum evaporated in order to obtain an oil with the depolymerized products.

The solid phase was washed with tetrahydrofuran (THF) and was stirred for 3 hours in a beaker. Then, was filtrated and the undissolved solid (coke) was oven-dried at 50 °C. The THF solution was vacuum evaporated to recover the unconverted lignin dissolved in it.

2.4. Analysis of the depolymerization products

Oil was characterized in order to establish the nature of the monomeric phenolic compound and to determine the molecular weight profile. 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, 60 m x 0.25 mm). The temperature program started at 50 °C then, the temperature is raised to 120 °C at 10 K min⁻¹, held 5 min, raised to 280 °C at 10 K min⁻¹, held 8 min, raised to 300 °C at 10 K min⁻¹ and held 2 min. Helium was used as the 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.

Matrix Assisted Laser Desorption/Ionization Time-of-flight mass spectrometry (MALDI-TOF) was carried out to check the oil molecular weight distribution in a Voyager-DE™ STRBiospectrometry™ Workstation of Applied Biosystems. It was also useful to know the depolymerization degree. A solution of DABP (3,4-diaminobenzophenone) 15 g L⁻¹ in a methanol-water mixture (volume ratio of 8:2) was used as matrix. The analyses were developed in negative mode.

Residual lignin was subjected to High Performance Size Exclusion Chromatography (HPSEC) to evaluate lignin average molecular weight (M_w), and 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 mm³ min⁻¹ and 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 pyrolysis was carried out using a CDS analytical Pyroprobe 5150. The pyrolysis temperature was set at 400 °C for 15 sec with a heating rate of 2 K msec⁻¹. Then the products were analyzed by GC-MS instrument described above. The oven program started at 50 °C and was held 2 min at this temperature. Then it was raised to 120 °C at K min⁻¹ and held 5 min, raised to 280 °C at K min⁻¹, held 8 min and finally raised to 300 °C at K min⁻¹ and held 10 min.

3. RESULTS

3.1. Yield of depolymerized products

In Table 1 are presented the yields of the products obtained after base catalyzed depolymerization of different lignins. First, regarding the oil yield, AL had the best result (18.48%) while FL presented the lowest yield of the desired product (12.95%). This difference means that AL had 42.7% more oil yield than FL, so it could be affirmed that the lignin nature is an essential factor on its depolymerization. Otherwise, as it could be expected AFL's oil yield was between AL and FL oil yields. Nevertheless, all oil yields obtained were higher than the obtained in previous work (11.5% of oil yield) with almost the same procedure (same temperature and catalyst concentration) [8].

In contrast, the values of residual lignin remained almost constant for the depolymerization of the three different lignins. There was almost no difference in the obtained yields whatever the lignin was. The range of the maximum and minimum yields of residual lignin was hardly 0.23%. Furthermore, it was the main fraction for all the studied cases. On the other hand, the behavior of coke production was completely different in three depolymerization studies. AL produced by far the lowest quantity of coke while FL and AFL had more than the double quantity of coke than the first lignin. These could indicate that the presence of residual formic acid in FL and AFL promoted repolymerization reactions inhibiting the action of NaOH. Otherwise, produced gas in the performed experiments was negligible and very similar in the three cases.

Table 1. Yields of depolymerization products referred to raw lignin introduced in the reactor (w/w).

	AL	FL	AFL
Oil (%)	18.48 ± 0.59	12.95 ± 0.37	16.28 ± 0.57
Residual lignin (%)	24.32 ± 0.06	24.37 ± 0.46	24.14 ± 0.19
Coke (%)	8.29 ± 0.73	17.71 ± 0.50	16.73 ± 0.94
Gas (%)	1.03 ± 0.04	1.17 ± 0.08	1.06 ± 0.04

3.2. Oil characterization

The characterization of the oil obtained in different depolymerization reactions by GC-MS shows differences in the concentration of the obtained phenolic compounds but not in the nature of them. In all cases, same compounds were produced but in different quantity as it can be observed in the Table 2.

Table 2. Yields (%) of obtained compounds referred to oil weight obtained in each case (w/w).

