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Improving base catalyzed lignin depolymerization by avoiding lignin repolymerization

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HIGHLIGHTS

- Olive tree pruning was considered as an interesting agricultural residue resource.
- Lignin revalorization as platform chemicals was studied.
- Repolymerization reactions were tried to be avoided to enhance chemicals production.
- Monomers production was dramatically improved when adding phenol as capping agent.

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ABSTRACT

Base catalyzed depolymerization was studied to revalorize lignin into monomeric phenolic compounds focusing in avoiding repolymerization phenomenon in order to improve oil yield. In this sense, two capping agents were evaluated in the oxidation of organosolv olive tree pruning lignin. Lignin to capping agent ratio was varied in order to establish its influence on phenolic oil yield and composition. The obtained phenolic products (oil) and by-products (char and residual lignin) were characterized to determine their composition and yield. Boric acid and phenol behaviors were completely different concerning their effect on the nature of the obtained products and on products yields. Boric acid avoided repolymerization although the active fragments seemed to prone to char formation instead of increasing oil monomeric compounds yield. Interestingly, phenol capping agent was proved to favor phenolic compounds production and at the same time, to avoid repolymerization phenomenon. The optimum capping agent to lignin ratio depended on the nature of the added capping agent since their action in lignin base catalyzed depolymerization was totally different.

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1. Introduction

Lignocellulosic biomass is a renewable, relatively carbon-neutral source of energy that is readily available, with a yearly supply of approximately 200 billion tones worldwide [1,2]. To date, effective utilization of these bioresources through biological routes is predicated on pretreatment technologies that can reduce biomass recalcitrance. The objective of pretreating lignocellulosics is to alter the structure of biomass and to make the cellulose and hemicelluloses more accessible/amenable to hydrolytic enzymes [3]. As a result of the lignocellulosic pretreatment, tones of lignin will be produced. In this sense, lignin revalorization will be a key economical factor for second generation bioethanol plants to be cost-effective. Lignocellulosic biomass from agricultural residues, forestry wastes, waste papers and energy crops has come under intense research scrutiny due to its potential use as a starting material

for bioenergy/biofuels and other bioproducts such as bioplastics and biochemicals [4]. Olive tree pruning constitutes a readily available lignocellulosic raw material that currently is yearly generated being an agricultural waste that has to be burned to prevent diseases propagation [5,6].

Lignin is one the main components of lignocellulosic biomass constituting the 20–30% of its weight. Lignin is a natural phenolic macromolecule present in the vegetal cell wall that is made up mainly of three phenylpropane units, namely guaiacyl alcohol (G), syringyl alcohol (S) and *p*-coumaryl alcohol (H). The lignin structure is very complex and consists in a three dimensional randomized net linked to hemicelluloses (lignin carbohydrate complexes, LCC). The main function of lignin in the plant is as a biological barrier and as a glue to retain hemicelluloses and celluloses linked shaping the cell wall.

Among all lignin application possibilities, bulk chemicals production seems to be one of the most promising pathways to add high added value to lignin products. In order to produce aromatic compounds from lignin, a wide range of chemical transformations

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to form valuable chemicals can be developed [7]. Base Catalyzed Depolymerization (BCD) consists in lignin oxidation mainly by the cleavage of the most lignin common bond, the β -O-4 ether bond, to produce phenolic compounds such as aldehydes, acids, and alcohols. Many studies [8–11] have been developed to better understand reaction mechanism and to improve products yields. However, results in literature and our own experience suggest that oil yield is restricted to reach values around 20% in base catalyzed lignin depolymerization. This limit is related to repolymerization phenomenon where instable lignin fragments undergo condensation reactions instead of forming monomeric products. Thring [11] evaluated the alkaline degradation of lignin by means of the combined effect of time and temperature reaction concluding that the identifiable monomeric products decreased with increasing severity of treatment, indicative of the increasing importance of pyrolytic and recondensation reactions occurring in lignin structure under the applied conditions. Moreover, even studies with lignin model compounds have suggested the importance of these recondensation reactions. Miller et al. [8] carried out experiments with lignin simple models (syringol, phenol and anisole) using water as solvent to improve BCD mechanism knowledge. They found that the more highly substituted compounds (syringol) appear to be less stable than compounds with lesser substitution (anisole). The product spectrum from the decomposition of syringol was more complex than that arising from the decomposition of the simpler compound anisole. However, they found that the poor material balance on aromatic rings suggested that a large fraction of the syringol may undergo retrogressive (polymerization) reactions or gasification.

In order to solve repolymerization reactions problems Roberts et al. [10] studied the use of boric acid to protect the phenolic OH groups and suppress repolymerization. In addition to blocking reactions of phenols, boric acid can also act as catalyst for the acidic ether hydrolysis. They found that the presence of boric acid increased the oil yields considerably (15% wt.) compared to the unanalyzed system (6% wt.). They proved that a combination of the BCD process and use of boric acid also affected product composition of the obtained oil. In general, with an increasing amount of NaOH, the molecular weight distribution was shifted towards lower molecular weight products, with increased monomer fraction of the oil. Phenol has also been studied as a good capping agent to prevent repolymerization reactions [12–15]. Okuda et al. [12] claimed that the reaction in the water–phenol mixture effectively decomposed lignin without producing the cross-linked higher molecular weight compounds. Their results showed that the water–phenol mixtures in supercritical conditions are excellent solvents for depolymerization of lignin.

