

Valorización de lignina mediante la obtención de catalizadores y productos químicos de interés

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Objectives and novelty

Lignin is a biopolymer obtained as by-product in the pulp industry and possibly, in the next future, in lignocellulosic biorefineries. The current purpose of lignin is the generation of electricity in the plants where is produced. Due to the exponential rise of the world population, its production has been surprisingly increased. According to the principles of green chemistry and zero waste processes, its valorization becomes imperative.

Therefore, the objective of the present work is the study of different alternatives for the integral valorization of residual lignin. To achieve this objective, two valorization routes are proposed i) its use as raw material for the preparation of carbon materials of high industrial interest, such as activated carbons and carbon fibers, ii) and as reactant for the production of high added value compounds, like catalytic depolymerization of lignin, using also lignin derived-catalyst, as summarized in Figure 1.

Results

Initially, the preparation of a carbon catalyst, from physical activation with CO_2 of a magnesium lignosulfonate, active for the dehydrogenation reaction of 2-propanol, was explored. The results showed that only a carbonization treatment at 900 °C produces hollow porous carbon spheres with apparent surface areas higher than 450 m^2/g . After partial activation with CO_2 , the resulting activated carbon presents an apparent surface area around 700 m^2/g and ca. 15%wt of Mg. The conversion of 2-propanol was higher than $X_{2\text{-propanol}} = 95\%$, showing a selectivity towards acetone near to $S_{\text{acetone}} = 100\%$, evidencing the high basic character of these carbon catalyst. On the other hand, the effect of the physicochemical properties of different lignins on the porosity of activated carbons chemically activated with

H_3PO_4 was analyzed. With the different experimental conditions evaluated, it was possible to prepare activated carbons essentially microporous (with A_{BET} higher than 2000 m^2/g) or with high contribution of mesopores (V_{meso} as large as 2.0 cm^3/g).

The activated carbon with the most developed mesoporosity was selected as the starting point for the preparation of active catalysts for oxidative and reductive lignin depolymerization. The oxidative depolymerization of lignin was studied on this activated carbon after its functionalization with nitro groups. The same carbon support was used to synthesize a copper-loaded catalyst, used for comparative purposes. In the catalyst functionalized with nitro groups, the formation of N-P species was observed, which presented the highest activity for the production of vanillin. This catalyst maintained its activity in the presence of oxygen in the reaction medium during successive reaction cycles. The maximum yield towards vanillin obtained was around 3.6% wt, which represented an increase of more than 30% with respect to the reaction without heterogeneous catalyst.

The lignin reductive depolymerization was carried out on three different catalysts. The activated carbon was loaded with Ni, Co-Mo and Ni-Mo yielding carbon materials with a strong interaction between the metal and the phosphorus contained in the activated carbon. The Ni-Mo catalyst presented a high concentration of a mixed phosphide MoNiP , which resulted in a yield to aromatic monomers and cycloalkanes of more than 12 % wt. In addition, for the sake of comparison, the reaction was also carried out using a commercial Ru-loaded activated carbon, which showed significantly lower yield towards bio-oil than the Ni-Mo phosphide-rich catalyst. Figure. 2 schematically represents the lignin oxidative and reductive depolymerization processes carried out in this work.

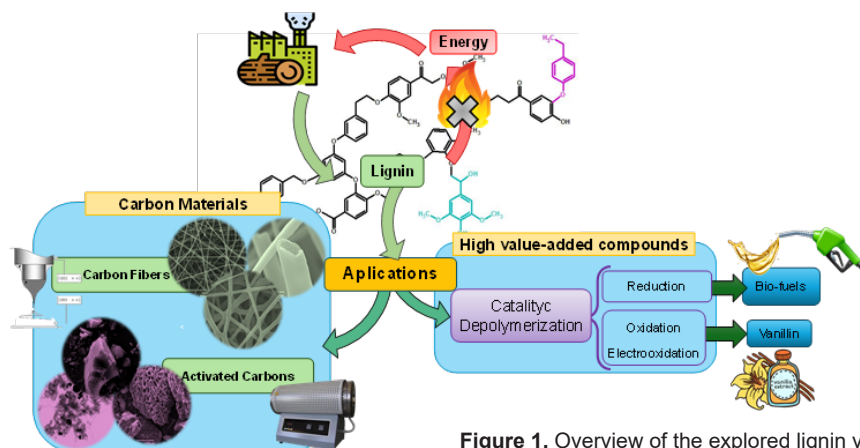


Figure 1. Overview of the explored lignin valorization routes.

