DUAL OXIDATION WAYS TOWARD LIGNIN EVOLUTION

Heber dos Santos Abreu[1]
Marcos Antônio Maria[2]
Jennifer Lemos Reis[2]

ABSTACT

During million years (MY) plants made up an efficient mechanism for their owner protection, neutralizing oxygen radicals (superoxide) in the cell wall. Evaluation of the oxygen paticipation on plant secondary metabolism, especially associated with the lignin formation, suggested two oxidation mechanisms: vertical and horizontal oxidation. The latter is mediated by enzymatic mechanisms, contributing to the structural profile of modern plants. Vertical oxidation is carried out in the cell wall and is responsible by lignin accumulation, while horizontal oxidation is elaborated into the cytoplasmatic compartment. These mechanisms are independent and play an important strategy to prevent destructive oxygen effect on the plant cells.

Key words: Lignin, oxidation, evolution

INTRODUCTION

At the beginning of land plant life since Silurian Period (411-439 millions years ago) (Myag), primitive vascular plants were small sized and contained at least 10-15% of lignin. Those plants survived under low oxygen atmosphere content (17.81 %), while earlier land plants in Ordovician Period (443-510 MYag) were not so able to accumulate lignin. However, in the Devonian Period, plants reached up to 40% of lignin and decayed later in the Mesozoic Era (ROBINSON, 1990). Between 335-245 million years, the atmosphere presented 35 % of oxygen, following by a rapid decreasing (ROBINSON, 1990). Distinctive progress of lignin accumulation and O-methylation rate were detected in plants that survived all that time. Such event takes plants to develop high biochemical flexibility, (GOTTLIEB et al. 1995). The number of oxygen atom linked to the aryl-group of *p*-hydroxyphenylpropanyl, guaiacyl and syringyl components, (GOTTLIEB, 1989), was also attributed to the oxygen effect on plants for million years. Lignin accumulation and its distribution in several botanic taxa have been reported (GOTTLIEB, 1989; GOTTLIEB et al. 1995; BOSÍSIO et al. 1995).

BIOCHEMICAL APPROACH

As mentioned above, in the horizontal oxidation, precursors of lignin are formed by enzymatic mediation. *p*-Coumaric acid for example is oxydated to caffeic acid and then methylated to ferulic acid until sinapic acid formation,

[1] DPF, IF, Universidade Federal Rural do Rio de Janeiro
[2] Universidade Federal Rural do Rio de Janeiro

respectively. The second biochemical reaction that is mediated by OMT (O-methyltransferase) methyl transfer group to 3- and 5-hydroxyl groups in the aromatic ring (LEWIS & SARKANEN, 1998; BOUT 1998; HETEN et al. 1998). This latter biochemical reaction displays to be gradual and takes long time (MY) to complet, while vertical oxidation seemed to be faster (Figure 1 and 2). Actually, the overall cell wall formation is unknown yet, even though, there are proposals that peroxide (H_2O_2) is used in the lignification (GROSS, 1977,1979; HIGUCHI, 1984; INZË & MONTAGU, 1995; VEIGA et al. 1999). Monolignols and peroxidase-H_2O_2 form phenoxy radicals that are take by unknown mediation mechanism of coupling to form lignin. Figure 1, describes dual ways of oxidation (vertical and horizontal oxidation) in the cell.

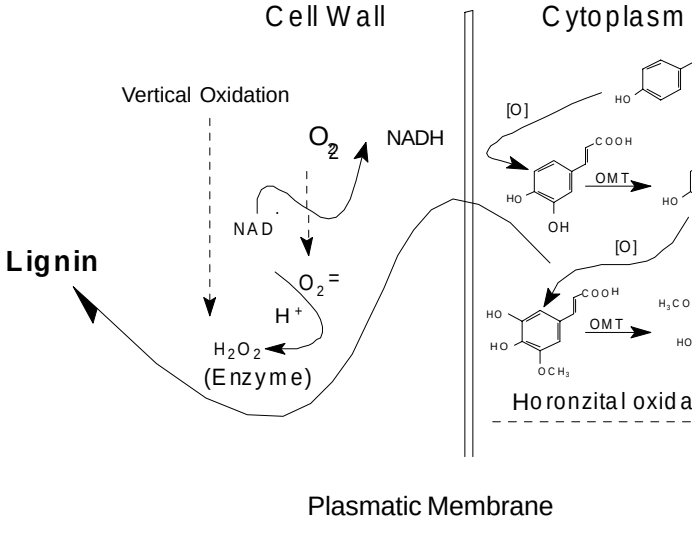
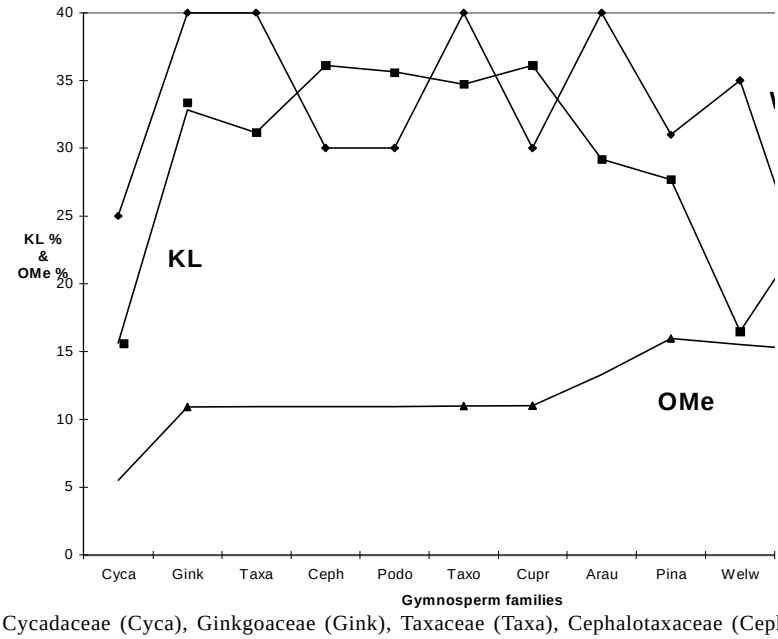