Nevertheless, in these studies researchers only paid attention to the molecular weight of the oil and not to tar, char or residual lignin where repolymerization reactions products are found. With this purpose, in the present work, improvement of base catalyzed lignin depolymerization was studied by the addition of different capping agents. Furthermore, revalorization of wastes was another challenge of this work; waste agricultural residues (olive tree pruning) were transformed into interesting bulk chemicals by

Table 1
Initial pH of the resulting reaction mixtures. All experiments were carried out adding 4% (wt.) of sodium hydroxide as catalyst.

Lignin	H ₃ BO ₃	Phenol	pH
1	0.75	–	12.7
1	1	–	12.6
1	2	–	10.0
1	–	0.75	12.7
1	–	1	12.7
1	–	2	11.4

lignin depolymerization. Organosolv olive tree pruning lignin was subjected to alkali oxidation conditions in order to produce phenolic monomeric compounds. Two capping agents were studied and compared, namely boric acid and phenol, to determine their effect on base catalyzed lignin depolymerization. Different lignin to capping agent ratios were evaluated in order to establish their influence in oil yield and composition. The obtained phenolic products (oil) and by-products (char and residual lignin) were characterized in order to determine their composition and yield.

2. Materials and methods

Olive tree pruning (*Olea europaea*, variety Arróniz) was used as raw material. The treatment for lignin extraction consisted on the digestion of the olive tree pruning in a mixture of ethanol–water (70% wt) at 200 °C for 90 min (previously optimized conditions [16]) in a pressure reactor. The liquid fraction (where lignin was dissolved) was separated from the solid fraction by filtration. Dissolved lignin was isolated by precipitation with two acidified water volumes (pH around 2). The suspension was centrifuged at 4000 rpm for 20 min to recover the lignin. Lignin was dried at 50 °C. Organosolv olive tree pruning lignin presented the following composition: acid insoluble lignin 71.90% ± 0.79, acid soluble lignin 1.63% ± 0.08, total sugars 2.94% ± 0.14 (glucose 1.75% ± 0.12, xylose 1.10% ± 0.03 and arabinose 0.09% ± 0.01) and ash content 0.39% ± 0.01.

Base catalyzed depolymerization is based on the base oxidation action on lignin structure. The reactions were conducted in a batch reactor – 5500 Parr reactor – with a 4848 Reactor controller. The reaction temperature was set at 300 °C for 40 min reaching pressures around 90 bars. Lignin:solvent (water) ratio was 1:20 (w/w). The catalyst (sodium hydroxide) concentration was set at 4% (wt.) [17]. Two capping agents (boric acid – pK_a 9.24 and phenol – pK_a 9.95) were studied, and their ratio (lignin:capping agent, w/w) was varied in order to study its influence on product yields. An experiment was carried out without capping agent as a reference. The resulting pH of each experiment is presented in Table 1.

The reaction mixture was then treated to separate the different products [10]. The reaction mixture was acidified with hydrochloric acid until reaching a pH around 1. A solid precipitated that was isolated by filtration using MN 640w filters. At this stage, residual lignin and char make up the isolated solid. Afterwards, this solid was solubilized in tetrahydrofuran (THF) and then filtered. The non-solubilized solid was char, and the residual lignin was solubilized in THF. THF was evaporated under vacuum to recover the residual lignin. The acidic filtrate was extracted with ethyl acetate in order to extract the phenolic monomers produced during lignin depolymerization. The yield of each product was calculated gravimetrically referring to the initial lignin weight. A scheme of the product separation procedure is presented in Fig. 1.

Oil was characterized in order to establish the nature of the monomeric phenolic compound and to determine the molecular weight profile. The phenolic oil was dissolved in ethyl acetate (HPLC grade). The solution was injected in a GC (7890A)-MS (5975C inert MSD with Triple-Axis Detector) Agilent equipped with a capillary column HP-5MS ((5%-Phenyl)-methylpolysiloxane, 60 m × 0.32 mm). The temperature program started at 50 °C then, the temperature is raised to 120 °C at 10 °C/min, held 5 min, raised to 280 °C at 10 °C/min, held 8 min, raised to 300 °C at 10 °C/min and held 2 min. Helium was used as carrier gas. Calibration was done using pure compounds (Sigma–Aldrich) to produce calibration curves – phenol, cresols (*o*-cresol, *m*-cresol and *p*-cresol), guaiacol, catechol, 4-methylcatechol, syringol, acetovanillone, 4-hydroxybenzoic acid, syringaldehyde, 4-hydroxy-3-methoxyphenylacetone and ferulic acid.

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