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Organosolv Black Liquor Hydrolysis to Obtain Low Molecular Weight Phenolic Compounds

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In this work, olive tree pruning was used as raw material to delignify it employing organosolv treatment. Obtained liquor was hydrolyzed at a high pressure reactor at 300 ºC for 40 min to depolymerize lignin it contains. Thus, lignin from the liquor was depolymerize avoiding the precipitation step. Different experiments were carried modifying organosolv black liquor. Products resulted after treatment were characterized by two techniques: Gas chromatography/Mass spectroscopy (GC/MS) and high performance size exclusion chromatography (HPSEC). Obtained oil after hydrolysis reaction of the organosolv black liquor had high concentration in guaiacol and syringol.

1. Introduction

Spain is the main producer of olive worldwide. This culture generates a lignocellulosic pruning residue estimated at 3000 kg/ha each year. Cultivators have to burn it in order to avoid diseases with the associated inconvenient costs and environmental concerns. Lignocellulosic biomass is mainly composed by cellulose, hemicelluloses and lignin. Lignin is the second most abundant natural polymer where p-hydroxyphenyl alcohol (H), guaiacyl alcohol (G) and syringyl alcohol (S) are the main precursors. These phenylpropane units form an amorphous three-dimensional structure and are linked mainly by aryl-aryl ether and carbon-carbon linkages (González Alriols et al., 2010).

Lignin can be extracted from lignocellulosic biomass by different methods, like kraft process, alkaline treatment, or organosolv processes. These last treatments employ organic solvents and water as reaction medium. Alcell® process, already used in the paper industry, uses a mixture of ethanol/water as solvent (Asiz and Sarkanen, 1989) allows the obtaining of lignin rich black liquor (Sannigrahi et al., 2010).

Lignin polyphenolic structure is ideally adequate to be transformed catalytically into lower molecular weight compounds such as phenols, aromatic acids, esters, ethers... replacing those obtained from petroleum (Sena-Martins et al., 2008; González Alriols et al., 2010). Several thermochemical conversion methods of biomass have been studied to depolymerize lignin to low molecular weight compounds (Huber et al., 2006; Windt et al., 2009; Saisu et al., 2003; Amen Chen et al., 2001). Among them, pyrolysis, Lewis acid-catalyzed solvolysis, base-catalyzed depolymerization, hydrogenolysis and hydrolysis have been the most investigated ones.

In hydrolysis process water is utilized to break lignin structure and to obtain low molecular weight compounds. Several studies have been performed to obtain phenolic compounds from lignin or its model compound under hydrothermal conditions (Saisu et al., 2003; Wahyudiono et al., 2007; Nenkova et al., 2011). Among hydrothermal treatments alkaline hydrolysis of lignin has been widely studied (Thring, 1994; Heitz et al., 1995; Nenkova et al., 2011). In these studies the main phenolic compounds

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obtained were guaiacol and syringol at low severities and catechol and its derivatives at high severities (Thring, 1994; Heitz et al., 1995).

The objective of this work was to obtain phenolic monomers from organosolv black liquor suppressing the precipitation step of lignin. Organosolv black liquor was treated at high temperatures and pressures in a batch reactor to achieve this goal. The obtained products (oil and residual lignin) were analyzed by different techniques (GC/MS and HSPEC). Coke was the main undesirable by-product formed during repolymerization reactions.

2. Materials and methods

2.1 Organosolv treatment

Organosolv treatment was carried out in a 1.5 L pressure stainless steel stirred reactor (Parr 4836) equipped with a heating mantle, mechanical stirrer, and manometer. The treatment was done according to previous optimized conditions (Toledano et al., 2011), using a solution of ethanol-water 70 % (v/v), in a solid: liquid ratio of 1:6 at 200 ºC for 90 min. After reaction, solid fraction was separated by filtration and then it was washed with the same solution used for the treatment followed by repeated washing with water.

2.2 Organosolv black liquor conditioning

Two types of liquor conditioning were done; in the first one, ethanol was removed from the liquor to promote hydrolysis reaction and in the other one, hemicelluloses were removed to see their influence. For the first case, 170 mL of the liquid fraction were placed in the oven at 50 °C for 24 h to remove most of the ethanol and thus concentrate the liquor without precipitating the lignin. For the second case, another 170 mL of liquor were also introduced in the oven for the same period of time after which, 3 volumes of ethanol were added to precipitate the hemicelluloses removing them by centrifugation. After this, the liquor without hemicelluloses was introduced in the oven for 74 h to remove the ethanol without precipitating the lignin. Thus, the effect of hemicelluloses on lignin depolymerization reactions could be analyzed.

