Chapter 3

MANGANESE COMPLEXES IN THE LIGNIN OXIDATION CATALYSIS

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ABSTRACT

Lignin is one of the major components of plants constituting up to 30% by weight and 40% by energy of the lignocellulosic biomass. The lignin oxidation reactions are very important not only in the context of traditional pulp-and-paper industry (lignin is oxidised/removed from wood in order to produce bleached pulp for the papermaking), but also with regard to the lignin valorisation toward the production of fine chemicals (*e.g.*: vanillin, vanillic acid, syringaldehyde).

Diverse transition metal complexes have been used as catalysts for the oxidation of lignin and lignin model compounds. This derives from the fact that some of these complexes mimic the reactive centres of natural enzymes (such as manganese peroxidase and lignin peroxidase) which, in nature, are involved in the biological delignification processes. Manganese complexes, in particular, have proved to be one of the most effective catalysts for the lignin oxidation with hydrogen peroxide or oxygen: manganese porphyrins, manganese complexes with triazacyclononane ligands or with heterocyclic amines, and a few polyoxometalates, among others were most commonly employed. In this book chapter, relevant results concerning the use of manganese complexes as catalysts for the lignin oxidation are discussed.

Keywords: Catalysis, lignin, lignin model compounds, oxidation, delignification, bleaching, lignocellulosic pulp, oxygen, hydrogen peroxide, manganese, porphyrins, heterocyclic amines, triazacyclononane ligands, polyoxometalates, ionic liquids

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INTRODUCTION

Besides cellulose and hemicelluloses, lignin is one of the major components of plants, constituting up to 30% by weight of the lignocellulosic biomass [1,2]. For papermaking in the pulp-and-paper industry, this component is oxidised/removed from the wood cell walls to produce bleached pulp, a fibrous material mainly composed of cellulose and hemicelluloses. As a consequence of the processing methodology, lignin is usually discarded as a waste material, regardless its high abundance and potential value. In fact, according to Zakzeski *et al* [1], only around 2% of the diverse lignins available from this industry are used commercially with the remaining being burned as a low value fuel.

However, lignin after a preliminary extraction from wood may be further processed in order to obtain specific products with higher commercial value. The lignins may be isolated from the wood using not only physical and chemical methods (including those derived from the conventional techniques employed in the pulp production industry), but also using biological pre-treatment processes. In particular, Kraft lignin and lignosulphonate lignin are obtained from the common kraft pulping and sulphite pulping processes, respectively. Posterior oxidation reactions of lignin may enable to obtain various monomeric products with additional value, such as vanillin (aromatic ingredient for food and perfumes), vanillic acid, syringaldehyde and 2,6-dimethoxybenzoquinone.

A paradigmatic example of selective oxidation of lignin may be found in nature, regarding the catalytic activity of numerous enzymes from fungi and bacteria, such as manganese peroxidase, lignin peroxidase and laccase. Each of these enzymes possess an active metal centre that, in the presence of hydrogen peroxide or oxygen, promotes the lignin oxidation and/or degradation. Thus, mimicking the reactive centres of natural enzymes by using appropriate systems containing transition metal catalysts may provide reactive paths for the lignin oxidation. Manganese complexes, in particular, have proved to be among the most effective catalysts for the lignin oxidation with hydrogen peroxide or oxygen.

This book chapter focuses on the use of manganese complexes as catalysts for the oxidation of lignin and lignin model compounds. A previous introduction to this review includes the description of the lignin structure, the types of lignin and the delignification methods commonly used in the pulp-and-paper industry.

1. LIGNIN, CELLULOSE AND LIGNIN OXIDATION

Lignin is a tridimensional heteropolymer built up of hydroxylated and methoxylated phenylpropane units (C_9). The α,β-unsaturated C_6C_3 precursors of lignin are the sinapyl alcohol (*1*), coniferyl alcohol *(2)* and *p*-coumaryl alcohol *(3)* (Figure 1) which gives rise in the lignin structure to the syringyl (S), guaiacyl (G) and *p*-hydroxyphenyl (H) units, respectively [2-4]. The structure of lignin varies in softwoods, hardwoods (Figure 2) and grasses regarding the proportion of S, G and H units. The "guaiacyl lignin" (G-type lignin), occurring in softwoods, is a polymerisation product of coniferyl alcohol. The "guaiacyl-syringyl lignin" (GS-type lignin), typical in hardwoods, is a copolymer of coniferyl and sinapyl alcohols, with the S/G ratio varying from 4:1 to 1:2. Typical lignins of

