Base catalyzed depolymerization of lignin: Influence of organosolv lignin nature

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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 they 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.

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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 anthraquione 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 lignins, 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 min 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 h 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 × 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-methoxypyphenylacetone, 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 × 7.5 mm) and PolarGel-M guard (50 mm × 7.5 mm) were employed. The flow rate was 700 mm$^3$ min$^{-1}$ and the analyses were carried out at 40 °C. Calibration was made using polystyrene standards (Sigma–Aldrich) ranging from 70,000–266 g/mol.

The pyrolysis was carried out using a CDS analytical Pyroprobe 5150. The pyrolysis temperature was set at 400 °C for 15 s 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 yield obtained were higher than the obtained in previous work (11.5% of oil yield) with almost the same procedure (same base catalyzed depolymerization of different lignins). First, 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 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].

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

<table>
<thead>
<tr>
<th>Product</th>
<th>AL</th>
<th>FL</th>
<th>AFL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil (%)</td>
<td>18.48 ± 0.59</td>
<td>12.95 ± 0.37</td>
<td>16.28 ± 0.57</td>
</tr>
<tr>
<td>Residual lignin (%)</td>
<td>24.32 ± 0.06</td>
<td>23.47 ± 0.46</td>
<td>24.14 ± 0.19</td>
</tr>
<tr>
<td>Coke (%)</td>
<td>8.29 ± 0.73</td>
<td>17.71 ± 0.50</td>
<td>16.73 ± 0.94</td>
</tr>
<tr>
<td>Gas (%)</td>
<td>1.03 ± 0.04</td>
<td>1.17 ± 0.08</td>
<td>1.06 ± 0.04</td>
</tr>
</tbody>
</table>

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 Table 2.

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 a 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].

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>AL</th>
<th>FL</th>
<th>AFL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>1.04 ± 0.12</td>
<td>1.34 ± 0.06</td>
<td>0.96 ± 0.17</td>
</tr>
<tr>
<td>Cresols</td>
<td>0.52 ± 0.03</td>
<td>0.80 ± 0.02</td>
<td>0.54 ± 0.04</td>
</tr>
<tr>
<td>Guaiacol</td>
<td>0.09 ± 0.02</td>
<td>0.10 ± 0.01</td>
<td>0.07 ± 0.01</td>
</tr>
<tr>
<td>Catechol</td>
<td>6.25 ± 1.20</td>
<td>11.80 ± 1.68</td>
<td>7.80 ± 1.24</td>
</tr>
<tr>
<td>3-methylcatechol</td>
<td>3.30 ± 0.34</td>
<td>4.40 ± 0.24</td>
<td>3.76 ± 1.01</td>
</tr>
<tr>
<td>4-methylcatechol</td>
<td>5.72 ± 0.02</td>
<td>7.00 ± 0.73</td>
<td>6.21 ± 0.91</td>
</tr>
<tr>
<td>4-hydroxybenzaldehyde</td>
<td>0.09 ± 0.01</td>
<td>0.10 ± 0.01</td>
<td>0.08 ± 0.02</td>
</tr>
<tr>
<td>4-ethylcatechol</td>
<td>2.40 ± 0.26</td>
<td>2.59 ± 0.23</td>
<td>1.99 ± 0.38</td>
</tr>
<tr>
<td>Acetovanillone</td>
<td>0.04 ± 0.01</td>
<td>N.D.</td>
<td>0.01 ± 0.00</td>
</tr>
<tr>
<td>4-hydroxy-3-methoxy-phenylacetone</td>
<td>0.07 ± 0.01</td>
<td>0.06 ± 0.01</td>
<td>0.05 ± 0.01</td>
</tr>
</tbody>
</table>
Throughout base catalyzed depolymerization of lignin, \( \beta-O-4 \) 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. According to the obtained results, in addition to the heterolytic cleavage of the \( \beta-O-4 \) 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 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. 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 into 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

![Fig. 1 – Molecular weight distribution of the oil from MALDI-TOF analysis.](image1)

![Fig. 2 – Molecular weight distribution of raw and residual lignins.](image2)
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.

### 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]. 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.

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 ($M_n$) molar mass 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>
<thead>
<tr>
<th></th>
<th>$M_w$</th>
<th>$M_n$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AL</td>
<td>16,416</td>
<td>1528</td>
<td>10.75</td>
</tr>
<tr>
<td>Residual lignin AL</td>
<td>13,214</td>
<td>805</td>
<td>16.41</td>
</tr>
<tr>
<td>FL</td>
<td>7924</td>
<td>1430</td>
<td>5.54</td>
</tr>
<tr>
<td>Residual lignin FL</td>
<td>14,335</td>
<td>773</td>
<td>18.54</td>
</tr>
<tr>
<td>AFL</td>
<td>15,088</td>
<td>1626</td>
<td>9.28</td>
</tr>
<tr>
<td>Residual lignin AFL</td>
<td>12,049</td>
<td>697</td>
<td>17.29</td>
</tr>
</tbody>
</table>

Fig. 3 – Repolymerization reaction between a phenolate and a carbenium ion [20].
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 Fig. 4 there were large 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 (14–16) 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 long-chain \( \omega \)-hydroxyfatty acids and \( \omega,\omega \)-dicarboxylic acids along with aromatic domains [24]. Dissolution of suberin may have 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 guiacol-subsituted compounds, which was in accordance with the nature of the lignins [13].

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 main 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 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.

Acknowledgments

Authors would like to thank the Department of Education, Universities and Investigation (BFI-2010-219 and project IT672-13), and the Department of Environmental and Territorial Policy (scholarship of young researchers) of the Basque Government for financially supporting this work.

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