L08
CONVERSION OF LIGNIN: CHEMICAL TECHNOLOGIES AND BIOTECHNOLOGIES

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The scientific activity of Dr. Claudia Crestini is focused on different aspects of Bioinorganic Chemistry. She is author of about one hundered pubblications on international journals. She is member of the wood related COST actions E23, E41, and of the managment commettee of E54 and FP602, she i salso member of the Scientific Commetee of the European Workshop on Lignocellulosic and Pulps EWLP since 2000.
In 2001 she activated the Italian Meeting on Lignin Chemistry.
Claudia Crestini was nominated and elected member of the International Academy of Wood Science in 2009.
Dr. Crestini is solely responsible for the establishment of Bioinorganic chemistry laboratory at the Tor Vergata university in Rome, one of the few Italian Laboratories with significant R&D activities in the field of development of new materials from lignins, bleaching, lignin structural characterization, catalysis, biomimetic catalysis and biotechnology in lignin and lignans oxidative modifications.
The main research fields are:

- Structural characterization of lignins by advanced NMR techniques. Development of heteronuclear NMR analyses of lignins.
- Biocatalysis in processes of lignin degradation, with a special focus on the study of manganese peroxidase, laccases and laccase-mediator systems.
- Development of supported catalysts and biomimetic catalysts for the activation of oxygen and hydrogen peroxide to the selective oxidation and functionalization of lignins and lignin model compounds.
- Oxidative catalysis in the oxidation of natural substances as unsaturated monoterpenes, cardanols, nucleosides, lignans.
- Development of new materials from lignins

Abstract
Novel processing methods and product concepts are required to extend the role of lignin for future biomass and biofuel applications in emerging platforms such as the biorefinery. The possible strategies of lignin valorisation are focused into two main directions, namely the selective functionalisation of the lignin polymer or in its oxidative depolymerization to get polyfunctional monomeric compounds. Here we report a panel of biocatalysis, organometallic catalysis and biomimetic catalysis processes developed by our research group for the activation of the environmental friendly oxidants oxygen and hydrogen peroxide in the oxidative functionalisation of lignin and lignin model compounds.

Introduction

Agricultural and forestry residues constitute a renewable source of lignocellulosic materials. Implementing concepts such as that of the biorefinery will allow the creation of high-value products that can improve profitability and can increase efficiency with respect to conventional mineral oil refinery. Despite the fact that the industrial use of biopolymers such as cellulose is considerable, lignin, the second most abundant biopolymer which accounts for 15-30% of biomass, is a under-utilized source of chemical energy. The use of lignin is nowadays still limited to thermovalorization processes as filler in composites, component in binders and coatings, or, at a lower extent, surfactant / dispersant additives, whereas its potential as a source of valuable phenols in the production of high value-added biopolymers in alternative to petrolchemistry is largely unexploited. Thus, novel processing methods and product concepts are required to extend the role of lignin for future biomass and biofuel applications in emerging platforms such as the biorefinery. The chemical heterogeneity of lignin is one of the main reasons for the lack of valorization of lignin residues that emerge from pulp and paper, and modern saccharification processes. Lignins are polyphenols characterised by a complex network of three main monomeric phenyl propanonic units bonded trough an array of different interunit bondings. The lack of a repetitive sequence, specific interunit bondings and specific subunits makes the structural characterization and upgrade of lignin a challenging task for the chemists.

Results and discussion

The possible strategies of lignin valorisation are focused into two main directions, namely the selective functionalisation of the lignin polymer in order to improve its compatibility and performance in composite and copolymer materials, or in alternative, in its oxidative polymerization to get polyfunctional monomeric compounds to be used as feed-stocks for polymer industry as an alternative to fossil fuels derived building blocks.

In this context special emphasis was devoted in the last years to the study of lignin oxidative functionalization processes, mainly due to the presence of high amounts of side-chain aliphatic OH, terminal phenolic OH groups and reactive benzylic positions, that can be selectively modified.

Here we report a panel of oxidative processes by means of biocatalysis, organometallic catalysis, biomimetic catalysis processes developed by our research group for the activation of the environmental friendly oxidants oxygen (O_2) and hydrogen peroxide (H_2O_2) in the oxidative functionalisation of lignin and lignin model compounds.

Laccases are able to actiate O_2 toward lignin oxidation, specially in the presence of oxidation mediators. The main oxidation pathways are found in phenolic lignin subunits oxidation with conseguent depolymerization and oxidative coupling products. Analogous behaviour was found in Mn peroxidase. However in this case coupling processes were found prevalent over depolymerization. Organometallic catalysts able to perform heterolytic oxygen transfer from hydrogen peroxide are able to oxidize lignin at different levels. According to the experimental conditions it is possible to tune the reaction selectivity towards phenolic groups and aromatic rings oxidation or toward side chain oxidation and depolymerization.