As an alternative, the use of lignin-derived carbon fibers electrocatalysts in the electrooxidative depolymerization reaction of lignin was also explored. Carbon fibers were prepared by electrospinning technique, whereby several lignin solutions containing metal precursors were spun into fibrillar morphology and finally carbonized, resulting in carbon fibers loaded with different metals in a single step. Consequently, electrocatalysts based on carbon fibers loaded with Ni, Co and Pd were successfully synthesized. Cyclic voltammetry experiments showed that Ni-containing carbon fibers exhibited higher activity than their Co and Pd counterparts. Electrochemical tests for lignin depolymerization revealed the need to cleave the lignin structure to allow migration of its fragments to the catalyst surface for oxidation. As a result, a yield to vanillin higher than 1% wt was obtained, at atmospheric pressure and room temperature, using the Ni-loaded electrocatalyst, also showing the same activity after several reaction cycles. Finally, a commercial Ni foam catalyst was compared, whose metal content was two orders of magnitude higher than the Ni content present in the carbon fibers. The activity of this commercial catalyst were significantly lower than the one presented by the electrocatalyst based on Ni carbon fibers.

(A_{BET} higher than 1000 m^2/g), suitable for use in catalysis applications or as adsorbents.

Conclusions

The main conclusion of this study raises the possibility of a full valorization of lignin through simple and cost-effective processes. To this end, lignin processing could be integrated within the facilities of a refinery equipped with second-generation ethanol production systems, only with minor modifications of some operation conditions which could significantly improve its overall sustainability. In this way, materials of high industrial interest such as activated carbon or carbon fibers, which can be obtained using non-expensive compounds and equipment, can be economically introduced into the utilities of a traditional refinery, bringing substantial profits.

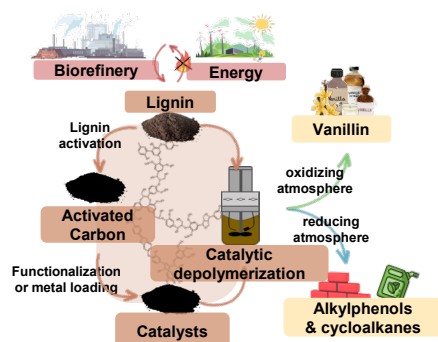
Related publications

[1] M. García-Rollán, F.J. García-Mateos, R. Ruiz-Rosas, J.M. Rosas, J. Rodríguez-Mirasol and T. Cordero, MgO-containing porous carbon spheres derived from magnesium lignosulfonate as sustainable basic catalysts, *J Environ Chem Eng* 11 (2023) 109060

[2] M. García-Rollán, N. Rivas-Márquez, S. Bertran-Llorens, P.J. Deuss, R. Ruiz-Rosas, J.M. Rosas, J. Rodríguez-Mirasol, T. Cordero, Bio-based vanillin production by oxidative depolymerization of Kraft lignin on a nitrogen and phosphorus functionalized activated carbon catalyst, *Energy Fuels* 38 (2024) 7018–7032

[3] M. García-Rollán, M. Toscano-de los Riscos, R. Ruiz-Rosas, J.M. Rosas, J. Rodríguez-Mirasol, T. Cordero, Oxidative electrochemical depolymerization of lignin using highly active self-standing electrocatalysts prepared by electrospinning of lignin, submitted to *Journal of Environmental Chemical Engineering*

Catalytic depolymerization



Electrocatalytic depolymerization

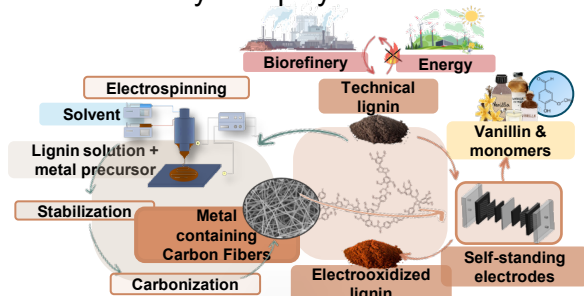


Figure 2. Overall process of lignin depolymerization by oxidative and reductive (A) and electrooxidative (B) pathways.

In order to fully introduce the processes presented herein within the framework of green chemistry and zero waste production, the valorization of the solid wastes obtained after lignin depolymerizations was finally studied. With this goal, this residue was chemically activated with phosphoric acid, obtaining activated carbons with a highly developed porosity