	AL	FL	AFL
<i>Phenol</i>	1.04 ± 0.12	1.34 ± 0.06	0.96 ± 0.17
<i>Cresols</i>	0.52 ± 0.03	0.80 ± 0.02	0.54 ± 0.04
<i>Guaiacol</i>	0.09 ± 0.02	0.10 ± 0.01	0.07 ± 0.01
<i>Catechol</i>	6.25 ± 1.20	11.80 ± 1.68	7.80 ± 1.24
<i>3-methylcatechol</i>	3.30 ± 0.34	4.40 ± 0.24	3.76 ± 1.01
<i>4-methylcatechol</i>	5.72 ± 0.02	7.00 ± 0.73	6.21 ± 0.91
<i>4-hydroxybenzaldehyde</i>	0.09 ± 0.01	0.10 ± 0.01	0.08 ± 0.02
<i>4-ethylcatechol</i>	2.40 ± 0.26	2.59 ± 0.23	1.99 ± 0.38
<i>Acetovanillone</i>	0.04 ± 0.01	N.D.	0.01 ± 0.00
<i>4-hidroxy-3-methoxy-phenylacetone</i>	0.07 ± 0.01	0.06 ± 0.01	0.05 ± 0.01

The main products present in the oil were catechol and substituted compounds: 3-methylcatechol, 4-methylcatechol and 4-ethylcatechol. Between the 16 and 25% of the produced oil was composed by these products. FL oil had 25.79% of these products as well as the highest content of all the other compounds except acetovanillone and 4-hydroxy-3-methoxy-phenylacetone. Otherwise, phenol and cresols were also produced in considerable amount. All these results were in concordance with other works where lignin and lignin model compounds were depolymerized under hydrothermal conditions [14, 15].

It could be appreciated that in all experiments the amount of guaiacol was very low and there was not presence of syringol which was in accordance with other works where it is stated that syringyl groups are more susceptible to BCD than guaiacyl groups [16]. Otherwise, as it was discussed above, the amount of phenol, cresols and catechol and its derivatives was very high. Regarding to these results, it could be affirmed that, apart from hydrolysis of ether-bonds demethoxylation of hydrolyzed compounds occurred, regardless of the nature of lignin. Several authors affirmed that guaiacol and syringol are formed easily from lignin ether-bonds hydrolysis [9]; Then, demethoxylation of these compounds lead to the obtaining of phenol, cresols and catechol [14, 17].

Throughout base catalyzed depolymerization of lignin, β -O-4 ether bond is heterolytically cleaved via the formation of a sodium phenolate derivative and a carbenium ion like transition state, which is immediately neutralized by a hydroxide ion. The sodium cations catalyze the reaction by forming cation adducts with lignin and, hence, polarizing the ether bond [8]. According to the obtained results, in addition to the heterolytic cleavage of the β -O-4 ether bond, dealkylation of side chains and hydrolysis of methoxy groups took place and lead to the formation of phenol, cresols and catechol.