herbaceous plants contain also significant amounts of H units and these lignins are referred to as the GSH-type [2-4]. The most common linkages between phenylpropane units in wood lignin are presented in Figure 3. In wood lignin, more than two thirds of the phenylpropane units are linked by ether bonds and the rest mainly by carbon-to-carbon bonds. The most abundant inter-unit linkage in lignin is β-*O*-4 and the other relevant linkages are the α-*O*-4, β-5, β-1, β-β, 4-*O*-5 and 5-5 biphenyl (Figure 3) [2]. In addition, lignin itself is also linked to polysaccharides.
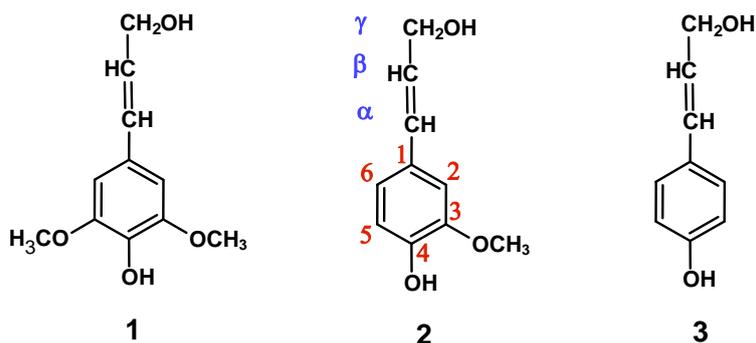

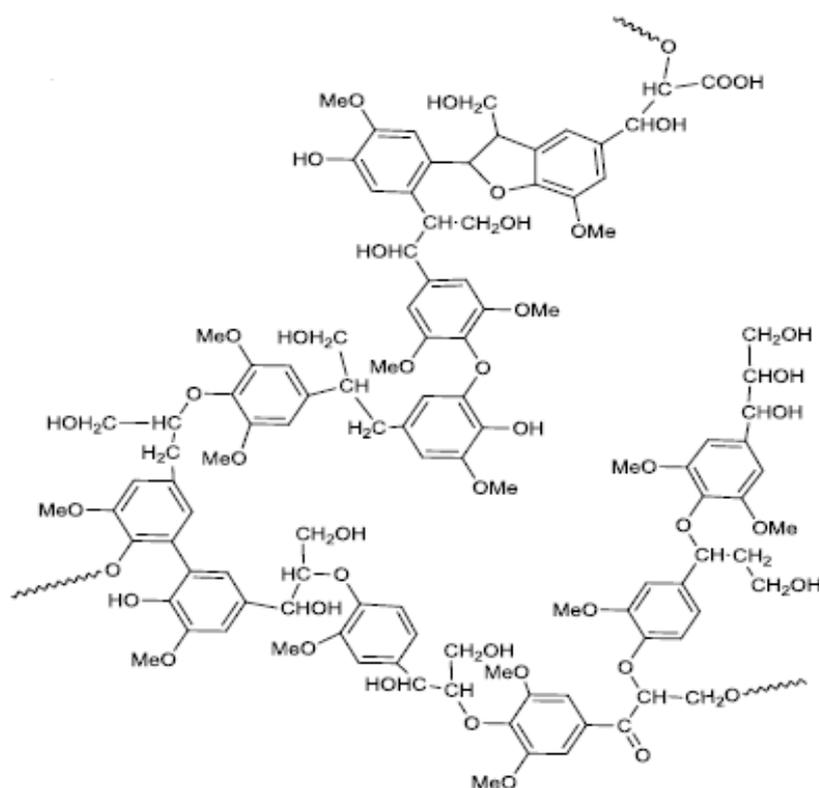Figure 1. Structures of lignin precursors (1 – 3).

