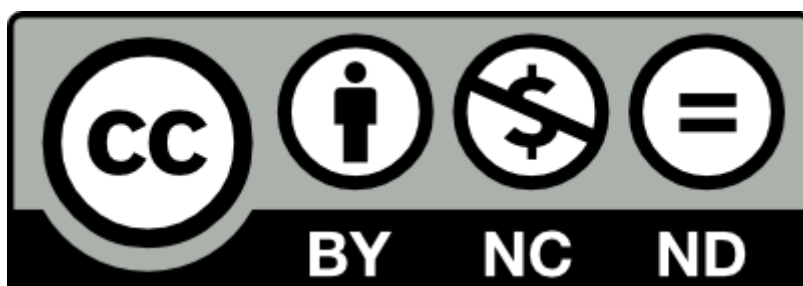


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**Abstract:** The aim of this work was to study the influence of a renewable capping agent (CA) in the production of monomeric compounds from the depolymerization of an organosolv lignin (*Pinus radiata*) by a base catalyzed depolymerization (BCD) process. After the delignification process of the *Pinus radiata* sawdust, the lignin contained in the black liquor was subjected to a first mild depolymerization process, without using any catalyst, in order to obtain two different products: a lignin which was the feed in the subsequent BCD process and a phenolic oil which was used as CA in the same BCD process. This process was carried out at 230 °C in three consecutive cycles of 20 min using different amounts of capping agent dissolved in a 4% wt. NaOH solution with a lignin:solvent ratio of 1:20. The use of a renewable capping agent derived from lignin was effective not only in terms of phenolic oil production increasing but also in maximizing the monomeric phenolic compounds concentration. The use of CA: lignin ratio of 1:1 resulted the most effective with 10.64% of oil yield and almost 44% of monomeric phenolic compounds concentration while minimizing de undesired by-products yield.

**Keywords:** Lignin, Capping agent, Depolymerization, Phenolic monomers, Organosolv.



# Study of a renewable capping agent addition in lignin base catalyzed depolymerization process

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## ABSTRACT

The aim of this work was to study the influence of a renewable capping agent (CA) in the production of monomeric compounds from the depolymerization of an organosolv lignin (*Pinus radiata*) by a base catalyzed depolymerization (BCD) process. After the delignification process of the *Pinus radiata* sawdust, the lignin contained in the black liquor was subjected to a first mild depolymerization process, without using any catalyst, in order to obtain two different products: a lignin which was the feed in the subsequent BCD process and a phenolic oil which was used as CA in the same BCD process. This process was carried out at 230 °C in three consecutive cycles of 20 min using different amounts of capping agent dissolved in a 4% wt. NaOH solution with a lignin:solvent ratio of 1:20. The use of a renewable capping agent derived from lignin was effective not only in terms of phenolic oil production increasing but also in maximizing the monomeric phenolic compounds concentration. The use of CA: lignin ratio of 1:1 resulted the most

effective with 10.64% of oil yield and almost 44% of monomeric phenolic compounds concentration while minimizing de undesired by-products yield.

**KEYWORDS:** Lignin, capping agent, depolymerization, phenolic monomers, organosolv.

## 1. Introduction

Lignin is one of the main components of the cell wall of vascular plants, with a mass content that can vary between 15-30% depending on the species [1] and it is considered the second most abundant polymer in nature after cellulose. Lignin is a polyphenolic compound composed by the polymerization of three hydroxy cinnamyl alcohol monomers, p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol that produce respectively p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) phenylpropanoid units. The amount of these phenylpropanoid units in the cell wall depend on the species. In this sense, hardwood lignins are mainly composed of G and S units and low H traces, whereas softwood lignins only presents G units and low levels of H units. Finally, lignins from grasses have similar amount of G and S units and present a higher level of H units than in other species. These phenylpropanoid units are linked to each other mainly via ether bonds ( $\alpha$ -O-4,  $\beta$ -O-4 and 4-O-5) and carbon-carbon bonds [2]. This confers to the lignin its three-dimensional structure that acts as a resin between cellulose and hemicelluloses [3] which is essential to provide structural integrity to the cell wall and for the stem resistance and stiffness. Due to this phenolic nature, lignin is considered as the most abundant renewable aromatic polymer on Earth [4] and is called to be an alternative to chemical compounds derived from petroleum [5].

Nowadays pulp and paper industry (P&P) is the main source of lignin and the Kraft method is the most employed one to generate chemical pulps. About 50 Mt of lignin are

generated as a by-product in this process [6], which are burned to generate energy [7]. However, due to the environmental issues that can be generated by Kraft process, the organosolv process has been gaining relevance in the fractionation of lignocellulosic feedstock [8]. The organosolv process consist in the delignification of the lignocellulosic biomass via cleavage of ether linkages of lignin [9] employing organic solvents such as ethanol, methanol, acetone, organic acids and polyhydric acids. Among these, the use of ethanol appears as the most favorable due to its low toxicity [10]. The organosolv process has several advantages compared to conventional methods such as the possibility of recovering the solvent by distillation, a lower environmental impact and obtaining a high quality lignin that can be used in different applications such as antioxidants, bio dispersants, polyurethanes foam and epoxy resins [11].

In order to obtain high added value compounds from lignin, different thermochemical methods have been studied. Among these, the BCD process has demonstrated to be a suitable method to transform organosolv lignin into low molecular weight compounds [12]. The use of different basic catalysts in the depolymerization of lignin from olive tree pruning was studied by Toledano et al. [13] concluding that the use of sodium hydroxide (NaOH) as catalyst increased the yield of the phenolic oil which is rich in monomeric compounds. In another study [14] it was concluded that the use of NaOH was suitable for the depolymerization of olive tree pruning lignin obtained through different organosolv processes. Usually most of these works have been carried out in conventional batch reactors; however, the use of microwaves has turned out to be environmentally friendlier and a more efficient option in terms of energy and economic saving and selectivity [15]. Using the microwave technology it is possible to increase the depolymerization reaction of lignin in solvolytic processes [16] since the microwaves facilitates the cleavage of the  $\beta$ -O-4 and C-C bonds [17].

Nevertheless, one of the main products that appears, as a result of the depolymerization of lignin is the char. Char is composed by coke and residual lignin that is generated by the repolymerization via condensation reactions of unstable fragments of lignin. To avoid these repolymerization reactions the effect of different co-solvents has been studied [18] concluding that the use of a mixture of water and p-cresol increased the yield of the tetrahydrofuran (THF) soluble compounds formed during the depolymerization. The effect of boric acid was studied as capping agent during the BCD reaction of organosolv lignin by Roberts et al. [19] and they concluded that the use of boric acid increased the oil yield while the repolymerization reactions were decreased. Additionally, Toledano et al. [20] compared the effect of boric acid and phenol as capping agents in BCD of the organosolv lignin from olive tree pruning and concluded that phenol reduced the amount of char and increased the yield of monomeric compounds. In the same way, other studies had concluded that phenol acts avoiding repolymerization reactions, however, due to the toxic nature of phenol, the aim of this work was to study the use of a renewable capping agent in substitution of this compound. This capping agent was obtained by the depolymerization, without using any catalyst, of the lignin contained in the black liquor from the delignification of pine sawdust through an organosolv process. As it was previously, mentioned one of the main obstacles during the depolymerization are the repolymerization and condensation reactions between the instable fragments of lignin which are in the medium [21]. The hypothesis was that the monomers, dimers and oligomers of the CA could act linking to the active sites of the instable molecules avoiding repolymerization between larger molecules.