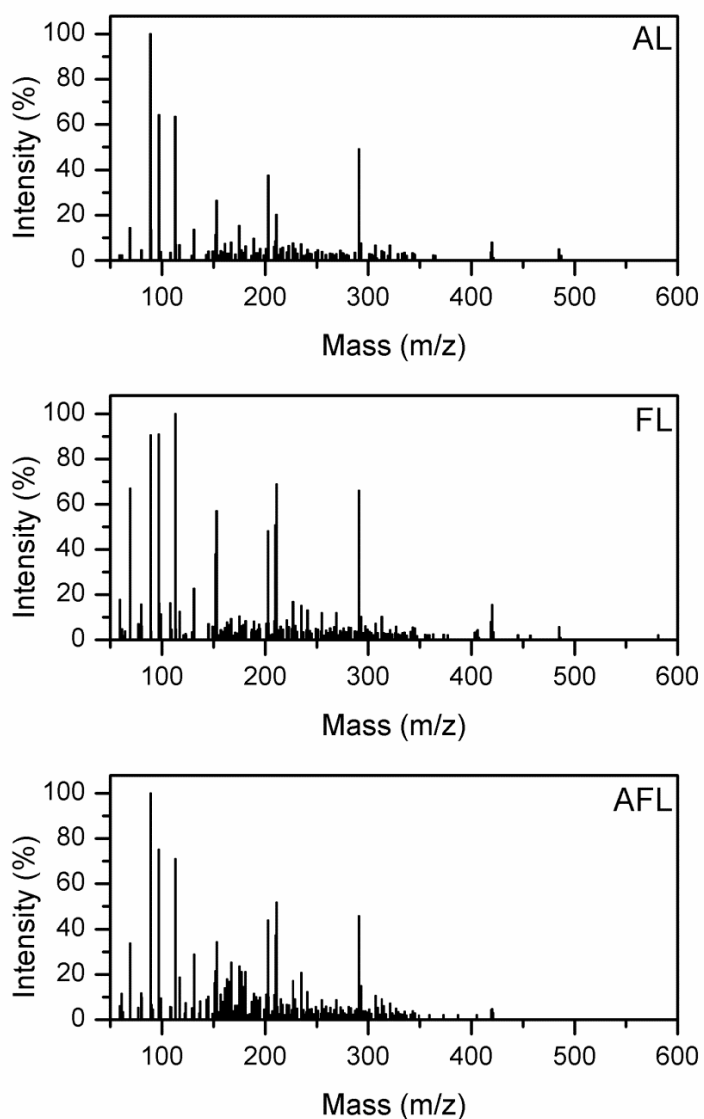
Otherwise, as it was mentioned above, FL yielded the most monomeric phenolic compounds of all studied samples. This behavior could be explained due to the lower molecular weight of FL [13] which promoted the obtaining of monomeric phenolic compounds. This fact could be

related to the demethoxylation, dealkylation and demethylation reactions which are more favored by lower molecular weight lignin fractions [18]. However, as indicated in the previous section, FL produced the lowest oil yield.

Maldi-Tof analyses were carried out in order to determine the MWD of the oil as it is shown in Fig. 1. It can be observed that the oil was composed by compounds with low molecular weights, as almost all of the compounds were below 350 g mol^{-1} . Taking in to account that olive tree pruning lignin is composed mainly by phenylpropanoid alcohols units, (guaiacyl alcohol and syringyl alcohol), which molecular weight range is between 180 and 210 g mol^{-1} , it could be concluded that most of the products obtained were not only monomers but also dimers.

Otherwise, the molecular weight distribution pattern was very similar in the three cases suggesting that the depolymerization reactions were the same for all the lignins and lead to similar compounds. AL and AFL patterns were almost identical while very slight differences were observed respect to FL. In this last lignin more intense peaks than the other two distributions could be found which indicated that more monomeric phenolic compounds were produced in the case of FL; a fact that was in accordance with the results of GC-MS. One of the main differences between FL and AL or AFL was the most intense peak. In AL and AFL corresponded to a molecular weight of 89 g mol^{-1} while in FL it was set at 110 g mol^{-1} . The peak at 89 g mol^{-1} could be attributed to the solvent used for oil characterization, ethyl acetate, while the peak at 110 g mol^{-1} could be assigned to catechol.

Figure 1. Molecular weight distribution of the oil from MALDI-TOF analysis.



