Depolymerization of different organosolv lignins in supercritical methanol, ethanol and acetone to produce phenolic monomers

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ABSTRACT

Olive tree pruning was delignified by organosolv processes (acetosolv, formosolv and acetosolv/formosolv) to extract different lignins. The obtained lignins (acetosolv lignin (AL), formosolv lignin (FL) and acetosolv/formosolv lignin (AFL)), were depolymerized using three different solvents (methanol, ethanol, acetone) under supercritical conditions in a batch reactor to produce high value added compounds. The recovered products (oil, char and residual lignin) were analyzed in order to determine their composition and to know the influence of employed solvent and lignin. Lignin was successfully depolymerized in all cases, and molecular weight of residual lignin was significantly reduced compared to raw lignin. The obtained oil had numerous phenolic monomers being syringol and guaiacol the main products in all studied cases. Depolymerization of AFL led to maximum yield of oil (38.04%) and acetone was the best solvent in terms of phenolic monomers production.

Keywords

Lignin, Supercritical solvents, Depolymerization, Monomeric phenols, Solvolysis

Introduction

The depletion of fossil fuels is causing biomass to become an important renewable feedstock for the production of fuels, chemicals, and energy. Plant biomass is composed around of 40-45 wt.% of cellulose, 25-35 wt.% of hemicellulose, 15-30 wt.% of lignin and up to 10 wt.% of other compounds[1]. Lignin is a natural polymer made up by the combination of three different phenylpropane monomer units, namely guaiacyl alcohol, *para*-coumaryl alcohol and syringyl alcohol[2]. Its three monomers are differentially methoxylated and vary in abundance in the polymer, depending on the plant species and plant tissue[3]. These phenylpropane units form an amorphous three-dimensional structure and are linked mainly by an aryl-aryl ether linkage[4] and in less proportion by C-C bonds[5]. Lignin's function is to provide mechanical stability to plant tissues and is very difficult to degrade by biochemical or chemical means[6]. However, due its chemical structure, lignin is a very promising source of renewable products and commodity chemicals.

Liquefaction of lignin or biomass in sub/supercritical fluids such as water[7,8], methanol[9,10], ethanol[11,12], carbon dioxide and acetone[13] has been studied by many researchers to obtain bio-oil or phenolic chemicals with low molecular weights. In the energy field, these phenolic chemicals can be used as antioxidant additives in gasoline to control gum formation. The phenol antioxidants are also very important to control the oxidative process in the new generation biodiesels that have very low content of sulfur[14]. Yokoyama et al.[7] studied lignin depolymerization under sub- and supercritical water and reported that higher water density increased the yield (maximum 40%) of oil and products containing hydroxyl groups and decreased the yield (minimum 30%) of char. Okuda et al.[8] gave a detailed of lignin depolymerization process under supercritical water. According to their proposal, lignin first decompose by hydrolysis and dealkylation yielding formaldehyde and low-molecular weight fragments that have reactive functional groups and compounds such as syringols, guaiacols,

catechols and phenols. Then, cross-linking between formaldehyde and these fragments occur, and the residual lignin gives higher-molecular- weight fragments. However, they found that when phenol was used in the reaction media, no char was produced, because char formation was depressed due to entrapment of active fragments (e.g., formaldehyde) and capping of active sites occurs by excess phenol.

Minami et al.[9] examined lignin reactivity, focusing on the 5-5, β-1, β-O-4, and α-O-4 linkages of lignin using some lignin model compounds. The results showed that the 5-5 and β-1 linkages were stable in supercritical methanol, whereas both β-O-4 and α-O-4 linkages were cleaved rapidly. Therefore, it was suggested that supercritical methanol treatment effectively depolymerized lignin to lower molecular-weight products by cleaving the ether linkages of lignin. Otherwise, lignin depolymerization and hydrogenation was studied under supercritical methanol by Barta et al.[10]. Lignin was disassembled to monomeric units with little or no formation of insoluble char. The process was catalyzed by a copper-doped porous metal oxide, and the products after hydrogen transfer contain virtually no aromatics and have greatly reduced oxygen content in order to use them in hydrocarbon fuels or fuel additives.

Lignin was hydrocracked at 260 °C under supercritical ethanol and hydrogen atmosphere by Tang et al.11. In that study, under supercritical ethanol conditions, and employing ruthenium based catalyst, lignin was depolymerized and stable monomers such as phenols, guaiacols, anisoles, esters, light ketones, alcohols, long-chain alkynes, etc. were produced[11]. In recent work[12], hydrothermal degradation of an alkali lignin was achieved in sub/supercritical ethanol-water or pure ethanol with and without a catalyst. 50/50 (v/v) water-ethanol co-solvent was proven to be the most effective solvent for degradation of the lignin in terms of the yield of degraded lignin. They have also found that low temperature cannot provide sufficient energy to break lignin ether bonds but that high temperature led to re-condensation and char formation.

Other solvents used in lignin depolymerization are carbon dioxide and acetone. Gosselink et al.[13] found that organosolv lignin was successfully depolymerized into 10-12% monomeric aromatic compounds under supercritical carbon dioxide/acetone/water fluid by using small amounts of formic acid as hydrogen donor. They also claimed that obtained yields were comparable to other technologies like base-catalyzed lignin depolymerization.

The purpose of this study was to examine, for the first time, olive tree pruning lignin depolymerization process under supercritical solvents. Several studies were performed with three different liginins, obtained from acidic organosolv pulping of olive tree pruning and employing three different solvents (methanol, ethanol and acetone). The resulted products and by-products (oil, residual lignin, char and gas) were measured and analyzed by different techniques (GC/MS, HPSEC and pyrolysis-GC/MS).

Materials and methods

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[15].

Lignin depolymerization in supercritical solvents

The reactions were carried out in a batch reactor – 5500 Parr reactor – with a 4848 Reactor controller. The reactor was sealed and purged with nitrogen gas in order to remove any reactive air and reach an inert atmosphere until reaching around 2 bar of nitrogen pressure. The reactions were conducted at supercritical conditions for all the solvents for 40 min under constant stirring. Three solvents were used for each lignin: methanol, ethanol and acetone. Lignin : solvent ratio was 1 : 20 (in weight) for all experiments. In each batch experiment 1 g of

lignin was introduced. The initial temperature of the reactor was 20 ºC and heating rate was 4 ºC/min in all cases. 3 replicates were performed for each experiment. More experimental conditions are showed in **Table 1**.

Separation of products

The products recovered after the reaction in the batch microreactor (oil and tar) were treated in order to separate the products (**Figure 1**). Firstly, the solid residue was separated from the liquid by filtration and then washed with the same solvent used in each reaction to remove any liquid from the solid.

The recovered liquid fraction was vacuum evaporated in order to obtain an oil with the depolymerized products[16]. The solid phase was washed with tetrahydrofuran (THF) and was stirred for 3 hours in a beaker. Then, was filtrated and the undissolved solid (char) was oven-dried at 50 ºC. The THF solution was vacuum evaporated to recover the unconverted lignin dissolved in it.