## **2. Materials and methods**

### **2.1. Materials**

*Pinus radiata* sawdust was obtained from Ebaki XXI S.A. in Bizkaia, Spain. Ethyl acetate, sodium sulfate anhydride, Dimethyl Furfural (DMF) and Tetrahydrofuran (THF) were purchased from Fisher Scientific, NaOH and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) were purchased from Panreac and ethanol was obtained from Scharlab.

## **2.2. Organosolv treatment**

*Pinus radiata* sawdust was subjected to an organosolv process of delignification using a dissolution of 50% EtOH/water (w/w) at 210°C and 75 min with constant stirring in a solid:liquid ratio of 1:8 [22]. These conditions were selected since the delignification yield was the highest. The treatment was carried out in a 1.5 L stainless 5500 steel Parr reactor with a 4848 Parr controller. Two volumes of acidified water (pH 2) were added to the black liquor obtained from this process to precipitate the lignin (LBD), which was separated by filtration. Several organosolv treatments under the same conditions were carried out to obtain enough black liquor for the following processes.

## **2.3. Black liquor characterization**

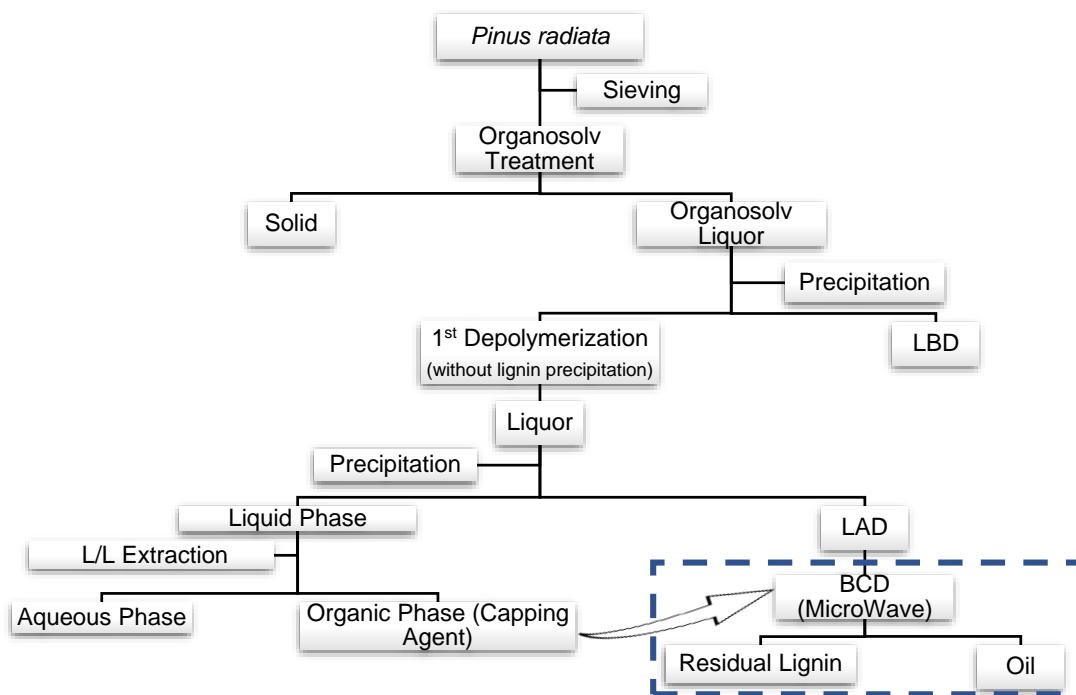
Organosolv liquor from delignification of *Pinus radiata* sawdust was characterized in terms of density, total dissolved solids (TDS), inorganic matter (IM) and organic matter (OM). Density was calculated by weighting a known volume sample of the liquor. TDS were determined by drying the sample for 24h at 105 °C, this method is based on TAPPI T264 cm-97 which is used to determine the moisture content of the sample. The inorganic matter (IM) was calculated burning the dried sample in an oven for 3h at 525 °C employing a method based on the TAPPI T211 om-93 standard used to determine the ash content. Finally, the organic matter (OM) could be determined by the difference between TDS and IM.

## **2.4. Depolymerization processes**

Two depolymerization reactions were carried out. Firstly, the depolymerization reaction of the lignin contained in the organosolv black liquor was carried out in a 1.5 L stainless 5500 steel Parr reactor with a 4848 Parr controller at 210 °C for 60 min. This treatment was conducted for the production of the phenolic-oil, which will be used as capping agent in the following BCD reactions. Secondly, the lignin isolated from the black liquor after this first depolymerization step (LAD) was dissolved in a 4% wt. NaOH solution employing a lignin:solvent mass ratio of 1:20. This mixture was subjected to a BCD reaction using the previously obtained CA in different proportions in weight respect to the lignin (0, 0.5, 1, 2). These BCD reactions were performed in a microwave reactor (FlexiWAVE MA186 with a 660 Terminal and EasyCONTROL software). The depolymerization reaction was carried out with constant stirring and using the following program: firstly, the temperature was raised to 150 °C in 135 seconds, this temperature was kept for 30 seconds and then raised again to the reaction temperature of 230 °C in 135 seconds. This temperature was kept for 20 min and then got down to 100 °C in 15 min. This sequence was repeated 3 times.

## **2.5. Product separation**

For the separation of the different products obtained during the process the next diagram was followed (Figure 1). For the separation of the monomeric compounds contained in the liquor after the BCD reaction, the method described by Toledano et al. [20], was used. The recovered liquor and solids (residual lignin and coke) were acidified until pH 1 employing HCl (37% wt.) in order to separate the solids from the liquor in two well defined phases, a solid phase and a liquid phase. The first one was composed of residual lignin and coke while the second, the liquid phase, was rich in phenolic compounds.



**Figure 1.** Scheme of the CA obtaining process and BCD process (blue box)

These two phases were separated by filtration and washed with acidified water (pH 1). A liquid-liquid extraction with ethyl acetate was carried out. In this way, the phenolic compounds were separated from the liquid phase obtaining an organic phase where the depolymerization products are dissolved. To remove the possible traces of moisture, anhydrous sodium sulfate was added to the organic fraction and then it was filtrated. Afterwards, the organic phase, free of moisture and solids, was evaporated in vacuum to separate the ethyl acetate from the oil rich in phenolic compounds. The solid residue was solubilized in 30 mL of tetrahydrofuran (THF) with constant stirring for 3h. Then, in order to separate the insoluble char from the residual lignin dissolved in the THF, the solution was filtrated. Finally, the THF solution was vacuum evaporated to recover the residual lignin (RL).

## 2.6. Product characterization

The chemical structure of the different lignins (LBD, LAD and residual lignins) were analyzed via FTIR employing a PerkinElmer Spectrum Two FT-IR Spectrometer



equipped with a Universal Attenuated Total Reflectance accessory with internal reflection diamond crystal lens. A total of 18 scans were accumulated in transmission mode with a resolution of  $4\text{ cm}^{-1}$  in a range of  $4000\text{-}600\text{ cm}^{-1}$ .