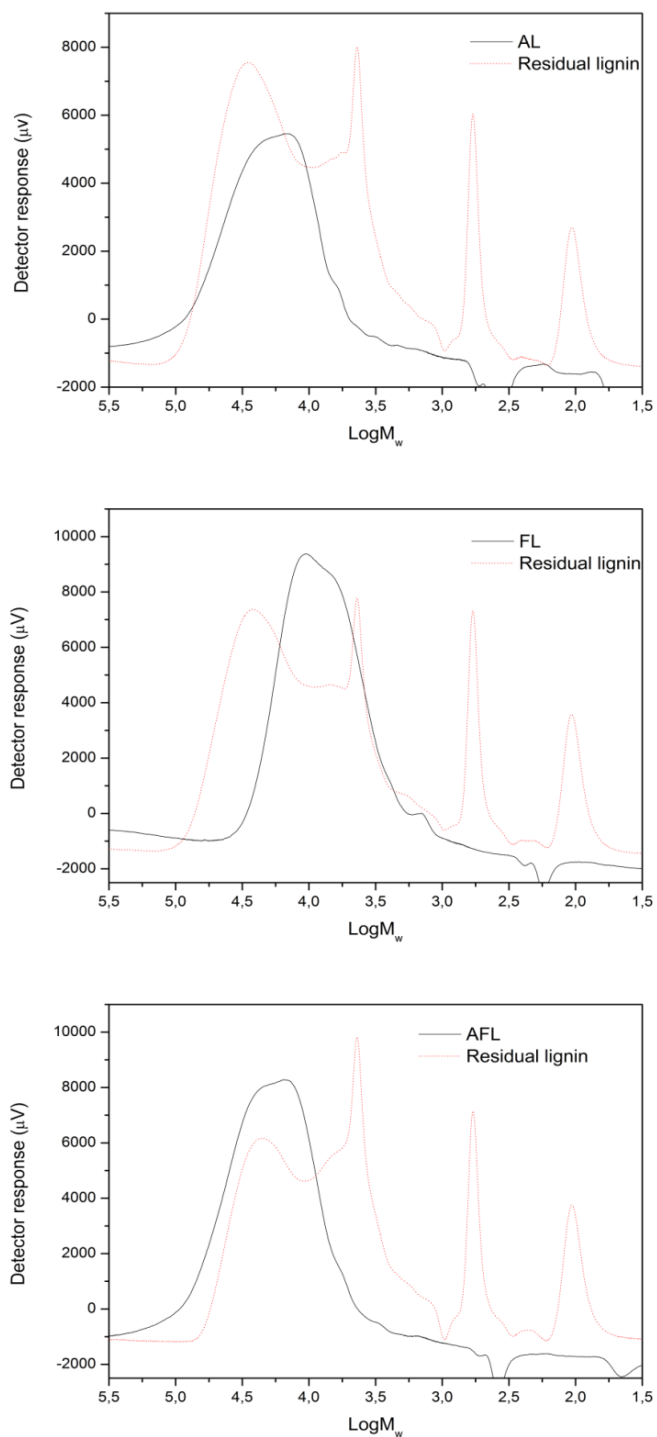
3.3. Residual lignin

Residual lignin was the main product obtained in all cases with around 24% of yield respect to the lignin introduced into the reactor. In order to know the changes produced in the residual lignins they were analyzed by HPSEC within the raw lignin used in each case as reference. Fig. 2 shows MWD of residual lignins and raw lignins.

In Fig. 2 for all residual lignins, four peaks can be observed, one related to the repolymerized lignin and the other ones related to a lower M_w lignin as a result of the depolymerization. The first peak of the residual lignin spectra for all the lignins, especially in AL and FL, confirmed that