Figure 2. Schematic representation of the chemical structure of hardwood lignin.
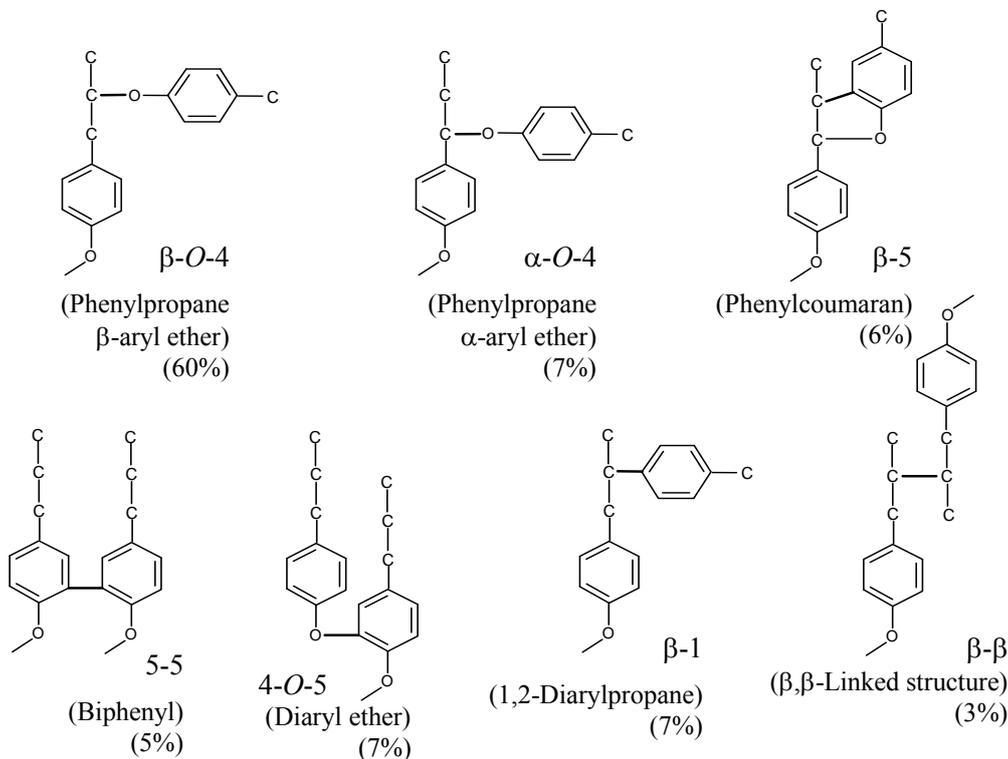
Figure 3. The most common linkages between phenylpropane units in wood lignin (percentage of linkage in typical hardwood lignin within brackets).

Lignin can be isolated from extractive-free wood as an insoluble residue after hydrolytic removal of the polysaccharides. The so-called Klason lignin is obtained after removing the polysaccharides from extracted (resin-free) wood by hydrolysis with 72% sulphuric acid. Other acids can be used as well for the hydrolysis, but the method has the serious drawback in that the structure of lignin is extensively changed during the hydrolysis. The polysaccharides may be removed by enzymes from finely divided wood meal. The resultant "cellulolytic enzyme lignin" (CEL) retains its original structure essentially unchanged. Besides CEL lignin, the "milled wood lignin" (MWL) has been widely used for structural studies. When wood meal is ground in a ball mill either dry or in the presence of non-swelling solvents (*e.g.*: toluene), the cell structure of the wood is destroyed and a portion of lignin (usually not more than 50%) can be obtained from the suspension by extraction with a dioxane-water mixture. MWL preparations always contain some carbohydrate material [2]. Lignins can also be obtained from the black liquor of the kraft pulping process (kraft lignin), from the sulphite pulping process (lignosulphonate lignin) or by the treatment of wood with various organic solvents (organosolv lignin). These latter types of lignin may be viewed as significant lignin sources for the production of fine chemicals by oxidation reactions [1].

Cellulose, which constitutes the main component of wood, is a linear homopolysaccharide composed of β-D-glucopyranose units, which are linked by β-(1→4)-glycosidic bonds (Figure 4). Along the chain direction, the repeating stereo regular unit is a cellobiose residue (1.03 nm) and each glucose residue is accordingly displaced 180º

with respect to its neighbours. Wood cellulose can consist of about 5000-6000 glucose units. Cellulose molecules have a strong tendency to form intramolecular and intermolecular hydrogen bonds, which accounts for its fibrous structure and high tensile strength. Besides the crystalline regions, cellulose also presents amorphous regions, which are more vulnerable to degradation. By contrast, hemicelluloses are predominantly branched hetero-/homopolysaccharides with a polymerisation degree between 100 and 200. The major hemicellulose of hardwoods is 4-*O*-methylglucuronoxylan while galactoglucomannan is the dominant hemicellulose of softwoods [2-4].

The lignin biodegradation in nature is a very complex process requiring the presence of several types of enzymes and redox mediators. At least three types of enzymes are considered to be involved in this process, namely manganese peroxidase (Mn-P) [5,6], lignin peroxidase (LiP) [7,8] and laccase [9,10]. Mn-P and LiP contain a Fe(III) prosthetic group and both require the presence of hydrogen peroxide as the oxidant. However, in addition, manganese peroxidase also needs the presence of Mn(II) chelates (*e.g.*: oxalate, tartrate, lactate) to oxidise lignin. On the other hand, laccase possesses a multicopper prosthetic group and uses oxygen as the terminal oxidant. The mechanisms of biological lignin oxidation are widely discussed elsewhere [5-10] and, thus, only their most relevant aspects, in the context of this paper, will be presented (see below).