Figure 1. Diagram showing vertical and horizontal oxidation in the cell.

Plants that have established ways to resist to oxygen destructive effects survived during million years and have showed high flexibility in the molecular lignin composition (Methoxylation degree), as well as a variable level of lignin accumulation in the xylem tissues. Contemporaneous gymnosperms kept original rate of lignin accumulation and compositional profile. Cycadaceae (15,6 % of lignin-245-256 MYag-23% of O_2) Ginkgoaceae (32,8%), Taxaceae (31,8), Cephalotaxaceae (36,1% 223,4-235 MYag-24,06% of O_2), Podocarpaceae (35,64), Taxodiaceae (34,73), Cupressaceae (36,1), Araucariaceae (29.2%), Pinaceae 27,7%), Welwitschiaceae (16,5%) and Ephedraceae (24,7%) are examples of families that sustain lignin with different level of accumulation and compositional ratio. Figure 2 shows the behaviour of lignin evolution. Woodness Index (up side) (GOTTLIEB, 1989; GOTTLIEB et al. 1995; BOSÍSIO et al. 1995), lignin content (middle), and methoxyl content (down side), were compared followed by the evolutive sequence of gymnosperm families. Comparative analysis of the lignin in plants and oxygen distribution (MY) (Figure 3) suggests different status of lignin evolution in each gymnosperm families.



Cycadaceae (Cyca), Ginkgoaceae (Gink), Taxaceae (Taxa), Cephalotaxaceae (Ceph), Podocarpaceae (Podoc), Taxodiaceae (Taxo), Cupressaceae (Cupr), Araucariaceae (Arau), Pinaceae (Pina), Welwitschiaceae (Welw), Ephedraceae (Ephe) and Gnetaceae (Gnet); KL (Klason Lignin), OMe (Methoxyl content), WI (Woodness Index)

Figure 2. Relationship among methoxyl content, lignin content and Woodiness Index for gymnosperm families (MARIA, 1997).

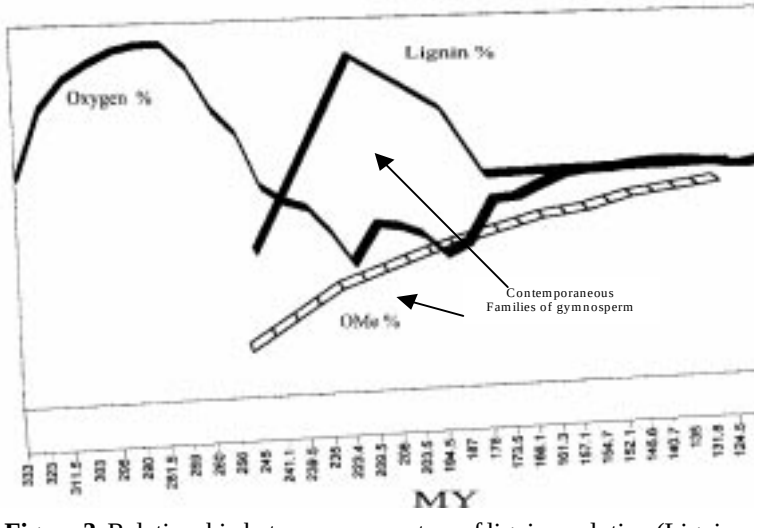


Figure 3. Relationship between parameters of lignin evolution (Lignin and OMe %) and atmospheric oxygen variation (MYag) adapted from (BOSÍSIO, 1995; TAYLOR & TAYLOR, 1993)

FINAL CONSIDERATIONS

This study has permitted to propose that plants under different atmospheric oxygen conditions may adapted an enzymatic control of lignin composition. However, the lignin accumulation occurred at each level of oxygen content, varying period by period. Therefore, plants that survived at high oxygen atmospheric content promoted high lignin accumulation, otherwise under low oxygen content plants accumulated less lignin. e.g. ferns, licopods, gymnosperms and angiosperms. It was also suggested that this event favored the horizontal oxidation on structural point of view contributing to β-O-4 unit (alkyl-β-aryl ether bond) formation (ABREU, 1999), which is an unit base dependent of oxidative mechanism.

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