2.3 Liquors physicochemical characterization

Organosolv liquors L1 and L2 were characterized before the hydrolysis reaction. Density was determined measuring the weight of the black liquor in a known volume previously weighed. Total dissolved solids (TDS) were determined after introducing a known volume of liquor for 24 h in an oven at 105 ± 3 ºC. Inorganic matter (IM) was determined after combustion of the sample at 525 ºC. Organic matter (OM) was determined by the difference between total dissolved solids and inorganic matter. Lignin content was determined by a gravimetric method adding 2 volumes of acidified water at pH 1.

Table 1. Black liquors physicochemical characterization.

Liquor	Density (g/mL)	TDS (%)	IM (%)	OM (%)	Lignin (%)
L1	0.942 ± 0.003	12.07 ± 0.08	0.071 ± 0.002	12.00 ± 0.08	5.46 ± 0.05
L2	0.853 ± 0.001	9.02 ± 0.06	0.052 ± 0.001	8.97 ± 0.06	4.31 ± 0.05

2.4 Organosolv black liquor hydrolysis

20 mL of each of the obtained liquors (L1 and L2) were introduced in a pressure batch microreactor -5500 Parr reactor- with a 4848 Reactor controller. The reaction conditions were 300 ºC and 40 min with constant stirring. Two experiments were done (H1, H2).

2.5 Products separation

The original liquor and the recovered liquor after the reaction time in the microreactor were treated in order to separate the products. Firstly, 2 volumes of acidified water at pH 1 were added to the liquor. In this way, residual lignin precipitated and then all the solids (coke and residual lignin in the case of hydrolyzed liquors) were separated from the liquid by filtration and washed to remove residual liquor.

This liquor 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 oil with the depolymerizated products.

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

2.6 Analysis of obtained products

Obtained oil was characterized to evaluate qualitatively and quantitatively the monomeric phenolic compounds dissolved in it. The oil was dissolved in ethyl acetate (HPLC grade) in a metric flask. The solution was injected in a GC (7890A)-MS (5975C inert MSD with Triple-Axis Detector) Agilent equipped with a capillary column HP-5MS ((5 % Phenyl)-methylpolysiloxane, 60 m x 0.25 mm). The temperature program started at 50 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, syringol, acetovanillone, veratrol, 4-hydroxybenzoic acid and 4-hydroxy-3-methoxyphenylacetone.

Residual lignin was subjected to High Performance Size Exclusion Chromatography (HPSEC) to evaluate lignin molecular weight (MW) and molecular weight distribution (MWD) employing 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.

3. Results and discussion

3.1 Hydrolysis process yields

The yields of products and by-products of depolymerization reactions of the organosolv liquors and oil yield obtained directly from the original liquors are presented in **table 2**. Oil yield (g dried oil)/(g liquor dry matter) was determined by weighing dried oil for 24 hours in a desiccators. Coke yield (g oven-dried coke/g liquor dry matter) was determined by weighing oven-dried coke and lignin yield (g oven-dried residual lignin/g lignin in liquor) was quantified by weighing oven-dried residual lignin.

Table 2. Yields of depolymerization reaction and oil yield obtained from organosolv liquor.

Experiment	Oil yield (%)	Coke yield (%)	Lignin yield (%)
L1	30.63	....	....
H1	17.50	35.55	14.77
L2	28.21	....	....
H2	19.28	49.09	9.56

The results in Table 2 showed the differences between the yield of the oil obtained after hydrolysis reaction of the liquor. It could be observed that oil yields from original liquors L1 and L2 were higher than the oil obtained from hydrolysis reactions H1 and H2. This result suggested that the compounds extracted with ethyl acetate in the case of original liquors (L1 and L2) were mainly dimmers and trimmers of higher molecular weight which amount after hydrolysis treatment was reduced because of dealkylation (Okuda et al., 2010) or repolymerization reactions (Roberts et al., 2011). This fact could explain the reduction of the amount of oil extracted after depolymerization reactions.

3.2.1Oil characterization by GC/MS

The oil obtained from original liquor and from hydrolysis reactions of the liquors was characterized by GC-MS technique.

Two types of produced phenolic products profiles can be distinguished. In the first, are the profiles of the oils obtained from the liquor without any treatment, the second type are the profiles of the oils after hydrolysis performed at high temperature and pressures. In Table 3 the composition of the oils is shown.