In pulp-and-paper industry, the removal of lignin (the inter-fibre bonding material) from wood is mostly carried out during the pulping process. The sulphate or kraft process is the dominant chemical pulping process [2,3,11-12]. Wood chips are impregnated with the pulping liquor containing sodium hydroxide and sodium sulphide (pH > 13 - 14) at liquor-to-wood ratios of about 4. The soaked chips are heated up to 160-180 ºC, for 1-3 h, in batch or continuous digesters. Alternatively, sulphite chemical pulping is carried out under acidic conditions (pH 1-4) at 135-155 ºC for 6-10 h in batch digesters using $SO_2/MHSO_3/MSO_3$ aqueous solution [2]. In the kraft process, the lignin depolymerisation takes place mainly through the cleavage of the alkyl-*O*-aryl ether bonds (α-*O*-4, β-*O*-4). Concomitant increase of the 5-5 biphenyl, β-5 and diphenylmethane structures is observed. After the kraft pulping, about 2-3% of lignin is left in unbleached hardwood pulps and about 3-5% in softwood pulps. The unbleached kraft pulps have a characteristic brown colour, mainly due to the lignin chromophore groups. On the other hand, it is believed that the lignin depolymerisation in sulphite pulping is minimal while lignin is removed from wood in the sulphonated form (lignosulphonates). The sulphite pulp is of yellow colour, much less coloured than the kraft pulp. No conventional pulping process allows the complete delignification (lignin removal) of wood without seriously affecting the strength properties of the fibres.
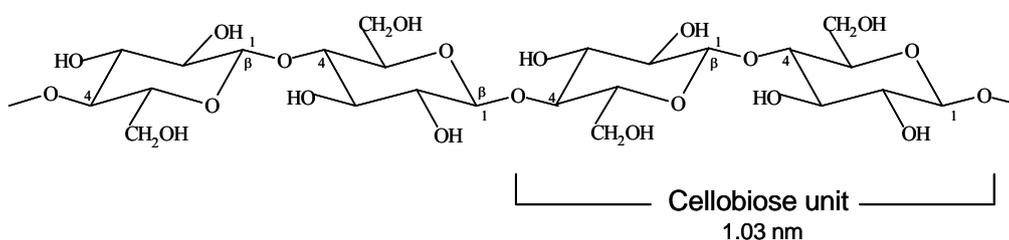

Figure 4. Simplified representation of cellulose structure.

Pulping is followed by the bleaching process [11-13] which is applied to remove the residual lignin present in the pulp and to achieve an adequate brightness (a measure of how much light is reflected from a handsheet of paper) by elimination of the chromophore groups. No significant cellulose damage should occur. The chemicals commonly used for pulp bleaching include oxidants such as chlorine, hypochlorite, chlorine dioxide, molecular oxygen, ozone and hydrogen peroxide, and NaOH, used in the alkaline extraction stage. Typically, there are two main process variables usually determined to evaluate the delignification degree and the polysaccharides degradation: kappa number and intrinsic viscosity. The kappa number is a parameter that estimates the amount of potassium permangante oxidisable moities in the pulp, mainly residual lignin. The intrinsic viscosity is an index related to the polymerisation degree of the polysaccharides. In the delignification process, the kappa number of the pulp must be reduced with the minimal decrease of intrinsic viscosity (main selectivity criterium).

To a large extent, the evolution of the bleaching technologies has been environmentally driven. In the last generation of bleaching technologies, the substitution of all kind of chlorine-based reagents is achieved by their substitution with molecular oxygen, ozone and hydrogen peroxide, in totally chlorine-free (TCF) sequences [13]. However, these oxygen-based oxidants are inferior to chloride dioxide with regard to the efficiency and the selectivity of pulp bleaching [14,15]. Due to the lignin autoxidation with release of oxygen-centred radicals, the pulp polysaccharides are seriously damaged thus hindering the progressive implementation of TCF technologies. This drawback could be overcome by using transition metal catalysts [16,17] that activate oxygen at low temperatures and control the oxidation to avoid free-radical steps, just mimicking the enzymes responsible for the lignin biodegradation in nature.

