

LGP2, Laboratoire de Génie des Procédés Papetiers, Grenoble INP (Coordinateur)
DCM, Département de Chimie Moléculaire, UJF
ARKEMA, Centre de Recherche Rhône-Alpes
Fibre Excellence

Background and objectives

Cellulosic pulps for paper production are obtained after wood delignification (cooking) and bleaching with chlorinated agents to remove residual lignin. The use of these cellulosic pulps in chemical applications (cellulosic textiles and plastics) is not possible because of the cellulose contamination with hemicelluloses and lack of reactivity. Special delignification (cooking) processes have to be used which are more complicated and which do not allow to produce cellulosic pulps for both paper and cellulose applications. This project aims at developing a new environmentally friendly catalytic bleaching process, using hydrogen peroxide, for pure cellulose production from a wood pulp of paper quality obtained with conventional cooking process. Cu(II)-di-imine complexes are used as catalyst for H₂O₂ delignification.

Catalyzed H₂O₂ delignification by the Cu(II)-phenanthroline complex

Mechanism explaining the higher lignin depolymerization with the catalyst (study using Lignin Model Dimer, i.e. LMD):

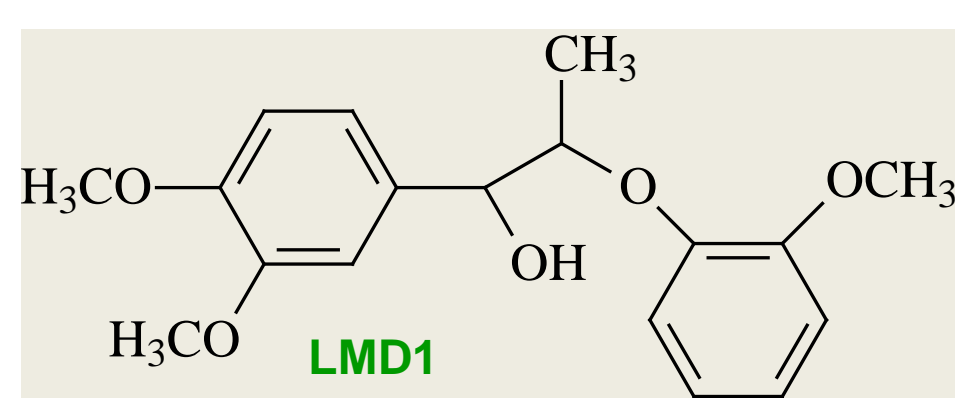


Fig 1. LMD1 = non phenolic Lignin Model Dimer 1-(3,4-diméthoxyphényl)-2-(2-méthoxy-phénoxy)propane-1-ol

1st step: oxidation of the alcohol group in the C- α position catalyzed by the Cu(II)-phenanthroline complex in alkaline medium - (no reaction without the catalyst). LMD1 is oxidized into LMD5