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, 30 m x 0.25 mm). The temperature program started at 50 ºC then; the temperature is raised to 120 ºC at 10 ºC/min, held 5 min, raised to 280 ºC at 10 ºC/min, held 8 min, raised to 300 ºC at 10 ºC/min 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.

Residual lignin was subjected to High Performance Size Exclusion Chromatography (HPSEC) to evaluate lignin molecular weight (MW) 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 x 7.5 mm) and PolarGel-M guard (50 x 7.5 mm) were employed. The flow rate was 0.7 mL/min and the analyses were carried out at 40 ºC. Calibration was made using polystyrene standards (Sigma-Aldrich) ranging from 70,000 to 266 g/mol.

Obtained char was subjected to a pyrolysis-GC/MS analysis. The pyrolysis was carried out using a CDS analytical Pyrobrobe 5150. The pyrolysis temperature was set at 600 ºC for 15 sec with a heating rate of 2 ºC msec^{-1}. Then the products were analyzed by GC-MS instrument described above. The oven program started at 50 ºC and was held 2 min at this temperature. Then it was raised to 120 ºC at 10ºC/min and held 5 min, raised to 280 ºC at 10ºC/min, held 8 min and finally raised to 300 ºC at 10 ºC/min and held 10 min.

Results and discussion

Yield of obtained products

The yield of the products was affected by both, lignin nature and solvent used in the reaction. The desired product (oil) was produced in higher quantity than other lignin depolymerization processes like alkaline hydrothermal treatments[17-19]. For all solvent and lignin used oil yield was above 20%, however some differences were observed (**Figure 2**).

According to the solvent, acetone gave the best oil yields for all lignins used in the reactions, while methanol was the worst solvent for oil obtaining. The obtained oil yield for acetone was always above 30% with a maximum of 38.04% for AFL oil. This result was higher than the oil yield obtained in another work for lignin depolymerization with a much longer reaction time

(3.5 h)[13]. Ethanol oil was the second solvent that gave best oil yields. In this case, AL had the highest yield with a 33.03% of oil. Finally, methanol had the lowest values of the desired product. It hardly reaches a 30% of initial lignin, so this solvent had the lowest capacity to break down lignin linkages in order to produce monomers and oligomers. In another work has reported that 5-5 linkages of the lignin are not reactive in supercritical methanol, however, ether linkages (β-O-4, α-O-4) have been found to be very reactive at this conditions[9]. Based on the obtained results, it can be concluded that acetone and ethanol are more effective to break lignin internal linkages than methanol, so ether linkages are even more reactive in acetone and ethanol than in methanol.

According to lignin nature, FL yielded the lowest oil yield for the three solvents used. The main difference between these three lignins was the molecular weight[15]. FL had the lowest molecular weight of all lignins while AL had the highest one and despite what other authors claimed[20], this parameter has influence in oil yield. As M_w was lower, the oil yield was lower too. This rule was fulfilled except in the case of AFL acetone oil where the maximum yield value was obtained.

The obtained yields for residual lignin were very low in all cases, always below 5% (**Figure 3**). These results were very low compared with other one obtained by other depolymerization methods[21].

According to used solvent, two different scenarios are described. Based on the tendency, it could be concluded that the alcohols (ethanol and methanol) had the same behaviour. The highest residual lignin yield was obtained for AL and the lowest one for FL, having the same tendency as the one described in the oil production.

Otherwise, acetone was the solvent with different behavior; its maximum was for FL while the minimum yield was obtained for AL. In absolute terms, ethanol was the one with more residual lignin in the cases of AL and AFL. However, for FL the yield of residual lignin was below

acetone. Otherwise, acetone had the lowest yield in AL and AFL but as mentioned above in FL L residual lignin yield for acetone was the highest one.

According to lignin nature, there was no clear trend. AFL had the highest yields of residual lignin for two solvents acetone and methanol, and in average, residual lignin was higher for this type of lignin. FL had the lowest yields for ethanol and methanol and on average was the lignin with the lowest residual lignin yield. Finally, AL was between these two types of lignin. The results of residual lignin yields were very different in this case depending on the type of solvent that had been used. For ethanol, the maximum residual lignin yield was obtained (4.89%). Otherwise, unlike FL and specially AFL, there were huge differences between the residual lignin yield results for AL, namely, the disparity between them was higher. For AFL the residual lignin yields range between the lowest one and the highest one was 0.76% while in AL the range was 1.71%, which represents an increment of 125%.

The char obtained in the depolymerization process of organosolv lignins was very high in all cases (**Figure 4**). For this undesired product clear tendencies could be described for both lignin nature and solvent used.

According to the solvent, it could be observed that acetone had the highest yield of char in all cases while ethanol had the lowest yield. These results proved that with acetone lignin suffers more transformations as both oil and char yield were higher than with the other solvents. Depolymerization reactions and recondensation reactions occurred with higher severity; this behavior could be due the higher solubility of the lignin in acetone.

According to lignin nature it could be seen that FL had the highest yield of char for all the solvents used and AL had the lowest yield. These results complement the ones obtained for the oil. As it has been discussed, oil yield of FL was the lowest one while char yield was the highest one; this indicated that for FL, repolymerization was enhanced over depolymerization reactions. Acetosolv lignin behaved the other way round, in this case oil yields were highest ones and consequently char yield was the lowest. It can be concluded that in AL,

9

depolymerization reactions governed the process. Moreover, as it was expected, AFL's char results were between AL and FL.

The gases were formed by cleavage of the aliphatic propane chain and removal of ring substituents[22]. However, there were not very high in any studied case (Figure 5). The value of the gases was below 1.63% in all experiments, so this fraction was negligible. Nevertheless, some tendency could be observed as, in all cases, the quantity of gases recovered with acetone was the highest one while the gases recovered with methanol were the lowest ones. This could indicate that the removal of ring substituents were more effective when acetone was used as solvent.

Oil characterization

Oil was characterized by GC-MS analysis in order to identify the compounds dissolved in it (**Table 2**). In the oil phase, 13 monomrric phenols were identified. In all cases, there were two main monomeric phenolic compounds in the oil: guaiacol and syringol. Moreover, the quantity of syringol was higher than guaiacol as the lignin was isolated from a hardwood which is G:S type with more syringol than guaiacol units[15,22]. Besides these compounds, the other products obtained were almost the same in all cases, which indicated that depolymerization reactions took place via the same mechanism in all cases.

A clear trend could be observed for the products obtained in each case. When acetone was used as solvent, lower concentrations of guaiacol and syringol were obtained. However, the quantity of phenol, cresols and catechol was higher. This means that with acetone, in addition to hydrolysis reactions dealkylation, demethoxylation and demethylation reactions were enhanced. Hydrolysis reactions lead to the formation of guaiacol and syringol by the cleavage of β-O-4 ether bond, afterwards, by demethoxylation reactions phenol, cresols and catechol are produced[23]. As it can be observed, with ethanol and methanol more syringol and guaiacol were recovered than with acetone. Furthermore, as the concentration of these two

compounds decreased the quantity of phenol, cresols and catechol increased, which was in accordance with the discussed before.