To determine the average molecular weight ( $M_w$ ) and polydispersity index ( $M_w/M_n$ ) of the different lignins (LBD, LAD and RL) a gel permeation chromatography (GPC) analysis was carried out using a JASCO instrument equipped with an interface (LC-NetII/ADC) and a refractive index detector (RI-2031Plus). Two PolarGel-M columns ( $300\text{ mm} \times 7.5\text{ mm}$ ) placed in series were employed. The flow rate of the mobile phase (N,N-Dimethylformamide) was  $700\text{ mm}^3\text{min}^{-1}$  and the analyses were performed at  $40\text{ }^\circ\text{C}$ . Calibration was made using polystyrene standards (Sigma-Aldrich) ranging from 70000 to 266 g/mol.

A pyrolysis was carried out to analyze the composition of lignins (LBD, LAD and RL) employing a CDS analytical Pyroprobe 5150. The pyrolysis temperature was set at  $600\text{ }^\circ\text{C}$  for 15 s employing a heating rate of  $2\text{ }^\circ\text{C msec}^{-1}$ . After the pyrolysis the products were analyzed in a GC (7890A)-MS (5975C inert MSD with Triple-Axis Detector) Agilent equipped with a HP-5MS ((5%-Phenyl)-methylpolysiloxane,  $30\text{ m} \times 0.25\text{ mm}$ ) capillary column. The temperature program started at  $50\text{ }^\circ\text{C}$  and held for 2 min, then the raised to  $120\text{ }^\circ\text{C}$  at  $10\text{ }^\circ\text{C}/\text{min}$ , kept 5 min, then increased to  $280\text{ }^\circ\text{C}$  at  $10\text{ }^\circ\text{C}/\text{min}$ , kept 8 min, raised to  $300\text{ }^\circ\text{C}$  at  $10\text{ }^\circ\text{C}/\text{min}$  and held 10 min. Helium was used as the carrier gas.

The capping agent employed for the BCD reactions and the oil obtained after these reactions were characterized by GC-MS. The sample was dissolved in ethyl acetate (HPLC grade) in a metric flask. The solution was injected in GC-MS instrument described previously. The temperature program started at  $50\text{ }^\circ\text{C}$ ; then, the temperature was raised to  $120\text{ }^\circ\text{C}$  at  $8\text{ }^\circ\text{C}/\text{min}$ , held at this temperature for 5 min, raised to  $280\text{ }^\circ\text{C}$  at  $8\text{ }^\circ\text{C}/\text{min}$ , held 8 at this temperature for min, raised to  $300\text{ }^\circ\text{C}$  at  $10\text{ }^\circ\text{C}/\text{min}$  and held at this

temperature for 2 min. Helium was also 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.

### 3. Results and discussion

#### 3.1. Black liquor

The results of the characterization of the recovered black liquor are shown in Table 1. As it was expected the pH value was typical result for an organosolv black liquor from *Pinus radiata* and was similar to the pH values obtained by Santos et al. [23]. During the organosolv process, the water in the medium is autoionized leading to hydronium ions that contribute to decrease the pH of the medium. In addition, these ions produce the rupture of the acetyl groups of hemicelluloses forming acetic acid and other organic acids from the degradation of hemicelluloses that contribute to decrease the pH [24,25]. On the other hand, it was noted that all the dissolved solids presented in the black liquor corresponded to the organic matter as would be expected for an organosolv black liquor.

**Table 1.** Black liquor characterization

<b>Black liquor</b>	
<b>pH</b>	3.78 ± 0.042
<b>Density (g/mL)</b>	0.90 ± 0.003
<b>TDS (%)</b>	2.80 ± 0.015
<b>IM (%)</b>	N.D.*
<b>OM (%)</b>	2.80 ± 0.015

\*N.D.: Non detected

#### 3.2. Lignin and capping agent

##### 3.2.1. Lignin

To determine the variations in terms of molecular weight, chemical structure and composition of the original lignin (LBD) and the lignin precipitated after the first “depolymerization” step (LAD), both lignins were subjected to different analysis.

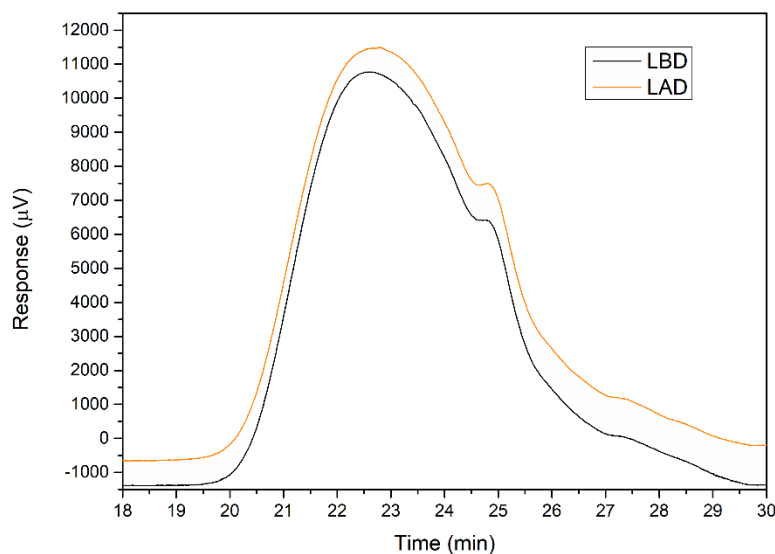
### 3.2.1.1. Molecular weight distribution

The molecular weight distribution of LBD and LAD are shown in the Figure 2 and the average molecular weight ( $M_w$ ), number-average ( $M_n$ ) and the polydispersity index ( $M_w/M_n$ ) are summarized in Table 2.

**Table 2.**  $M_w$ ,  $M_n$  and PI of LBD and LAD

Sample	$M_w$	$M_n$	$M_w/M_n$
LBD	3567	1036	3.442
LAD	3638	1010	3.601

The obtained lignin samples after precipitating the lignin contained in the black liquor from the organosolv process, presented similar  $M_w$ ,  $M_n$  and polydispersity values than the ones obtained by Dominguez et al. [22], which was the expected result because similar experimental conditions were used. The molecular weight distribution of the lignin samples is presented in Figure 2.