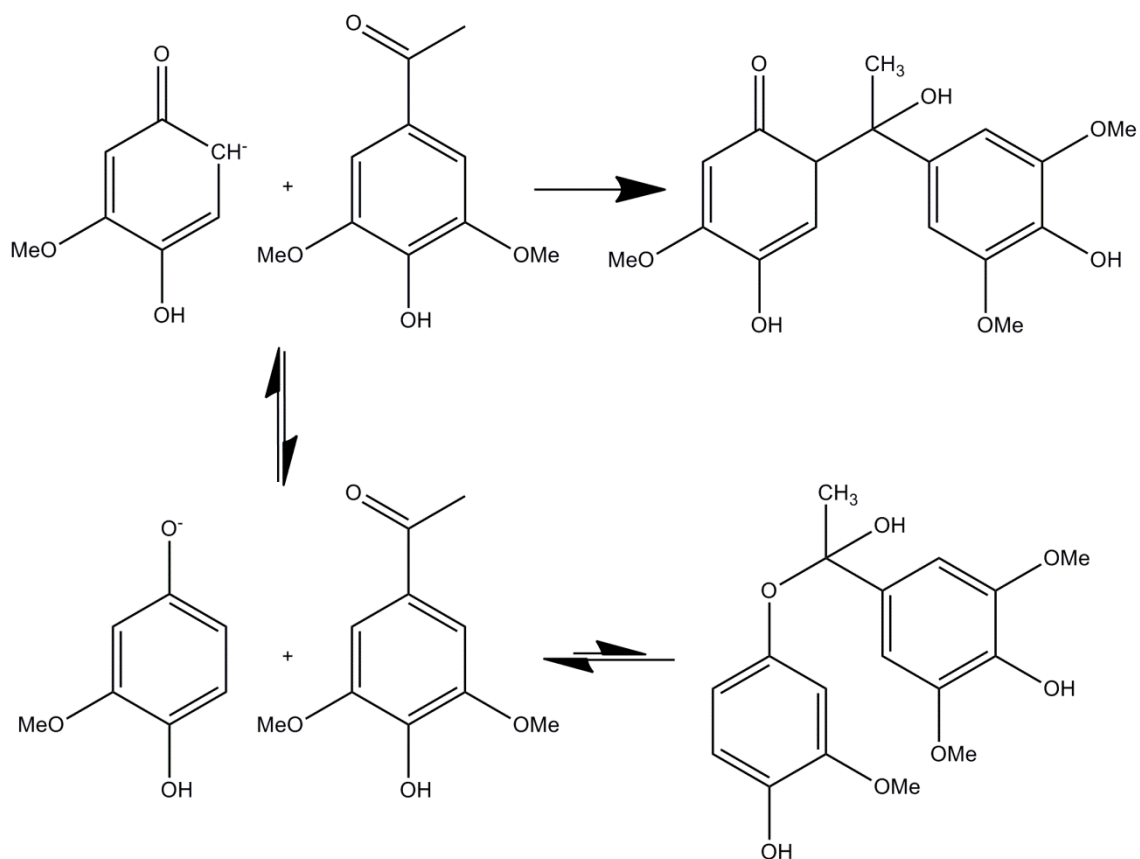
part of the residual lignin has suffered a repolymerization and consequently had a higher M_w than the original lignin. Many authors have reported that the quinone intermediate formed during alkaline hydrolysis of lignin could re-polymerize with the newly formed phenolate side chain through C-C linkages causing an increase in the molecular weight [19, 20].

Figure 2. Molecular weight distribution of raw and residual lignins.



The phenolate ion could also exist as a carbanion with a negative charge in *ortho* or *para* position of the phenolic hydroxyl group [21]. In Fig. 3 it is shown an oligomerization reaction by the aldol addition. The addition of the carbanion species to the ketone species will, consequently, induce an easy formation of carbon-carbon bonds between these compounds [21]. This oligomerization occurs for all lignin samples, and was not affected by the M_w of the raw lignin.

Figure 3. Repolymerization reaction between a phenolate and a carbenium ion [20].



After this first peak other three peaks appears in the chromatogram indicating lower molecular weight fractions than the original lignin as a result of depolymerization. The shape of the peaks was very similar in all lignin samples and had almost the same M_w which indicated that the formation of these residual lignins took place via the same mechanism and lead to almost same residual lignin samples.

In Table 3 weight-average (M_w), number-average (M_n) molecular weight and polydispersity (M_w/M_n) of raw and residual lignins are represented. In AL and AFL residual lignin, could be

observed that M_w decreased respect to the respective raw lignin while in FL increased. This behavior was in accordance with discussed above claiming that formic acid promoted repolymerization reactions. Otherwise, the polydispersity of all residual lignins increased noticeably indicating very different M_w fractions as it has been observed in Fig. 2. In addition, it is again appreciable that all residual lignins are more similar to each other than the raw lignins, with a M_w between 14,335 and 12,049 and very high polydispersity in all cases.

Table 3. Weight-average (M_w), number-average (M_n) molar mass and polydispersity (M_w/M_n) of raw and residual lignins.

	M_w	M_n	M_w/M_n
AL	16,416	1528	10.75
Residual lignin AL	13,214	805	16.41
FL	7924	1430	5.54
Residual lignin FL	14,335	773	18.54
AFL	15,088	1626	9.28
Residual lignin AFL	12,049	697	17.29

In order to know better the composition of this residual lignin and the changes that had suffered in its own structure, a pyrolysis-GC-MS analysis was made to all raw and residual lignins. As it can be appreciated in the Fig. 4 there were huge differences between the raw lignins and residual lignins. However, the chromatograms between raw lignins and more especially between residual lignins were very similar to each other. In Table 4 the compounds which had more than 2% of the area of the whole chromatograms are listed and specified.