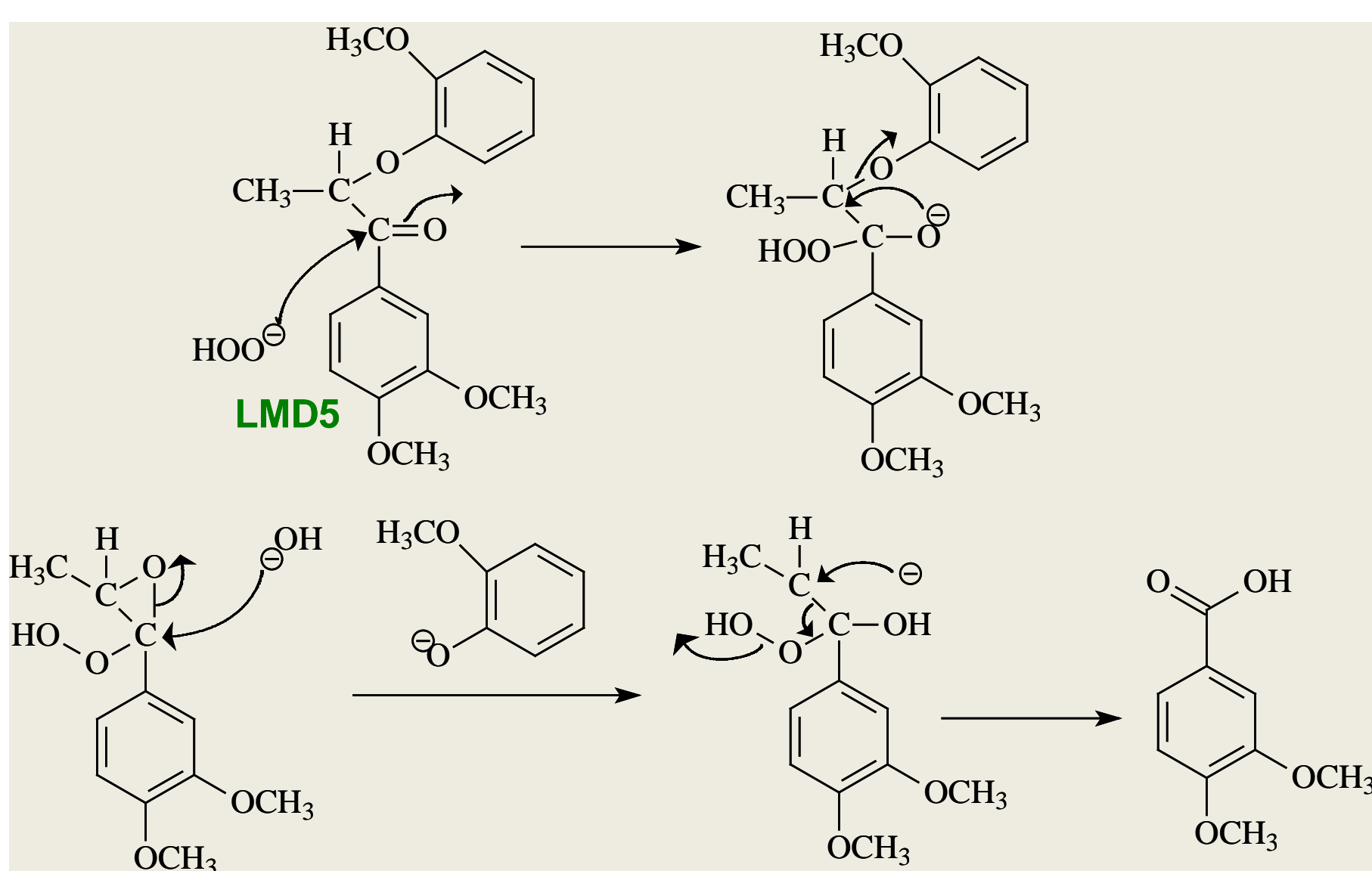


Fig 2. β -O-4 ether linkages in alkaline medium (LMD=Lignin Model Dimer)

2nd step: cleavage of the β -O-4 ether linkages of LMD5 in alkaline medium (does not require the catalyst)

Screening of Cu(II)-di-imine catalyst

Quantification of the veratryl alcohol consumption (non phenolic lignin model) and veratryl aldehyde production after the catalyzed oxidation.