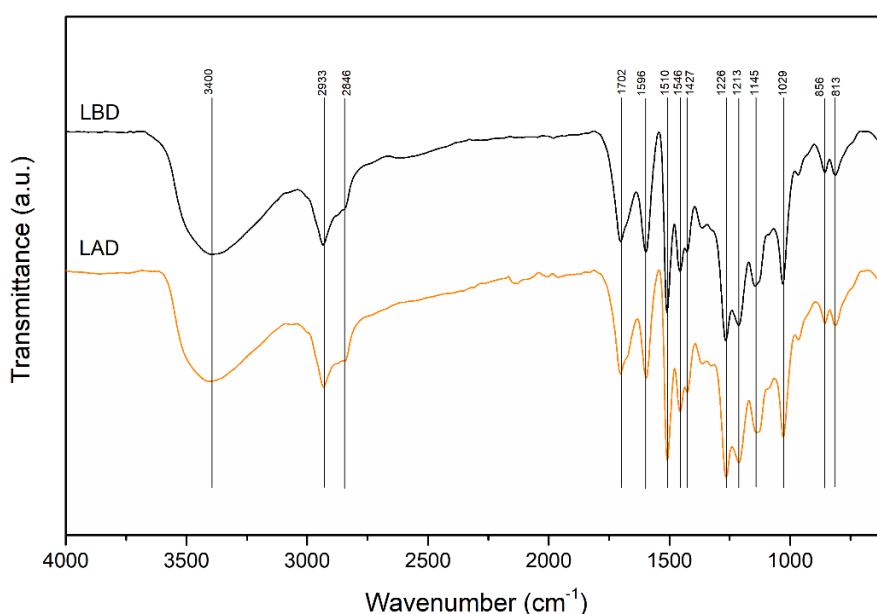


**Figure 2.** Molecular weight distribution of LBD and LAD

During the depolymerization process the pH of the liquor was slightly reduced (pH=3.61) due to the degradation products of the hemicelluloses, increasing by this way the concentration of hydronium ions in the medium which could help in the cleavage of lignin bonds. However, this slight increase in the concentration of hydronium ions was not enough to increase the degree of depolymerization of lignin due to the mild conditions of the depolymerization treatment [26]. This also indicated that the repolymerization reactions were very limited or non-existent. Therefore, as it was expected LAD turned out to be similar to LBD in both molecular weight and polydispersity index.

### 3.2.1.2. Chemical structure

The chemical structures of the lignins were characterized by FTIR. As it can be observed in Figure 3, there were no differences between the two samples, which confirms that, due to the low severity of the depolymerization reaction, there were no repolymerization reactions that could alter the structure of the LAD lignin respect the LBD.



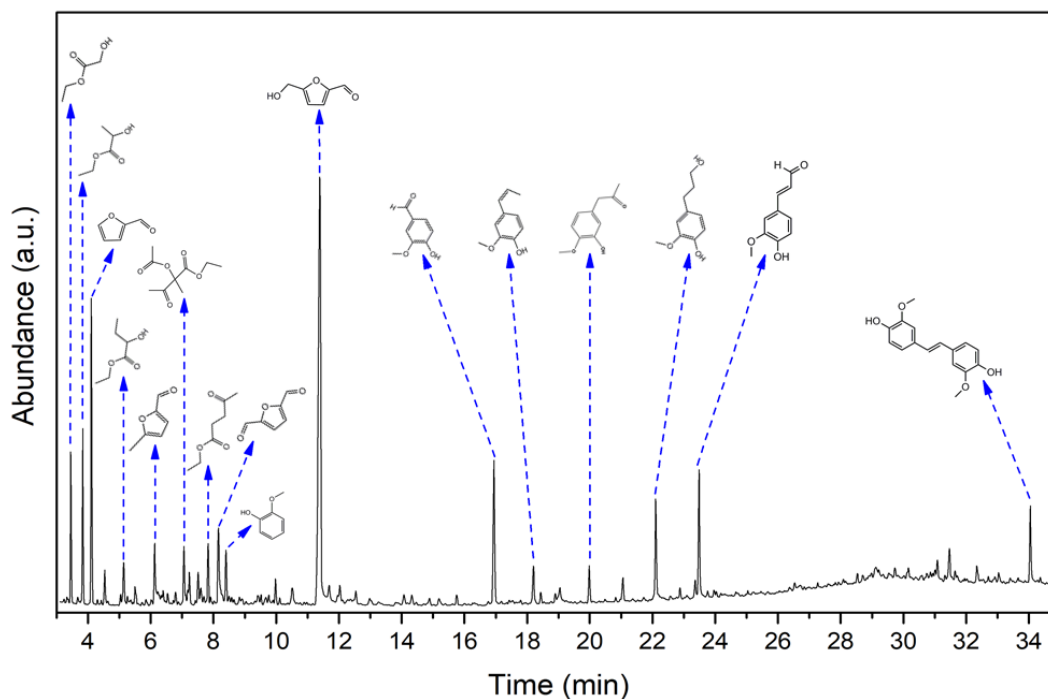
**Figure 3.** FTIR spectra of LBD and LAD

This can be confirmed by analyzing different peaks associated with lignins whose condensed structures were typical of repolymerization reactions. In this sense, it can be

observed that the peak at  $1705\text{ cm}^{-1}$  had the same intensity in both samples. This peak, associated with the carbonyl group [27], is usually more intense in the residual lignins that are formed in the repolymerization reactions because, after the cleavage of the  $\beta$ -O-4 bonds of the lignin, a double bond is formed between the carbon and the oxygen that stabilizes the unstable fragments of lignin with a carbonyl group [28]. Additionally, the signals at  $1213\text{ cm}^{-1}$  and  $1140\text{ cm}^{-1}$  had the same intensity in the two samples. These signals correspond to the C-C + C-O + C=O stretching and to the C-H bonds in-plane deformation of the G rings respectively and are usually more intense when G units are condensed. The same happened with the signals at  $856\text{ cm}^{-1}$  and  $813\text{ cm}^{-1}$ , characteristics of the C-H group out of plane at positions 2,5 and 6 in the guaiacyl units [27]. It should be noticed as well that the intensity of the peak associated with the vibration of the aromatic ring in guaiacyl units ( $1510\text{ cm}^{-1}$ ) [27] did not varied in intensity, indicating that both samples had the same aromatic nature. Therefore, it could be concluded that the chemical structure of LAD lignin did not change with respect to the structure of LBD lignin.

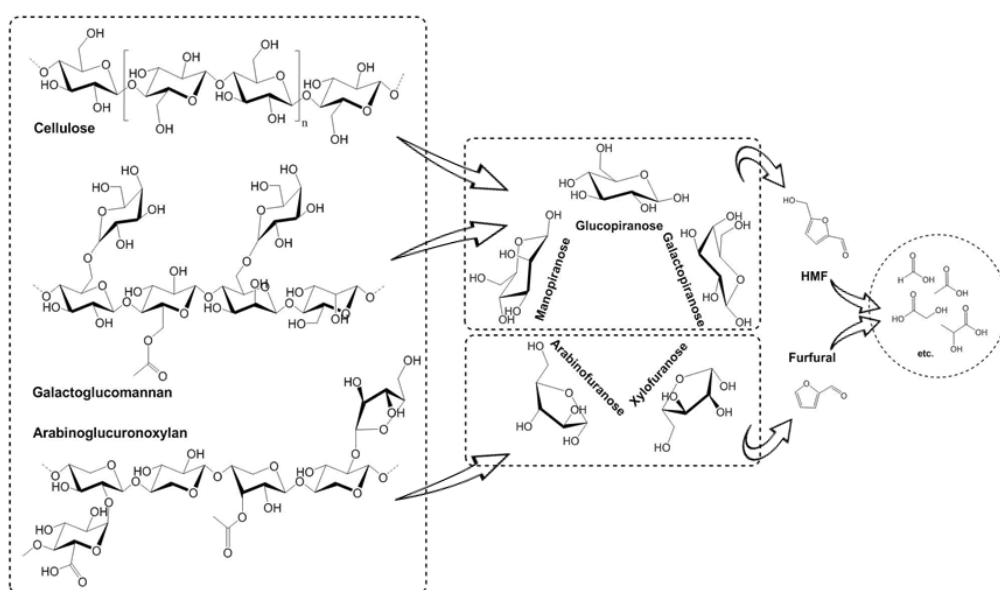
### **3.2.2. Capping agent**

The capping agent was mainly composed, as it can be observed in Figure 4, by degradation products of hemicelluloses, mainly HMF and furfural. During the organosolv delignification process, cellulose amorphous region and hemicelluloses were depolymerized giving rise to soluble oligosaccharides and monosaccharides. As shown in Figure 5, soluble monosaccharides were degraded by dehydration in their corresponding furans. The hexoses are mainly decomposed in HMF while the pentoses are decomposed in furfural. If the reaction conditions are the appropriate, these compounds can degrade to give acids such as formic, acetic, glycolic and lactic [29,30].