Table 3. Concentration of compounds in the obtained oil (%) referred to oil weight (w/w).

Obtained products	**Concentration [%w/w]**			
	L1	**H1**	**L2**	**H2**
Phenol	0.07	0.76	0.29	1.03
o-cresol	....	0.17	....	0.17
p-cresol and m-cresol	....	0.44	....	0.40
Guaiacol	0.19	6.02	0.20	7.17
Catechol	....	0.20	....	0.08
Syringol	0.42	8.48	0.51	11.08
Acetovanillone	....	0.05	0.02	0.05
Veratrol	....	0.05	0.04	0.04
4-hidroxybenzoic acid	0.15	0.18	....	0.31
4-hidroxy-3-methoxy-phenylacetone	0.14	0.20	0.12	0.16

The oils from hydrolysis reactions had high amount of guiacol and syringol. The decomposition of the lignin by hydrolysis and dealkylation yielded low molecular-weight fragments that have functional reactive groups and compounds such as syringols and guaiacols (Okuda et al., 2004). Therefore, in H1 and H2 reactions, guaiacols and syringols are the main products of the oil. Otherwise, the amount of these two phenolic compounds is higher in the case of H_2 which suggested that the absence of hemicelluloses improved hydrolyisis reaction of the lignin.

On the other hand, hydrolysis reaction performed was strong enough to produce small amounts of phenol, cresols and catechol that are mainly produced at high severities and employing base catalyst (Thring, 1994; Heitz et al., 1995).

3.2.2 Lignin characterization by HPSEC

Lignin present in the black liquor and residual lignin obtained after hydrolysis of the black liquor were subjected to HPSEC to evaluate lignin molecular weight and molecular weight distribution.

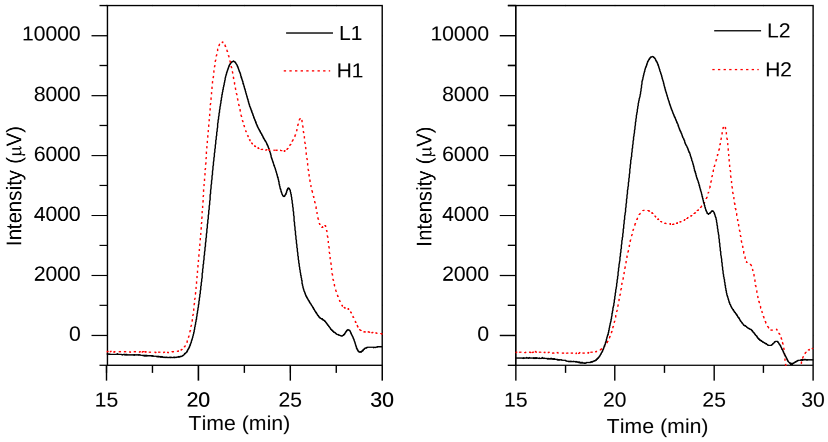

Figure 1. HPSEC analysis: molecular weight distribution of lignins.

In Figure 1**,** chromatograms of original lignin from liquors (L1 and L2) and residual lignins after hydrolysis reactions (H1 and H2) are presented. The chromatograms of residual lignins had two main peaks, but the behavior was completely different. In the chromatogram of H1 residual lignin, large part of it had higher molecular weight than original lignin due to repolymerization of the reaction intermediates/oligomer products to form C–C linkage (Chakar and Ragauskas, 2004). However, in the chromatogram of H2 residual lignin, there was not larger molecular weight fraction.
Otherwise, the second peak in the residual lignins chromatograms was associated to lower molecular weight lignin as a result of the depolymerization reactions of lignin or oligomerization of unstable fragments However, the proportion of this low molecular weight lignin was higher in the case of H2 reaction. All these difference between the two residual lignins, H1 and H2, indicated that the presence of hemicelluloses affected significantly in depolymerization reactions.

4. Conclusions

Olive tree pruning was subjected to organosolv treatment to obtain very rich in lignin black liquors which were treated at high temperatures and pressures in order to depolymerize the lignin they contained. Performed hydrolysis reaction resulted in oil with high percentage of guaiacol and syringol. In addition, cresols, phenol and catechol were formed during the hydrolysis treatment. However, high amounts of undesirable coke were obtained in these reactions. Otherwise, the presence of hemicelluloses changed the experimental results of black liquors hydrolysis hindering the depolymerization of the lignin.

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