All raw lignins presented almost the same compounds but in different proportion which indicated that the nature of three lignins was similar but with some differences. As it was expected, AL and FL lignins were more different between them whereas AFL was a mixture of both of them. In AFL and more especially in AL, phenolic compounds (from 1 to 13) were the main products of the pyrolysis [22]. However, in FL fatty acids were the main compounds (14 to 16) which indicated that FL had some lipids in its composition [23]. In AL and AFL chromatograms the main peak was related to methoxyeugenol (12) while in FL the most abundant compound was the stearic acid (16). These fatty acids are common in suberin which

present aliphatic domains composed of branched polyester moieties mainly composed of long-chain ω -hydroxyfatty acids and α,ω -dicarboxylic acids along with aromatic domains [24]. Dissolution of suberin may have been occurred during pretreatment and while lignin separation process, these fatty acids may have precipitated and so, considered as lignin [25]. Otherwise, most of the phenolic products of the three lignins came from syringol-substituted compounds and guaiacol-substituted compounds, which was in accordance with the nature of the lignins [13].

Figure 4. Pyrolysis-GC-MS chromatograms of raw and residual lignins.

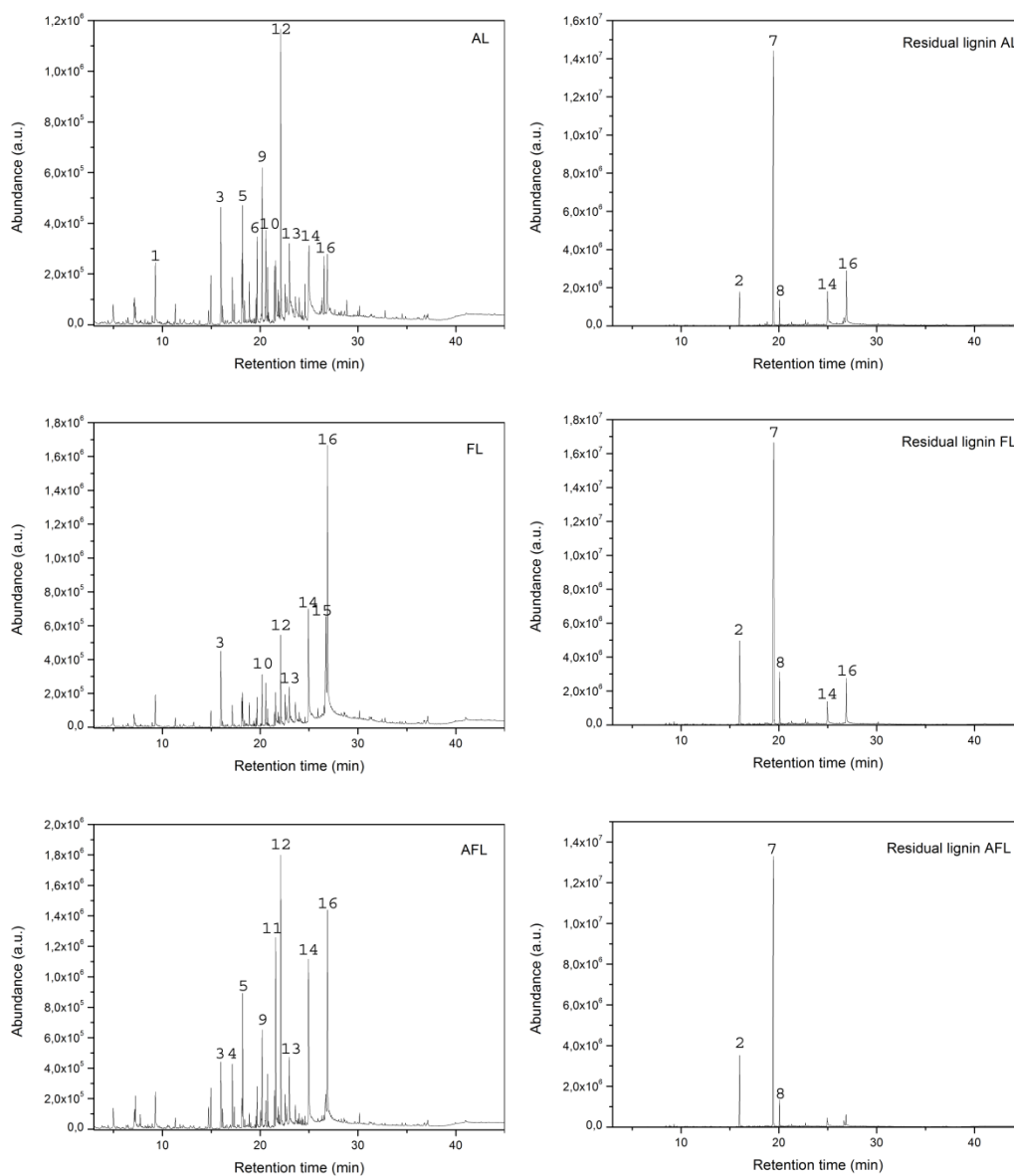


Table 4. List of pyrolysis products identified by Pyrolysis-GC-MS of raw and residual lignins.

No.	Retention time (min)	Compound name (Type) ^a	M _w (g/mol)
1	9.29	Guaiacol (G)	124.14
2	15.98	2-tert-Butyl-p-Cresol (H)	164.25
3	15.99	Syringol (S)	154.16
4	17.17	Vanillin (G)	152.15
5	18.22	Isoeugenol (G)	164.20
6	19.45	Butylated Hydroxytoluene (S)	220.35
7	19.69	Guaiacylacetone (G)	180.20
8	20.08	Phlorobutyrophenone (S)	196.20
9	20.21	Acetophenone (AH)	120.15
10	20.58	2,4'-dihydroxy-3'-methoxy-Acetophenone (G)	182.17
11	21.61	Syringaldehyde (S)	182.17
12	22.12	Methoxyeugenol (S)	194.23
13	23.00	Homosyringic acid (S)	212.20
14	25.00	Palmitic acid (FA)	256.42
15	26.73	Oleic acid (FA)	286.42
16	26.86	Stearic acid (FA)	284.47

a. Compounds categories: Guaiacol type phenols (G), syringol type phenols (S), p-hydroxyphenyl type phenols (H), aromatic hydrocarbons (AH) and fatty acids (FA).