**Figure 4.** GC-MS chromatogram of Capping Agent (CA)

A higher concentration of HMF versus furfural was noted since pine hemicelluloses are mainly composed of hexoses [31] that degrade into HMF. It was also possible to observe the presence of ethyl glycolate and ethyl lactate that are formed by esterification of glycolic acid and lactic acid with the ethanol, which was in the medium during the posterior depolymerization process of the organosolv black liquor.



**Figure 5.** Scheme of pine wood cellulose and hemicelluloses degradation adapted from [32]

However, in addition to the products derived from the degradation of hemicelluloses, there were also lignin derived compounds. These compounds were first formed during the delignification of the raw material and after the subsequent depolymerization of black liquor via hydrolytic cleavage of the  $\alpha$  and  $\beta$  aryl ether bonds of lignin [9]. Due to this rupture, smaller fragments of lignin were produced that were solubilized in the medium [33]. These unstable fragments can repolymerize or stabilize as monomers forming part of the CA such as guaiacol, dihydroconiferyl alcohol, coniferyl aldehyde or dimers such as 3,3'-dimethoxystilbene-4,4'-diol (Figure 4).

### **3.3. Depolymerization process of LAD**

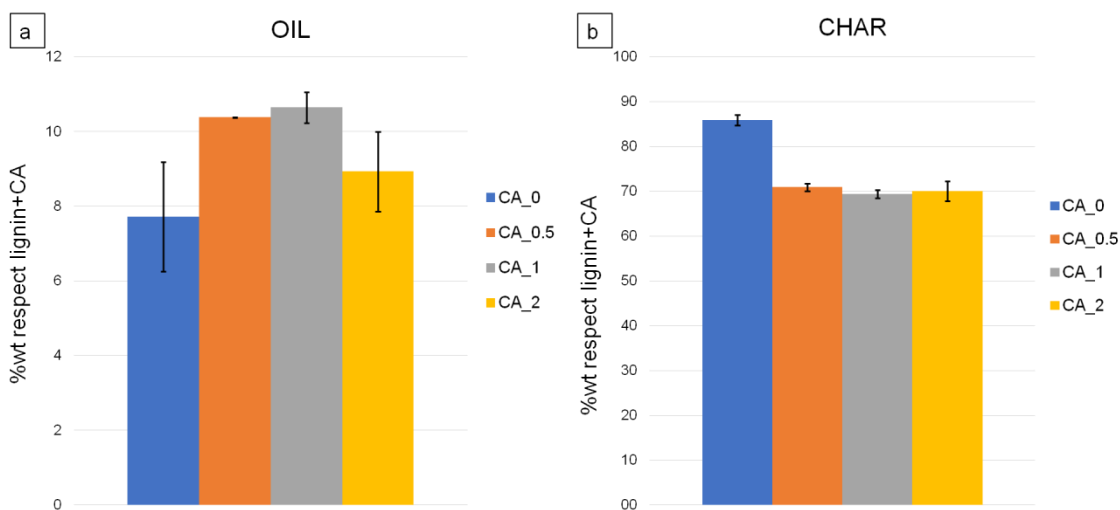
#### **3.3.1. Yield of depolymerized products**

As a result of the base catalyzed depolymerization reaction of LAD, three products were mainly obtained, namely: an oil rich in monomeric compounds and a solid fraction, called char, which is composed of residual lignin and coke. Oil and char yields (%wt.) were calculated respect to the total organic matter that was used in the reactions (lignin and capping agent) and are presented in Figure 6a and 6b, respectively. An experiment without capping agent (CA\_0) was carried out in order to evaluate the effect of the CA during the depolymerization reaction, obtaining an oil yield of 7.72%. Even though, as expected, the oil yield increased in those experiments where the capping agent was used, in all cases the yield turned out to be low due to the mild conditions of the treatment. This comes to be in agreement with the results obtained by Roberts et al. [19] who observed that the oil yield increased at higher temperatures.

Furthermore, it should to be noted that, in the experiments where CA:lignin ratios of 0.5:1 (CA\_0.5) and 1:1 (CA\_1) were used, very similar oil yields were obtained (10.38% and 10.64% respectively), while an excess of CA, ratio 2:1 (CA\_2), did not have a positive

effect, obtaining an 8.93% oil yield. This decrease is an unexpected result considering previous studies in which phenol was used as a capping agent. For example, Toledano et al. observed that an excess of phenol resulted in an increase in the oil yield [20]; nonetheless the calculations were made with respect to the initial lignin and yields greater than 100% were obtained. In addition, in the same study, they proved that an excess of boric acid as capping agent was necessary to obtain a higher oil yield. In another study carried out by Belkheiri et al. [34] in which lignin Kraft LignoBoost was depolymerized in a reactor with recirculation using phenol as a capping agent, it was observed that the yield in oil was very similar regardless of the amount of phenol used.

Otherwise, it could also be observed that the experiments were more reproducible in the cases where a CA:lignin ratio of 0.5:1 and 1:1 were used. Regarding the char yields, it was observed as it was expected, that the capping agent acted decreasing repolymerization products.



**Figure 6.** Oil (a) and Char (b) yield (%wt.) respect to the total organic matter

However, it is remarkable the high char values that were obtained. This high yield of char could be explained by the high residence time employed in the BCD reactions since, according to Ouyang et al. [17], the recondensation reactions could be favored by high residence times under microwave irradiation conditions. In this way, the highest char



yield was obtained for the blanc experiment while in the rest of experiments this product decreased considerably with respect to the blanc by  $29.88 \pm 0.747\%$  in average. However, as it can be seen in Figure 6b, the char yield in the experiments where capping agent was used was practically the same, which denotes that the concentration of capping agent had little influence on the production of char.