Otherwise, the lignin that gave best results in term of monomeric phenolic products yield was AL. Regardless to the solvent used for its depolymerization, this lignin gave the maximum yields of phenolic products comparing to the other two lignin samples. This suggests that the many diverse fractions of different M_w may allow an easier breakdown of the molecule to form phenolic monomer compounds since this lignin has the highest polydispersity. This behavior was the contrary of what is expected for lignin depolymerization. It is supposed that lignins with lower Mw are easier to break and to form phenolic monomers[20]. However, FL had the lowest Mw but the structure of AL was easier to break in order to obtain monomeric compounds.

In conclusion, the most suitable option for lignin depolymerization by supercritical solvents in order to obtain phenolic antioxidants was to use acetosolv lignin with acetone as solvent.

Residual lignin characterization

In **Table 3** are shown the number-average (M_n), weight-average (M_w) molecular weight and polydispersity (M_w/M_n) of the residual lignin (relative to polystyrene standards) obtained after lignin depolymerization by supercritical solvents. HPSEC results were very enlightening. Residual lignin molecular weight decreased in all cases compared to the corresponding untreated lignin proving that depolymerization phenomenon occurred. The M_w decreased considerably in all cases and moreover polydispersity also betrayed a significant decrease. This behavior was contrary to the one occurred for base catalyzed depolymerization of lignin[24]. All recovered residual lignins did not show any repolymerization phenomena which indicated that usual repolymerization reactions which mainly are described as carbon to carbon bond formations between monomers intermediates and original lignin[25] did not form residual lignin and in this case lead to char formation.

Residual lignin from methanol experiments had the lowest both M_w and polydispersity regardless of liginin nature. The decrease of M_w in these residual lignins respect to the raw lignin was always higher than 80% and in the case of AFL the reduction in the M_w was as high as 86%. On the other hand, residual lignin polydispersity of all experiments carried out was lower than the corresponding untreated lignin fraction which is the normal trend for polymer degradation[20].

In **figure 6**, the molecular weight distribution of the raw lignins and all obtained residual lignins is showed. As it can be observed, all residual lignins had lower molecular weight fractions than original lignin. A very intense peak could be observed at Log 3.6 corresponding to an approximately 3900 g/mol fraction in residual lignins regardless the solvent employed in the reaction. This peak has also been observed in other studies where same lignins were depolymerized[21]. These results suggest that this olive tree pruning lignins are formed by different complex and condensed parts that are separated when the lignin is subjected to the depolymerization reactions. Under supercritical solvents the β-O-4 ether bond in easily broken down but the C-C linkages that formed the complex structures are not cleaved. As a result of this, the lignin is decomposed in diverse parts of different Mw that are identified by the GPC analysis of the residual lignins. This peak was even more intense in the case of FL residual lignins which indicated that low M_w lignin fractions were higher in the case of this type of lignin. Otherwise, the shape of the distribution was similar in all cases which suggested that the formation of the residual lignins took place via the same mechanism regardless both, lignin or solvent nature.

Char characterization

In order to study the nature of the char formed during lignin thermal degradation under supercritical solvents, a pyrolysis-GC-MS analysis was performed. In **figure 7** pyrograms from

AL and chars obtained after the depolymerization of this lignin by the three different solvents are showed as an example. It can be noticed that the nature of the recovered char was completely different compared to the raw lignin. This means that the lignin suffered several transformations to form char. However, this insoluble fraction in THF had some similarities regardless the nature of the raw lignin and the solvent used in the reaction.

In **table 4**, the compounds that had more than 1% of the area of the whole pyrogram (figure 5) are specified. In the majority of the char samples creosol (2-methoxy 4-methylphenol) was the main compound of the pyrolysis. However, when methanol was used as solvent, the main compound forming the char was syringol. Besides these two compounds many other phenolic compounds can also be found in the structure of the char. Despite this slight difference, the nature of the chars is very similar as many compounds are repeated in their chromatograms. Besides syringol and creosol many other phenolic compounds can also be found in the structure of the char. Taking this into account, it could be concluded that the char, just like lignin, had an aromatic nature. Otherwise, the nature of these phenolic compounds was the same in all char samples which indicated that the formation of this fraction took place via same mechanism regardless the nature of lignin and with very slight different depending on the solvent.

The main difference between this char and both, raw lignin and residual lignin, is the solubility in THF. Lignin and residual lignin were soluble in THF while char was an insoluble fraction. This behavior from char may be due to its highly condensed structure and high M_w. As an indicative of this condensed structure of the char was the existence of Stigmastan-3,5-diene as a product in the char´s chromatograms. This compound is highly branched and condensed and it only appeared in the chromatograms of char pyrolysis, which explains the different nature of char respect to the raw and residual lignin and consequently its insolubility in THF.

Conclusions

Different organosolv lignins were treated under supercritical solvents in this work. Lignin was successfully depolymerized under studied conditions and high yields of oil were obtained in all cases, moreover, the Mw of lignin was considerably reduced. As a negative point, char yield was very high compared to other depolymerization methods.

In the oil phase, 13 phenols, mainly guaiacol and syringol and their alkylated forms, were identified. Acetone was the best solvent for lignin depolymerization in terms of oil yield. Furthermore, lignin suffered higher degradation (demethoxylation, dealkylation and demethylation reactions) in acetone and consequently yielded more products like cresols or catechol. In terms of lignin nature, AL was more easily depolymerized. It yielded more oil and the concentration of phenolic monomeric compounds was higher when this lignin was used regardless the solvent employed in the reaction.

In conclusion, the most suitable option for lignin depolymerization by supercritical solvents was to use acetosolv lignin with acetone as solvent.

Supplementary information

The list of compounds and the pyrograms from the pyrolysis-GC/MS analysis of FL and AFL lignins and respective chars.

References

(1) Wahyudiono; Sasaki, M.; Goto, M. Recovery of phenolic compounds through the decomposition of lignin in near and supercritical water. *Chem. Eng. Process.* **2008**, 47(9-10), 1609-1619.

(2) Fang, Z.; Sato, T.; Smith Jr., R. L.; Inomata, H.; Arai K.; Kozinski, J.A. Reaction chemistry and phase behavior of lignin in high-temperature and supercritical water. *Bioresour. Technol*. **2008,** 99 (9), 3424-3430.

(3) Kleinert, M.; Barth, T. Phenols from lignin. *Chem. Eng. Technol.* **2008**, 31 (5), 736-745.

(4) Chakar, F.S.; Ragauskas A.J. Review of current and future softwood kraft lignin process chemistry. *Ind. Crops Prod.* **2004**, 20 (2), 131-141.

(5) Bauer, S.; Sorek, H.; Mitchell, V. D.; Ibáñez, A.B.; Wemmer, D. E. Characterization of Miscanthus giganteus Lignin Isolated by Ethanol Organosolv Process under Reflux Condition. *J. Agric. Food Chem.* **2012**, 60 (33), 8203-8212.