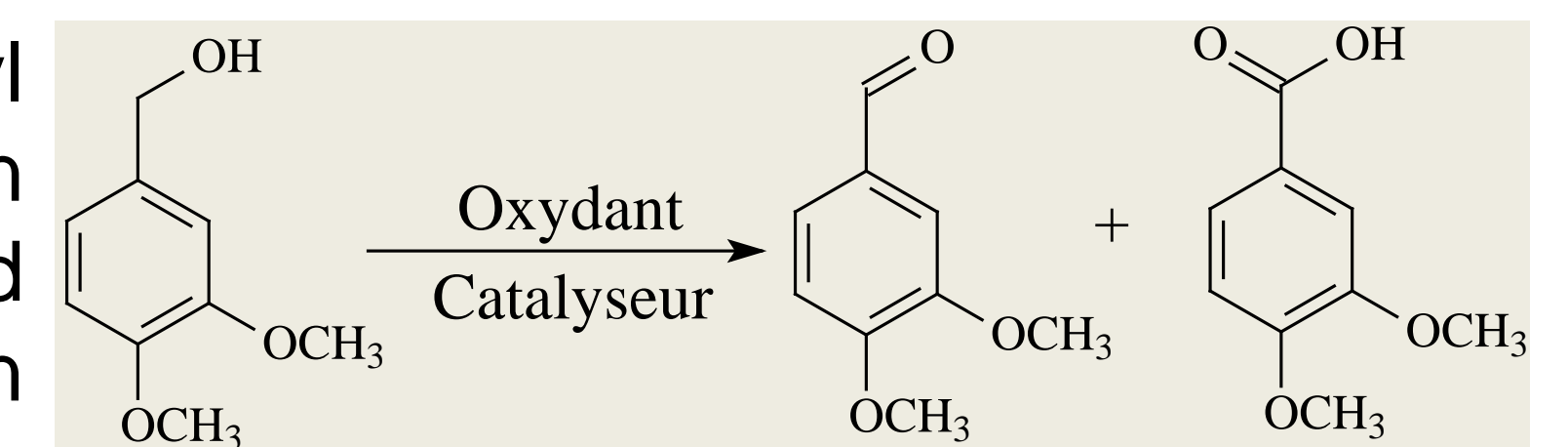
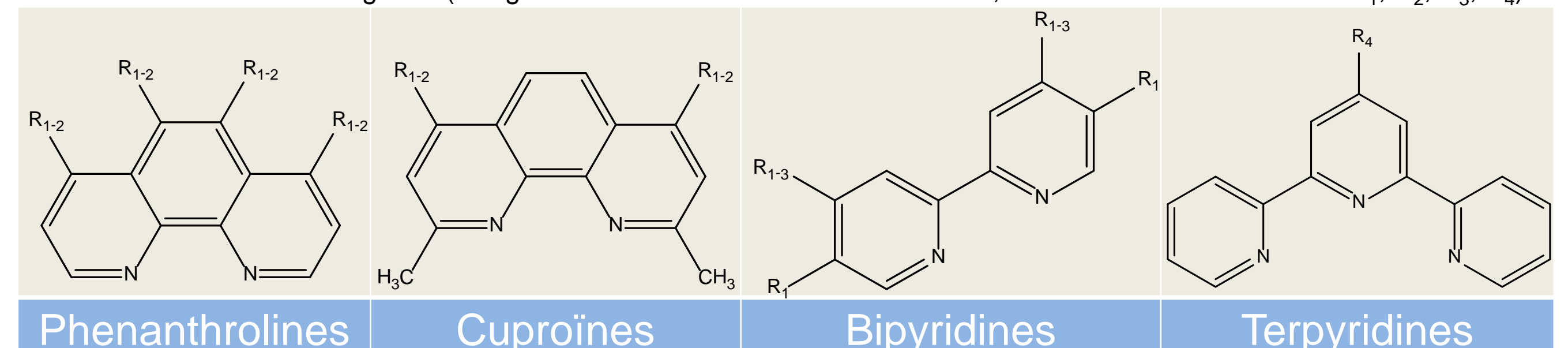


Fig 3. Oxidation of the veratryl alcohol into aldehyde and acid, in the presence of the Cu(II)-phenanthroline complex

Table 1. Selected di-imine ligands (22 ligands from several families were tested, with or without substituents R₁, R₂, R₃, R₄)



➔ Cu(II)-phenanthroline type complexes are the most active.

Produced celluloses and technical and economical evaluation of the process

A bleaching/purification process has been developed which includes H₂O₂ delignification, catalyzed (or not), and pre- and post-chlorine free treatments (cold caustic extraction E and ozonation Z)

Table 2. Celluloses properties

Cellulose	Brightness, %ISO	Viscosity, mL/g	S18, %	Cu, ppm	Heavy metals, ppm
Viscose target	90-92	400-600	3-3.5	1	<10
(aQ)(OP)EZ	90.3	874	3.3	<5	<0.5
(aQ)(OP) _{cat} EZ	91.2	437	3.4	<5	<0.5

➔ The produced celluloses exhibit similar properties as **viscose** pulps in terms of purity.

Table 3. Economical evaluation of the integration of the process in an existing bleached pulp production line (10% of the total production is used for pure cellulose production)

€ per produced tones	Cellulosic pulp	Pure cellulose	
		Catalyzed process	Without catalyst
Targeted sale price	580	880	
Wood cost	350	432	432
Chemicals cost	50	173	53
Gross profit	180	275	395

➔ The gross profit is better for pure cellulose than for cellulosic pulp. The process is working without catalyst, but the cellulose viscosity is too high for viscose application, (acceptable for other uses).

CONTACT:

Dr. Nathalie Marlin, Laboratoire de Génie des Procédés Papetiers, Grenoble INP
Nathalie.Marlin@Grenoble-inp.fr