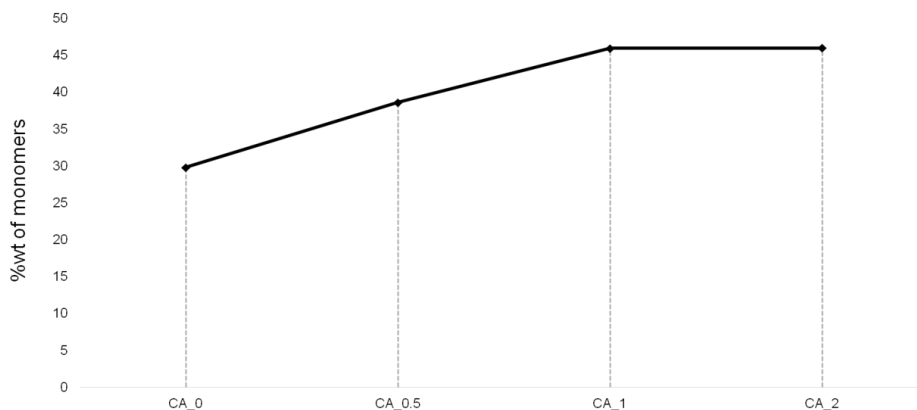
It should be noted that the material balances were not closed at 100% in any of the experiments; this loss of matter occurs because, during the depolymerization reaction, gaseous products are generated [14] which were not quantified in this case. Moreover, some products generated in the reaction remained in the aqueous phase after the liquid-liquid extraction process. This loss of material for the oil and char fractions was more evident in those experiments in which the capping agent was used, especially for CA\_2, compared to the blank experiment. This could be due to the fact that, during the BCD depolymerization reaction, the degradation compounds of the hemicelluloses that are presented in the capping agent could react creating compounds such as acetic acid [28] that are retained in the aqueous phase.

### **3.3.2. Characterization of depolymerized products**

#### **3.3.2.1. Oil characterization**

The monomer concentration in the oil is represented in Figure 7, in which, the effect of the capping agent in monomers obtaining can be observed. There was a clear evidence that the use of the capping agent favored the concentration of these compounds in the oil. In fact, it can be observed that, as the ratio of capping agent was increased, the yield of monomers in the oil increased up to 54.26% (CA\_2) with respect to the blanc experiment (CA\_0). This improvement was also evident in the experiments CA\_0.5 and CA\_1 where the concentration of monomers increased with respect to the blanc experiment, by 29.49% and 54.04%, respectively. However, it can be highlighted the fact that an excess of

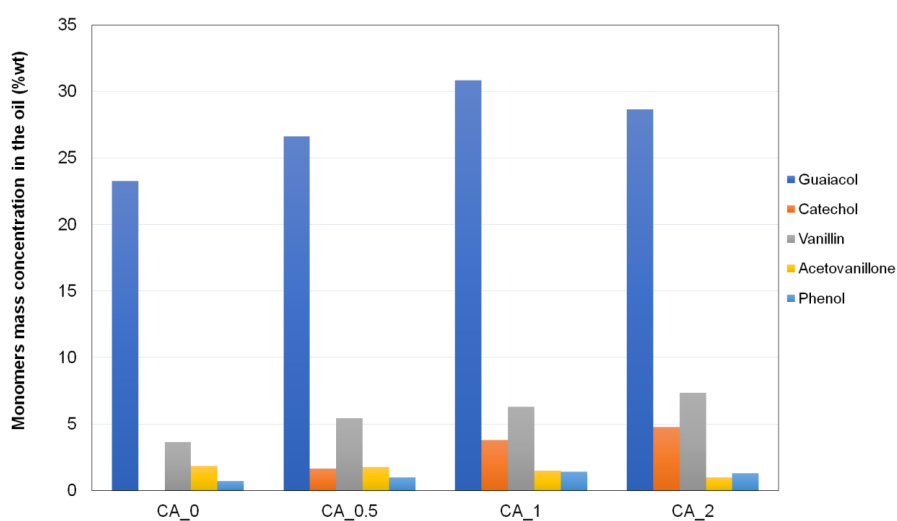
capping agent did not entail a significant improvement, since for CA\_2 there was no enhancement with respect to the experiment CA\_1. This little improvement in monomers yield in CA\_2 respect to CA\_1 (54.26% vs. 54.04%, respectively) as well as the decrease in oil yield (16.07% of decrease) did not justify the use of the highest CA proportion.



**Figure 7.** Phenolic monomers concentration (%wt.) in the oil.

Regarding the compounds presented in the oil, it should to be pointed out that the main compound in all the experiments was guaiacol (Figure 8). This product was formed by the hydrolysis of the ether bonds of lignin. However, as it can be observed in the blank experiment, the reaction conditions were not sufficiently severe to obtain some decomposition products of guaiacol such as catechol and cresols, obtained through the demethoxylation of guaiacol units [14] and only a small amount of phenol was obtained. The addition of the capping agent favored the production of these monomers and also incremented the concentration of guaiacol obtaining the maximum for the experiment CA\_1. Moreover, catechol was formed in the experiments where CA was used, increasing its yield as the CA: lignin ratio was increased. All these indicates that the presence of CA prevented the union of the unstable fragments of lignin during the BCD reaction favoring the formation of monomers. In addition, the demethoxylation of the monomers which

were already present in the CA, favored the production of catechols and cresols. On the other hand, due to the oxidative character of the atmosphere in which the depolymerization reactions were carried out, the second most abundant compound in all the reactions was vanillin, coming from the oxidation of lignin [35]. In addition, it could be observed that, in those experiments in which the capping agent was used, the amount of vanillin increased. This could be due to the oxidation of those monomers present in the capping agent such as guaiacol, dihydroconiferyl alcohol and the coniferyl aldehyde.

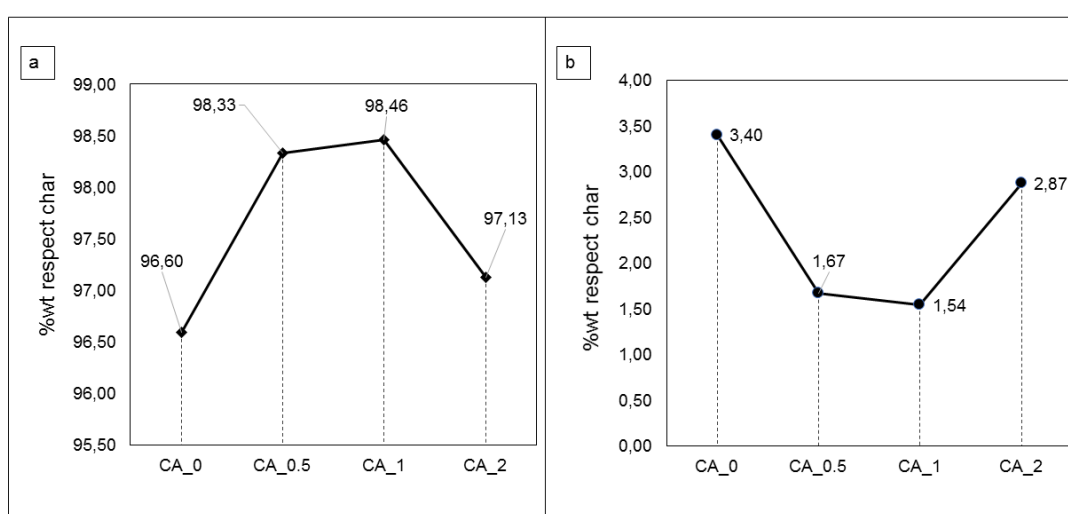


**Figure 8.** Monomers mass concentration (%wt.) presented in the oil.

### 3.3.2.2. Char characterization

As mentioned above, char is one of the main products obtained during BCD of lignin. Char is mainly composed by residual lignin and coke to a lesser extent which is the least desired product due to its limited revaluation opportunities. RL and coke percentage are calculated respect the recovered char and are shown in Figure 9a and 9b respectively. For all reactions, the residual lignin yield was higher than 95% while the coke did not exceed 3.5% in the worst case (CA\_0). In addition, the yield of RL increased in all experiments where CA was used decreasing the coke yield at the same time. In this sense, the lowest yield of RL and obviously the highest yield of the undesirable coke was obtained for the blanc experiment, 96.6 % and 3.40% respectively. At the same time as the CA:lignin ratio