(6) Ralph, J.; Lundquist, K.; Brunow, G.; Lu, F.; Kim, H.; Schatz, P. F.; Marita, J. M.; Hatfield, R. D.; Ralph, S .A.; Christensen, J. H.; Boerjan, W. Lignins: Natural polymers from oxidative coupling of 4-hydroxyphenyl- propanoids. *Phytochem. Rev.* **2004**, 3 (1-2), 29-60.

(7) Yokoyama, C.; Nishi, K.; Nakajima, A.; Seino, K. Thermolysis of organosolv lignin in supercritical water and supercritical methanol. *J. Jpn. Petrol. Inst.* **1998**, 41 (4), 243-250.

(8) Okuda, K.; Umetsu, M.; Takami, S.; Adschiri, T. Disassembly of lignin and chemical recovery-rapid depolymerization of lignin without char formation in water-phenol mixtures. *Fuel Process Technol*. **2004**, 85 (8-10), 803-813.

(9) Minami, E.; Kawamoto, H.; Saka, S. Reaction behavior of lignin in supercritical methanol as studied with lignin model compounds*. J. Wood Sci.* **2003**, 49 (2), 158-165.

(10) Barta, K.; Matson, T. D.; Fettig M. L.; Scott, S. L.; Iretskii A. V.; Ford P. C. Catalytic disassembly of an organosolv lignin via hydrogen transfer from supercritical methanol. *Green Chem*. **2010**, 12 (9), 1640-1647.

(11) Tang, Z.; Zhang, Y.; Guo, Q. Catalytic Hydrocracking of Pyrolytic Lignin to Liquid Fuel in Supercritical Ethanol*. Ind .Eng. Chem. Res.* **2010**, 49 (5), 2040-2046.

 (12) Cheng, S.; Wilks, C.; Yuan, Z.; Leitch, M.; Xu, C. Hydrothermal degradation of alkali lignin to bio-phenolic compounds in sub/supercritical ethanol and water-ethanol co-solvent. *Polym. Degrad. Stabil*. **2012**, 97 (6), 839-848.

(13) Gosselink, R. J. A.; Teunissen, W.; van Dam J. E. G.; de Jong, E.; Gellerstedt, G.; Scott, E. L.; Sanders, J. P. M. Lignin depolymerisation in supercritical carbon dioxide/acetone/water fluid for the production of aromatic chemicals. *Bioresour. Technol.* **2012**, 106, 173-177.

(14)Bennett, J. Advanced fuel additives for modern internal combustion engines. In *Alternative Fuels and Advanced Vehicle Technologies for Improved Environmental Performance*; Folkson, R., Ed.; Woodhead Publishing Ltd: Cambridge, U.K., **2014**, p.165-94.

(15) Erdocia, X.; Prado, R.; Corcuera, M.A.; Labidi, J. Effect of different organosolv treatments on the structure and properties of olive tree pruning lignin*. J. Ind. Eng. Chem.* **2013**, 20 (3), 1103-1108.

(16) Kim, J. Y.; Oh, S.; Hwang, H.; Cho, T.S.; Choi, I. G.; Choi, J. W. Effects of various reaction parameters on solvolytical depolymerisation of lignin in sub- and supercritical ethanol. *Chemosphere* **2013,** 93 (9), 1755-1764.

(17) Saisu, M.; Sato, T.; Watanabe, M.; Adschiri, T.; Arai, K. Conversion of lignin with supercritical water-phenol mixtures. *Energy Fuels* **2003**, 17 (4), 922-928.

(18) Nenkova, S.; Vasileva, T.; Stanulov, K. Production of phenol compounds by alkaline treatment of technical hydrolysis lignin and wood biomass. *Chem. Na.t Compd.* **2008**, 44 (2), 182-185.

(19) Toledano, A.; Serrano, L.; Labidi, J. Organosolv lignin depolymerization with different base catalysts. *J. Chem. Technol. Biotechnol.* **2012**, 87 (11), 1593-1599.

(20) Toledano, A.; Serrano, L.; Labidi, J. Process for olive tree pruning lignin revalorisation. *Chem. Eng. J.* **2012**, 193-194, 396-403.

(21) Erdocia, X.; Prado, R.; Corcuera, M. A.; Labidi J. Base catalyzed depolymerization of lignin: Influence of organosolv lignin nature. *Biomass Bioenerg*. **2014**, 66, 379-386.

(22) Pandey, M. P.; Kim, C. S. Lignin Depolymerization and Conversion: A Review of Thermochemical Methods. *Chem. Eng. Technol.* **2011**, 34 (1), 29-41.

(23) Toledano, A.; Serrano, L.; Labidi, J. Extraction and revalorization of olive tree (Olea europea) pruning lignin. *J. Taiwan Inst. Chem. Eng.* **2013**, 44 (4), 552-559.

(24) Toledano, A.; Serrano, L.; Labidi, J. Improving base catalyzed lignin depolymerization by avoiding lignin repolymerization. *Fuel* **2014**, 116, 617-624.

(25) Roberts, V. M.; Stein, V.; Reiner, T.; Lemonidou, A.; Li, X.; Lercher, J. A. Towards quantitative catalytic lignin depolymerization. *Chem. Eur. J.* **2011**, 17 (21), 5939-5948.

Tables

Table 1. Experimental conditions of lignin depolymerization under supercritical solvents.

	AL	FL	AFL
Methanol	300 ºC, 120 bar	300 ºC, 118 bar	300 ºC, 118 bar
Ethanol	300 ºC, 88 bar	300 ºC, 92 bar	300 ºC, 86 bar
Acetone	300 ºC, 66 bar	300 ºC, 66 bar	300 ºC, 67 bar

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

	AL ac	AL et	AL met	FL ac	FL et	FL met	AFL ac	AFL et	AFL met
Phenol	0.07±0.00	0.06±0.01	0.06±0.01	0.04±0.00	0.05±0.00	0.04±0.00	0.04±0.00	0.04±0.00	0.04±0.00
Cresols	0.15±0.01	0.07±0.01	0.06±0.01	0.09±0.02	0.06±0.00	0.05±0.00	0.08±0.00	0.05±0.01	0.05±0.01
Guaiacol	1.17±0.09	1.19±0.03	1.38±0.06	0.90±0.07	1.07±0.03	0.90±0.06	0.77±0.04	0.95±0.03	1.01±0.02
Catechol	0.09±0.00	0.08±0.01	0.00±0.00	0.06±0.00	0.06±0.01	0.00±0.00	0.03±0.00	0.02±0.00	0.02±0.00
3-methoxycatechol	0.59±0.08	0.64±0.12	0.38±0.06	0.62±0.11	0.69±0.10	0.33±0.07	0.32±0.00	0.34±0.04	0.59±0.02
4-hydroxybenzaldehyde	0.34±0.07	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Syringol	2.27±0.21	2.47±0.17	3.13±0.39	1.77±0.11	2.03±0.13	2.07±0.03	1.47±0.09	2.01±0.01	2.25±0.10
Vanillin	0.00±0.00	0.01±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Acetovanillone	0.05±0.01	0.07±0.00	0.07±0.01	0.06±0.01	0.09±0.01	0.08±0.01	0.05±0.00	0.07±0.01	0.09±0.01
4-hidroxy-3-methoxy-phenylacetone	0.20±0.07	0.27±0.02	0.32±0.00	0.15±0.04	0.23±0.03	0.18±0.04	0.14±0.01	0.18±0.02	0.32±0.01
Vanillic acid	0.12±0.01	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Syringaldehyde	0.00±0.00	0.04±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
3,5-dimethoxy-4-hidroxyacetophenone	0.14±0.03	0.20±0.00	0.20±0.03	0.17±0.03	0.22±0.03	0.25±0.00	0.14±0.01	0.00±0.00	0.00±0.00

