Towards lignin valorization by catalytic oxidation in aqueous media

Cédric Cabral Almada1, Sandra Tapin-Lingua2, Denilson Da Silva Perez2, Pascal Fongarland1, Laurent Djakovitch1
1 Institut de Recherches sur la Catalyse et l’Environnement de Lyon - IRCELYON - UMR 256, CNRS Université de Lyon 1, 2 avenue Albert Einstein 69626 Villeurbanne cedex, France
2 Institut Technologique Forêt Cellulose Bois-construction Ameublement - FCBA, Domaine Universitaire BP 251, 38044 Grenoble Cedex 9, France
*cedric.cabral-almada@ircelyon.univ-lyon1.fr

Introduction

With the depletion of fossil fuels, the need to develop green technologies to produce energy or chemicals increased. Lignocellulosic biomass is a promising candidate regarding its renewability and availability at a low price. Lignin, which represents ca. 30%, is a macromolecule formed by the random polymerization of three: p-coumaryl, coniferyl and sinapyl alcohol [1]. This results in a three-dimensional phenolic bio-polymer. Those structures depend on the source and extraction process. Nowadays it is essentially produced by the Kraft process (paper pulp production) and used as an energy source for it [2]. Nevertheless, a part of that lignin can be redirected for other applications without endangering this industry.

In order to valorize lignin, we studied its transformation to produce aromatic building blocks for polymers or fine chemicals by catalytic oxidation using heterogeneous catalysts in aqueous media under mild conditions.

Materials and Methods

In this work, a softwood lignin, provided by FCBA after extraction and purification from a Kraft black liquor by precipitation with H2SO4, was engaged. Alkaline solutions of lignin (0.5%wt) were treated in the presence of Au/TiO2 catalyst in a 300mL batch reactor under 40bar air at temperature varying from 50°C to 150°C. At completion, the catalyst was separated by filtration. The complexity of the reaction mixture encouraged us to design a protocol allowing evaluation of the transformation that occurred during the reaction. High molecular weight molecules were precipitated by HCl addition and separated by centrifugation giving so-called “precipitate”. Then, the remaining aqueous phase was washed with dichloromethane to recover monomeric fraction while oligomeric fraction remained in water. This fractionation allowed careful analyses of the different fractions by complementary techniques (IR, NMR, GC-MS, LC-MS…).

Results and Discussion

The influence of different parameters was evaluated throughout our study. It was shown that base loading has a great impact on the rate of lignin depolymerization. Indeed, increasing NaOH concentration resulting in a decreased “precipitate” amount. However, it seems that addition of catalyst had no notable effect on this aspect (fig. 1). In both cases, the recovered precipitate looks alike but completely different from the starting lignin. As a matter of fact, IR analysis showed disappearance of a characteristic band of lignin corresponding to aromatic vibrations together with apparition of bands corresponding to carbonyls.

Concerning the monomeric fraction, rising the amount of base improved the yields toward the target molecules; however, adding the catalyst lowered the yields in monomers by favoring over-oxidation (fig. 2).

In conclusion, the catalytic oxidation of lignin has been realized in an alkaline media under mild conditions. While the base seems to favor the formation of monomeric compounds, the use of gold catalyst lowered them due to over-oxidation. These aspects will be discussed in details.

Significance

This work falls within a biorefinery approach in which every compound of the lignocellulosic biomass is valorized. Indeed, the goal is to produce bio-based high-added value compounds from lignin, supplied by the paper industry, such as vanillin, a milestone for many applications (polymer, pharmaceuticals…).

References