was increased the yield of RL increased up to 98.46% for the experiment with a ratio of 1:1 reducing simultaneously the formation of coke up to 45.33% respect to the blanc experiment. However, this trend was reversed when an excess of capping agent was used which seems to indicate that an excess of CA was not beneficial. It must to be pointed out that coke was not analyzed in this case due to the low amount that was recovered after the reactions. On the other hand, residual lignin was characterized in order to study its chemical structure and composition.



**Figure 9.** Residual lignin (a) and Coke (b) yields (%wt.) respect char

### 3.3.2.2.1. Residual lignin characterization

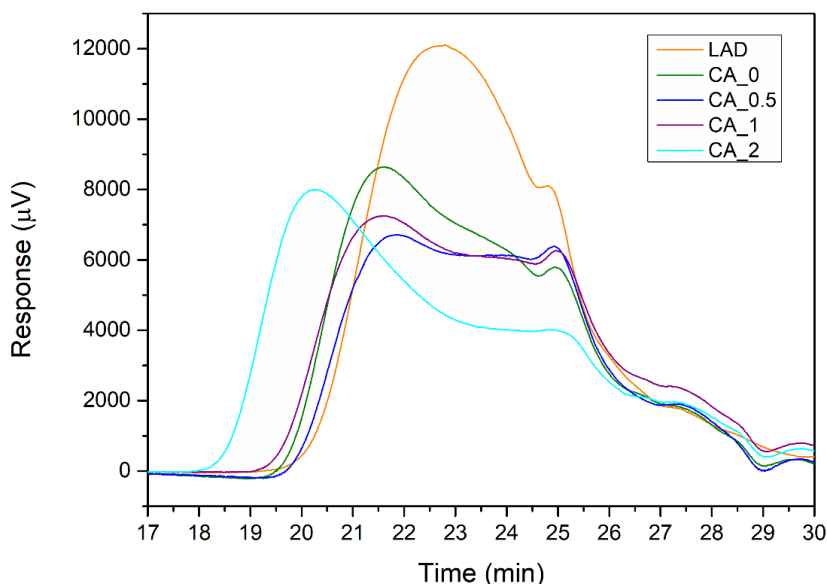
As it was mentioned above, residual lignin was the main product of lignin depolymerization in all cases. In order to determine the composition and structural changes that residual lignins had suffered, the samples were subjected to various analyses and compared with the LAD which was used as reference.

The molecular weight distribution of residual lignins were determined by GPC. The resulting chromatograms are shown in Figure 10 and summarized in Table 3. In Figure 10 it is shown a first peak in all chromatograms of residual lignins appearing at a shorter retention time. This indicates that repolymerization and condensation reactions occurred simultaneously during the depolymerization reactions, resulting in a higher Mw fraction

than the LAD. On the other hand, comparing the residual lignins of the experiments where the CA was used with the blanc experiment, it was observed that a low CA ratio had contributed to decrease the Mw and the polydispersity index of the lignin. This could be because the monomers, dimers and trimers that were present in the CA linked to the reactive sites of the unstable lignin fragments avoiding repolymerization between larger lignin molecules. However, as the CA ratio was increased, an increase in the molecular weights and the polydispersity index was observed, reaching the maximum when an the highest of CA:lignin ratio was used.

**Table 3.** Mw, Mn and PI of LAD and different RL

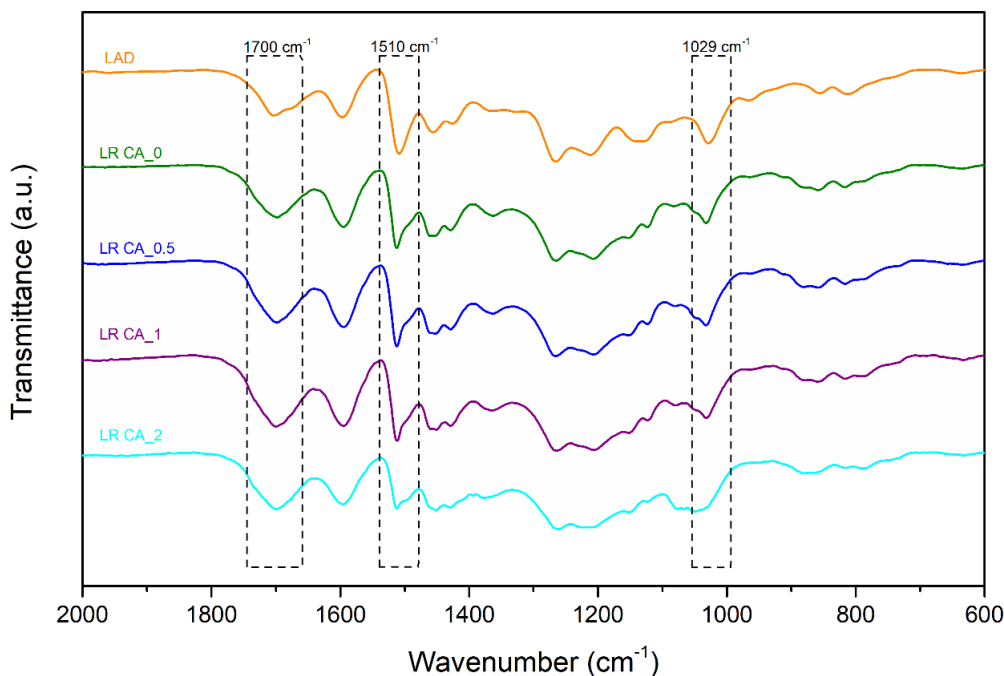
Sample	Mn	Mw	Mw/Mn
LAD	1010	3638	3.60
RL CA_0	1082	5812	5.37
RL CA_0.5	930	4631	4.98
RL CA_1	995	6099	6.13
RL CA_2	1519	16921	11.14



**Figure 10.** Molecular weight distribution of Residual Lignin and LAD

In order to determine the chemical structure of residual lignins they were subjected to a FTIR analysis and compared with the LAD to analyze the possible changes they suffered during the depolymerization reactions.