Table 3. Residual lignin HPSEC results. Weight-average (M_w), number-average (M_n) molecular weight and polydispersity (M_w/M_n) of residual lignins.

	M_w	M_n	Mw/Mn
AL	16,416	1528	10.75
AL acetone	2971	687	4.33
AL ethanol	3467	675	5.14
AL methanol	2441	609	4.01
FL	7924	1430	5.54
FL acetone	2633	625	4.21
FL ethanol	2641	608	4.34
FL methanol	1461	471	3.10
AFL	15,088	1626	9.28
AFL acetone	3451	609	5.67
AFL ethanol	3224	776	4.15
AFL methanol	2086	638	3.27

Table 4. Compounds with more than 1% of the total chromatogram area identified in the pyrolysis of AL and chars recovered after depolymerisation reactions with the three different solvents.

Compound	RT (min)	% of chromatogram area			
		AL	Char AL acetone	Char AL ethanol	Char AL methanol
Toluene	4.058	---	2.59	1.76	---
Furfural	4.987	1.49	---	---	---
Benzaldehyde	7.158	1.74	---	---	---
Phenol	7.415	---	---	2.25	1.02
o-cresol	8.645	---	1.64	1.51	---
p-cresol	8.986	----	---	---	1.88
2-methoxyphenol	9.290	2.52	---	---	---
3,5-dimethylphenol	10.294	---	1.67	---	---
3,4-dimethylphenol	10.692	---	1.38	---	---
2-methoxy-4-methylphenol	11.348	---	7.57	4.49	2.74
3-methyl-1,2-Benzenediol	13.102	---	2.34	----	1.28
3-methoxy-1,2-Benzenediol	13.257	---	6.60	2.94	2.76
2-methoxy-4-ethylphenol	13.811	---	1.51	---	---
4-methyl-1,2-Benzenediol	14.058	---	2.32	1.74	---
2-Methoxy-4-vinylphenol	14.967	2.04	---	---	---
Syringol	16.020	4.89	5.55	3.69	3.24
3,4-dimethoxyphenol	16.245	---	2.33	1.47	1.10
Vanillin	17.167	1.83	---	---	---
Vanillic acid	18.153	---	4.27	3.78	2.72
Isoeugenol acetate (E)	18.220	3.43	---	---	---
Acetovanillone	18.917	1.41	---	---	---
Guaiacylacetone	19.690	2.65	---	---	---
Acetoveratrone	20.210	4.69	---	---	---
2,4'-Dihydroxy-3'-methoxyacetophenone	20.580	3.41	---	---	---
Methoxyeugenol	21.920	9.78	---	---	---
Homosyringic acid	23.000	4.01	---	---	---
1-(2,4,6-trihydroxyphenyl),2-Pentanone.	23.208	1.47	---	---	---
Aspinidol	23.624	2.51	---	---	---
Palmitic acid	24.978	7.64	2.17	2.03	2.36
Stearic acid	26.860	2.92	1.87	2.58	1.41
Stigmastan-3,5-diene	37.128	---	1.12	1.88	1.34

Figure 1. Separation sequence for product isolation after lignin depolymerisation under supercritical solvents.
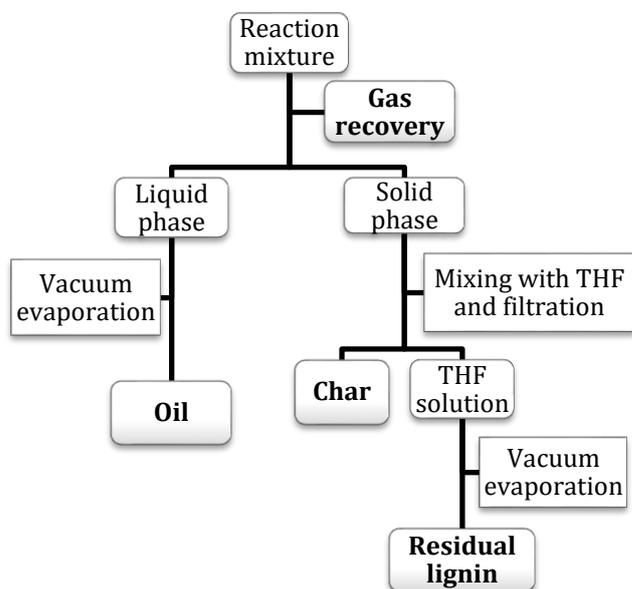

Figure 2. Obtained oil yields for different lignins and used solvents. Oil yields (%, w/w) are referred to initial lignins weights.
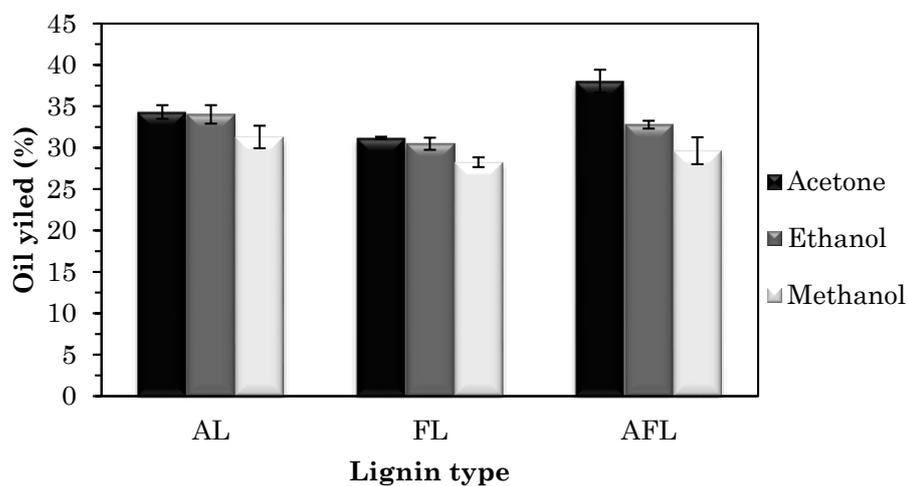
Figure 3. Obtained residual lignin yields for different lignins and used solvents. Residual lignin yields (%, w/w) are referred to initial lignins weights.
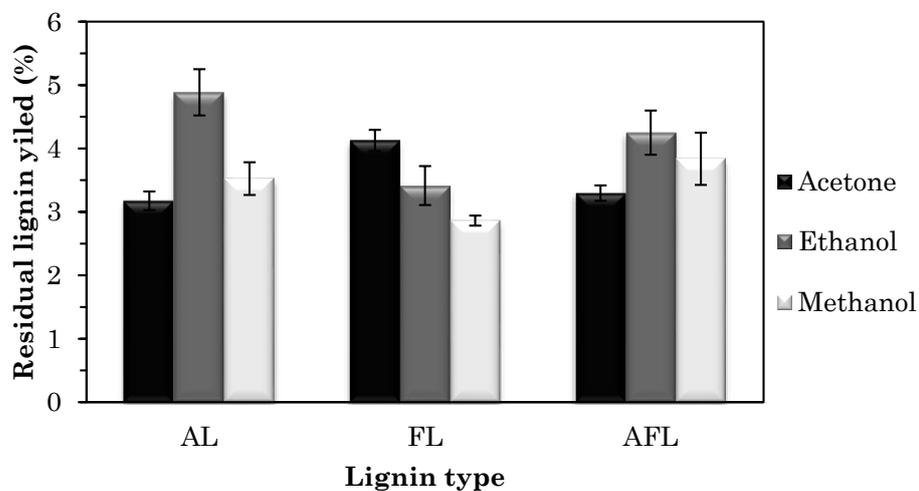