In residual lignins the chromatogram was completely different to raw lignins which indicated that the nature of recovered lignin after depolymerization reaction changed. In these residual lignins one main peak related to butylated hydroxytoluene (7) could be observed. This compound is the major component of the degradation products of residual lignins pyrolysis in all cases and it took more than 53% of the chromatogram area. Besides this, two other signals of phenolic compounds could be appreciated in all chromatograms: 2-tert-Butyl-p-Cresol and

phlorobutyrophenone. In addition, palmitic and stearic acid also appeared in the three chromatograms but in very low quantity. For example, in the case of AFL these two compounds took less than 2 % of the area of the whole chromatogram. As it could be observed the chromatograms of residual lignins were very similar between them so it could be concluded that the nature of the recovered residual lignin was not affected by the composition of the raw lignin.

4. CONCLUSIONS

Different organosolv olive tree pruning lignins were hydrothermally depolymerized employing NaOH as catalyst. The objective of this work was to study the differences occurring in base catalyzed depolymerization using three different lignins obtained by ~~several~~ organosolv methods. The desired product yield (oil) was higher in AL and AFL depolymerization processes. Nevertheless, FL oil was richer in phenolic monomers because of the lowest M_w of this lignin. Otherwise, coke yield was low in AL and relatively high in the other two cases which indicated that formic acid encouraged repolymerization reactions as it reduced the action of the catalyst. Finally, the nature and quantity of residual lignin in all cases was the same, notwithstanding the lignin used in the reaction was. The repolymerization and depolymerization reactions that took place in the formation of residual lignin were similar in the three studied cases and the nature, yield and M_w of the residual lignins were comparable regardless of the nature of the raw lignin.

To sum up, two statements could be made for BCD of different organosolv lignins: Low M_w lignins lead to more monomeric phenolic compounds but lower oil yield; and obtained residual lignin is independent of raw lignin nature.

ACKNOWLEDGEMENTS

Authors would like to thank the Department of Education, Universities and Investigation and Department of Agriculture, Fishing and Food of the Basque Government (scholarship of young researchers training) for financially supporting this work.

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