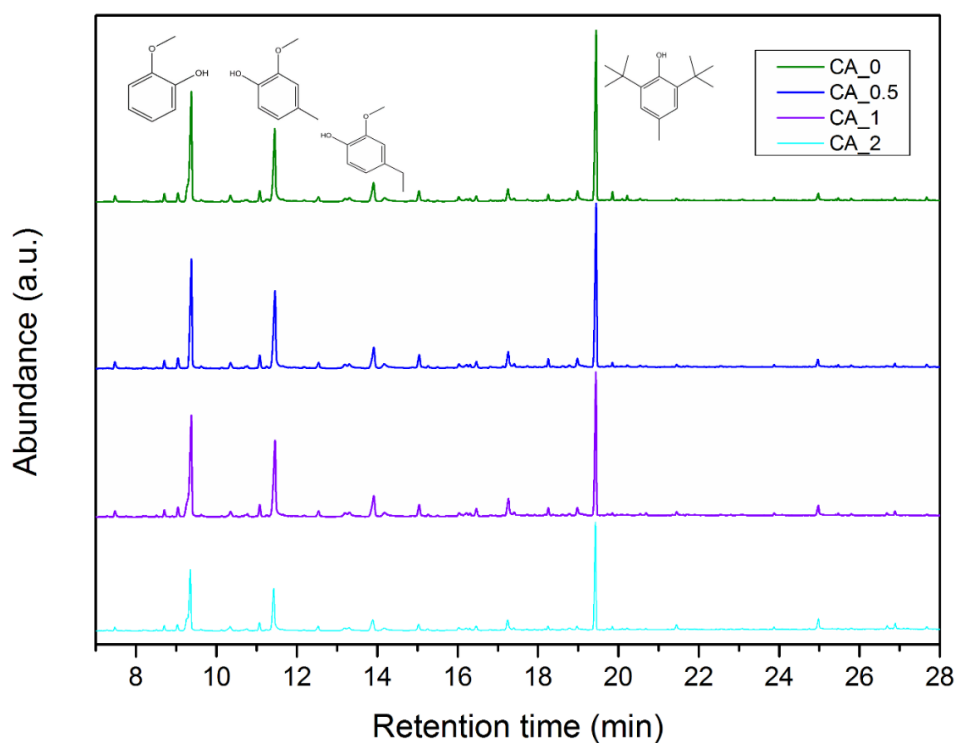
In Figure 11 the FTIR spectra in the fingerprint area of all lignins are shown. It could be observed that the intensity of the peak at  $1700\text{ cm}^{-1}$ , which is associated with the carbonyl group, is more intense in the residual lignins as it was mentioned above. Nevertheless, the main difference between them lies in the intensity of the peaks at  $1510\text{ cm}^{-1}$  and  $1028\text{ cm}^{-1}$ , both associated with the aromatic ring in guaiacyl units. The intensity of both peaks decreased as the concentration of CA in the BCD reactions increased. This confirms the results obtained in the analysis of the oil composition where it was seen that increasing the concentration of the CA, the amount of both guaiacyl and its derivatives was increased, which means that LAD has lost guaiacyl units during BCD reaction. On the other hand, no other significant differences were observed in lignins spectra, indicating that residual lignins maintained its aromatic structure. This could be explained by the mild conditions employed in the BCD which were not harsh enough to change the structure of the residual lignins.



**Figure 11.** FTIR spectra of RL and LAD

Finally, and with the purpose of understanding better the composition of this residual lignin, a pyrolysis-GC-MS analysis was carried out to all residual lignins. The

chromatograms of the residual lignins are represented in Figure 12. A list of compounds whose area was greater than 1% with respect to the total area of the chromatogram is specified in Table 4. As it can be appreciated in Figure 12, there were no differences between all residual lignins which presented the same compounds. In all cases, Butylated Hydroxytoluene (BHT) appears as contamination because it is used as a stabilizer of the THF that was employed in the separation of coke and residual lignin. The most abundant compound of residual lignin was guaiacol followed by 4-methylguaiacol and 4-ethylguaiacol. It should be noted that these three compounds represent more than 40% of the total area of the chromatograms in all cases respect of residual lignin. Among them, as mentioned above, the compound with the highest area was guaiacol with an average area of  $25.35 \pm 6.36\%$ . On the other hand, 4-methylguaiacol represented  $20.43 \pm 2.09\%$  while 4-ethylguaiacol showed an area of  $6.55 \pm 0.31\%$ . Finally, the high abundance of guaiacyl compounds that are presented in the residual lignins could explain the low oil yield obtained in the depolymerization processes.



**Figure 12.** Py-GC-MS of Residual Lignins

**Table 4.** Pyrolysis products identified by Pyrolysis-GC-MS of residual lignins

RT (min)	library/ID	Area (%)			
		CA_0	CA_0.5	CA_1	CA_2
3.34	Furan, 2,5-dimethyl-	N.D.	N.D.	N.D.	1.26
7.47	Phenol	1.03	1.17	1.04	1.01
8.70	O-Cresol	1.11	1.09	N.D.	1.13
9.03	m-Cresol	1.35	1.63	1.52	1.49
9.35	Guaiacol	22.71	19.13	22.47	12.50
10.34	Phenol, 2,4-dimethyl-	1.30	1.14	1.30	1.93
11.07	3-Methylguaiacol	1.56	1.86	1.74	1.97
11.42	4-Methylguaiacol	14.84	16.93	16.64	13.53
12.53	3,4-Dimethoxytoluene	N.D.	1.13	N.D.	1.28
13.89	4-Ethylguaiacol	4.68	5.06	5.40	4.74
14.18	4-Methylguaiacol	1.61	1.62	1.65	1.69
15.03	4-Vinylguaiacol	1.80	2.27	2.32	2.00
16.46	Guaiacylpropane	N.D.	1.02	1.27	1.30
17.24	Vanillin	2.22	2.86	3.35	3.23
18.99	Acetovanillone	1.47	1.46	1.32	N.D.
19.43	Butylated Hydroxytoluene	26.46	25.57	20.82	23.60
21.45	Methyl Homovanillate	N.D.	N.D.	N.D.	1.34
24.98	n-Hexadecanoic acid	1.20	1.01	1.85	2.47
26.89	Octadecanoic acid	0.39	0.52	N.D.	1.24

#### 4. Conclusions

The depolymerization of organosolv lignins from *Pinus radiata* using a renewable capping agent had a positive effect on the oil yield compared to the blank experiment. In addition, the yield of monomeric compounds also increased, especially the yield of guaiacol and vanillin. It could also be observed, that the use of the capping agent favored the demethoxylation of the guaiacyl units to form monomers such as catechol, decreasing the repolymerization reactions and reducing, as it was expected, the solid yield respect to the blank experiment. On the other hand, it was observed that as the capping agent ratio increased, the yields in oil and monomeric compounds also increased, obtaining the maximum oil yield for the experiment CA\_1. However, this tendency was reversed when an excess of capping agent was used as it can be seen in experiment CA\_2 where the oil yield decreased. Nevertheless, the monomers yield was the highest for the experiment



where an excess of capping agent was used but this increment was negligible. In addition, the GPC analysis demonstrated that an excess of the CA resulted in a residual lignin with higher molecular weights. Finally, the chemical structure and composition of all residual lignins were similar to each other; in all cases guaiacol and its derivatives were the main compounds after residual lignins pyrolysis so their structures maintained an aromatic nature which will be positive for further valorization. Taking all this into account, the use of CA:lignin ratio of 1:1 was selected as the most suitable option for lignin depolymerization process as it can act like any other commercial capping agent, such as phenol.

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