Figure 4. Obtained char yields for different lignins and used solvents. Char yields (%, w/w) are referred to initial lignins weights.
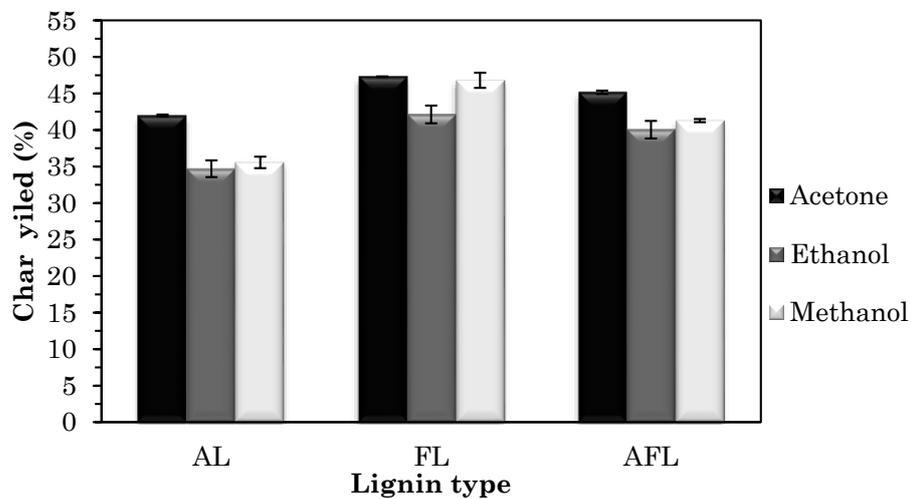
Figure 5. Obtained gas yields for different lignins and used solvents. Gas yields (%, w/w) are referred to initial lignins weights.
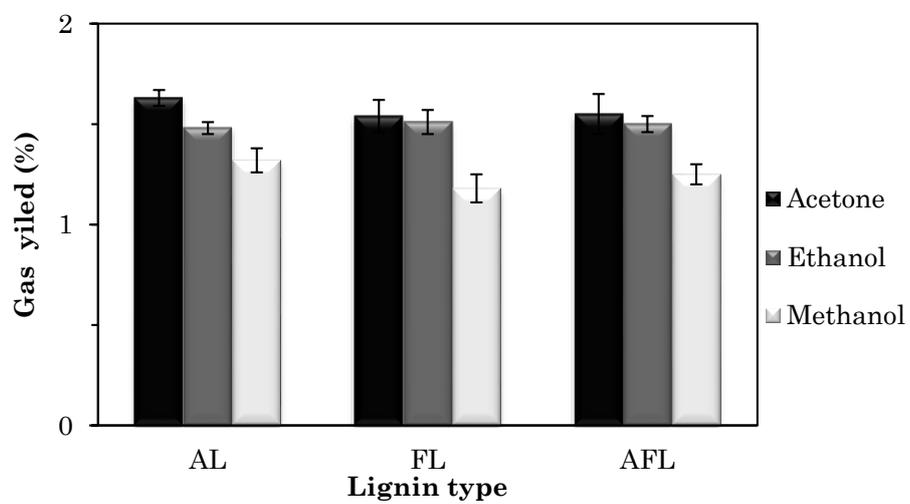
Figure 6. Molecular weight distribution of raw lignin and residual lignins samples.
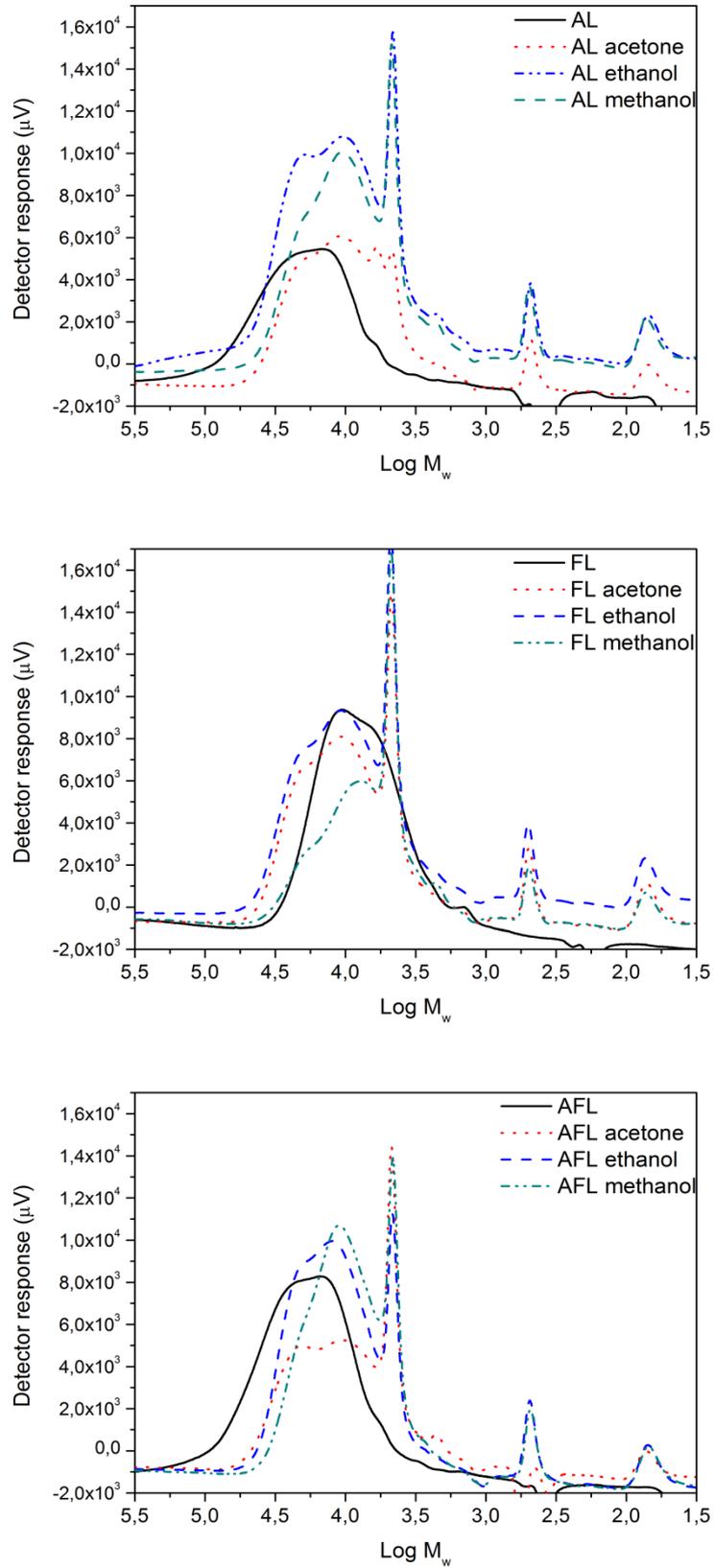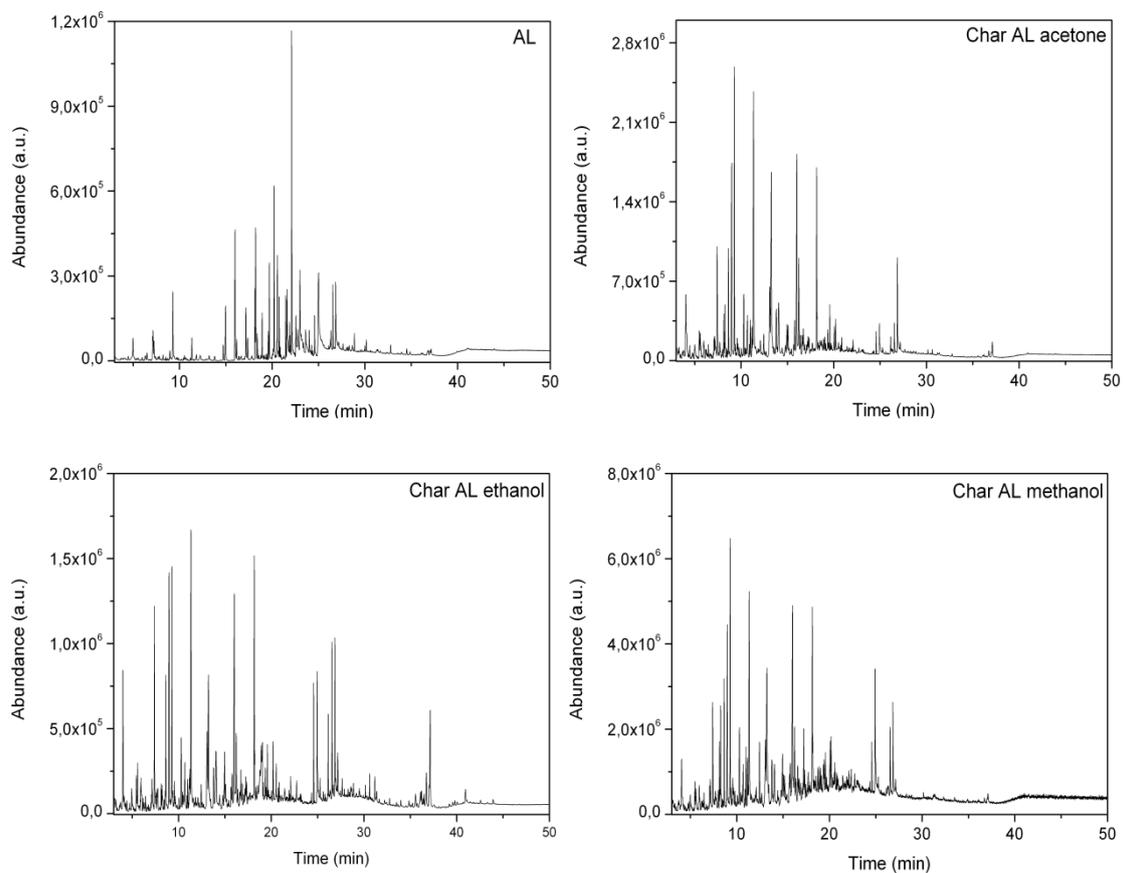
Figure 7. Pyrograms of AL and chars recovered after depolymerization reactions with the three different solvents.

For table of contents use only
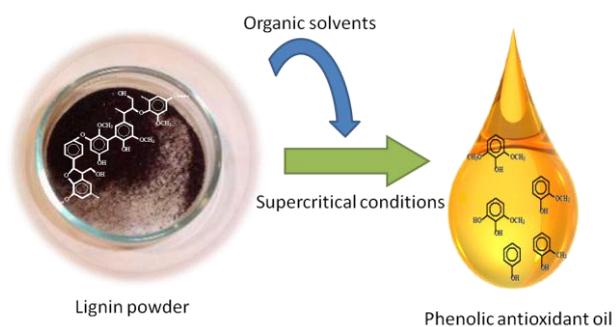
Synopsis: This study enables the obtaining of phenolic monomers from lignin employing only different green organic solvents like ethanol, acetone or methanol.

Manuscript title: Depolymerization of different organosolv lignins in supercritical methanol, ethanol and acetone to produce phenolic monomers

Authors: Xabier Erdocia, Raquel Prado, Javier Fernández-Rodríguez, Jalel Labidi

Supplementary information

Depolymerization of different organosolv lignins in supercritical methanol, ethanol and acetone to produce phenolic monomers

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- Number of pages: 5
- Number of figures : 2
- Number of tables : 2

Table S1. Compounds with more than 1% of the total chromatogram area identified in the pyrolyisis of FL and chars recovered after depolymerisation reactions with the three different solvents.

Compound	RT (min)	% of chromatogram area			
		FL	Char FL acetone	Char FL ethanol	Char FL methanol
Toluene	4.057	---	1.69	2.17	---
Furfural	4.987	1.10	---	---	---
Phenol	7.420	---	1.71	1.53	1.09
Limonene	8.285	---	1.80	1.51	---
2-methylphenol	8.648	2.52	1.19	1.33	---
4-methylphenol	8.972	---	3.01	2.58	---
2-methoxyphenol	9.284	1.56	4.19	4.18	---
2,4-dimethylphenol	10.289	---	1.32	1.38	1.35
2-methoxy-4-methylphenol	11.334	---	5.35	6.18	---
3-methyl-1,2-benzenediol	13.067	---	1.86	2.53	---
3-methoxy-1,2-Benzenediol	13.222	---	3.58	4.85	3.26
4-methyl-1,2-benzenediol	14.043	----	---	2.02	1.03
Syringol	15.995	4.26	4.11	4.27	3.64
3,4-dimethoxyphenol	16.225	---	1.01	1.43	1.22
Vanillin	17.161	1.16	---	---	---
Vanillic acid	18.143	1.12	2.14	2.64	2.90
Isoeugenol acetate (E)	18.220	1.38	---	---	---
Acetovanillone	18.917	1.14	---	---	---
Guaiacylacetone	19.69	1.24	---	---	---
Lauric acid	20.084	2.51	1.53	---	---
Acetoveratrone	20.210	1.94	---	---	---
2,4'-Dihydroxy-3'-methoxyacetophenone	20.580	1.98	---	---	---
Syringaldehyde	21.591	1.83	---	---	---
Methoxyeugenol	22.111	3.47	---	---	---
Palmitic acid	24.941	7.64	3.87	5.42	2.70
Stearic acid	26.875	2.92	5.22	1.65	2.37
Stigmastan-3,5-diene	37.119	---	1.08	1.08	1.00

Table S2. Compounds with more than 1% of the total chromatogram area identified in the pyrolyisis of AFL and chars recovered after depolymerisation reactions with the three different solvents.

Compound	RT (min)	% of chromatogram area			
		AFL	Char AFL acetone	Char AFL ethanol	Char AFL methanol
Toluene	4.048	---	1.13	3.03	1.56
Furfural	4.992	1.31	---	---	---
Phenol	7.418	---	1.18	3.08	1.58
2-methylphenol	8.649	2.37	1.19	2.01	1.66
4-methylphenol	8.978	---	1.94	5.22	2.02
2-methoxyphenol	9.284	1.86	2.92	3.27	2.01
2,5-dimethylphenol	10.295	---	---	1.99	---
4-ethylphenol	10.624	---	---	---	1.16
3,4-dimethylphenol	10.687	---	---	1.58	
2-methoxy-4-methylyphenol	11.334	---	4.51	5.54	2.22
3-methyl-1,2-benzenediol	13.069	---	1.03	1.98	1.28
3-methoxy-1,2-benzenediol	13.228	---	3.70	3.90	1.67
4-methyl-1,2-benzenediol	14.031	----	---	1.72	1.88
2-methoxy-4-vinylphenol	14.967	1.79	---	---	---
Syringol	16.001	2.95	3.98	3.43	2.83
3,4-dimethoxyphenol	16.234	---	1.23	1.18	1.10
Vanillin	17.167	2.56	---	---	---
Vanillic acid	18.154	1.19	2.66	2.28	1.10
Isoeugenol acetate (E)	18.224	4.24	---	---	2.22
D-Allose	18.79	1.14	---	---	---
Guaiacylacetone	19.685	1.26	---	---	---
Lauric acid	20.084	---	1.10	---	---
Acetoveratrone	20.205	3.15	---	---	---
2,4'-Dihydroxy-3'-methoxyacetophenone	20.580	1.26	---	---	---
Syringaldehyde	21.603	6.20	---	---	---
Methoxyeugenol	22.122	8.25	---	---	---
Homosyringic acid	22.994	2.75	---	---	---
Palmitic acid	24.941	9.95	3.04	2.95	1.48
Oleic acid	26.708	2.73	---	---	---
Stearic acid	26.873	9.17	1.89	3.24	1.75
Stigmastan-3,5-diene	37.119	---	1.03	1.18	2.66

Figure S1. Pyrograms of FL and chars recovered after depolymerization reactions with the three different solvents.
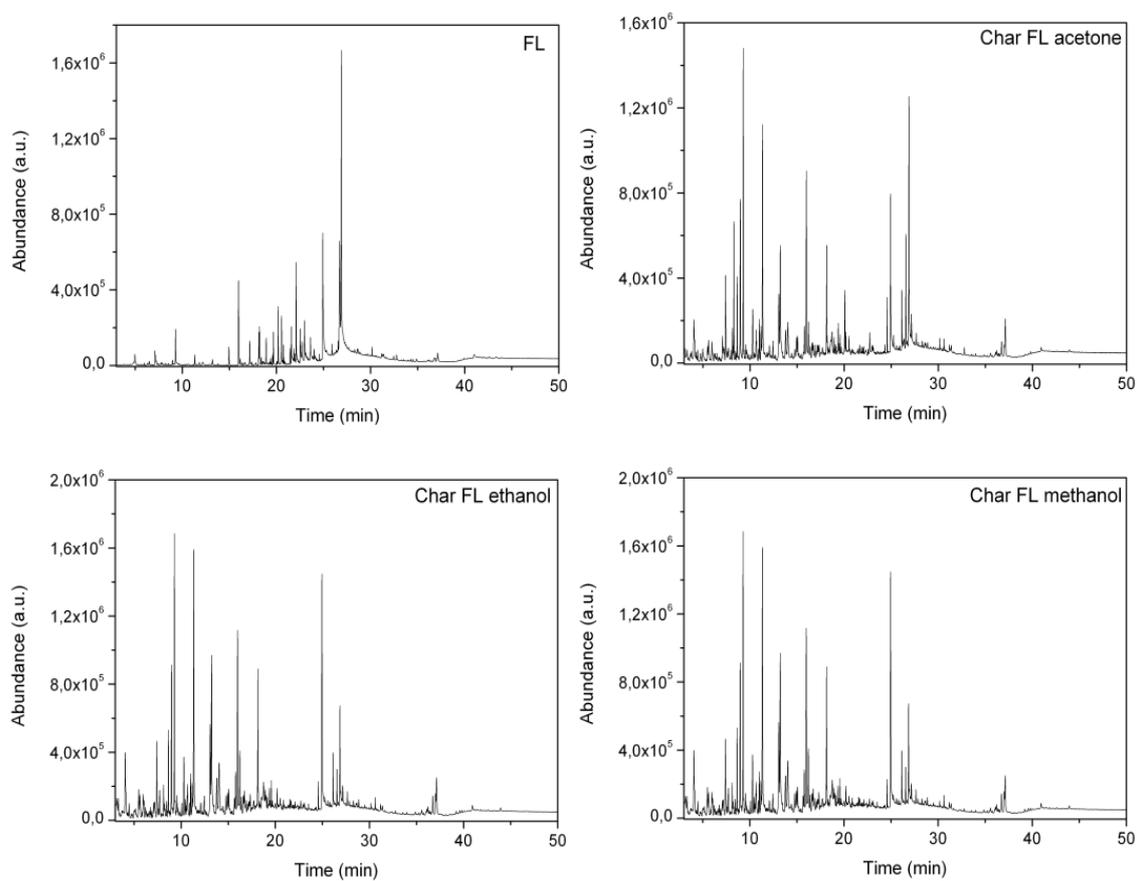
Figure S2. Pyrograms of AFL and chars recovered after depolymerization reactions with the three different solvents.