2. MANGANESE PORPHYRINS-CATALYSED LIGNIN MODELS/LIGNIN OXIDATION

Metalloporphyrins have been proposed as catalysts for the oxidation of lignin and lignin models, aimed to mimic the active centre of LiP or Mn-P, two metalloenzymes participating in the depolymerisation of native lignin by wood-rotting fungi [18]. The catalytic cycle of these enzymes involves, firstly, a two-electron oxidation of iron (III) protoporphyrin (IX) (the prosthetic group of the enzymes), by hydrogen peroxide, to give the oxo-iron(IV)-protoporphyrin IX radical - a highly reactive species (Figure 5, compound I). Then, in the case of LiP, the latter species oxidises lignin and returns to its initial state by two separate one-electron reductions (Figure 5). This enzyme may be inactivated when exposed to an excess of hydrogen peroxide. In the case of Mn-P, after the first two-electron oxidation of the enzyme by hydrogen peroxide, the formed oxo-iron(IV)-protoporphyrin IX species oxidises Mn(II) to Mn(III), which is stabilized by chelating agents such as oxalate or malonate. The resulting Mn(III) complex is then able to oxidise phenolic lignin structures (Figure 5). Thus, in contrast to lignin peroxidase, Mn-peroxidase also needs the presence of manganese complexes in order to degrade lignin.
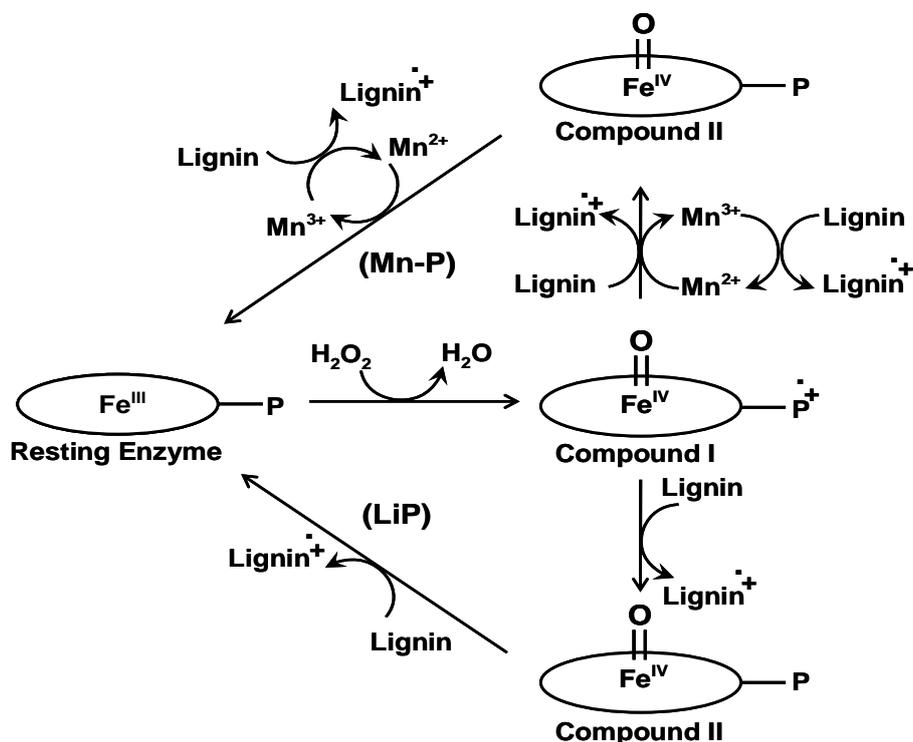
Figure 5. Catalytic cycle of lignin peroxidase (LiP) and manganese peroxidase (Mn-P). The first step (compound I formation) is common for both the enzymes.

Aimed to mimic the active centres of LiP and Mn-P, several types of metalloporphyrins have been considered. Besides the more frequent use of iron porphyrins [1,14] special attention has also been paid to the analogous manganese porphyrins.

2.1. Manganese Porphyrins in the Oxidation of Lignin Model Compounds with Hydrogen Peroxide or KHSO$_5$

Crestini *et al* [19,20] have studied the oxidation of 5-5 biphenyl and diphenylmethane-type lignin model compounds with hydrogen peroxide in the presence of water soluble manganese porphyrins. The catalytic efficiencies of Mn^{III}TDCSPP, Mn^{III}TSPP and Mn^{III}TPyMeP (the corresponding structures are presented in Figure 6) were compared with that of Fe^{III}TDCSPP. In general, manganese porphyrins had higher catalytic activity than the iron analogous. This could be due to the higher stability of the Mn porphyrins under oxidising conditions. Among the several metalloporphyrins tested, MnTPyMeP was shown to be the best catalyst. A 59% of conversion of 2,2',3,3'-tetramethoxy-5,5'-dimethylbiphenyl was obtained with MnTPyMeP in a dioxane/pH 6 buffer mixture at room temperature.

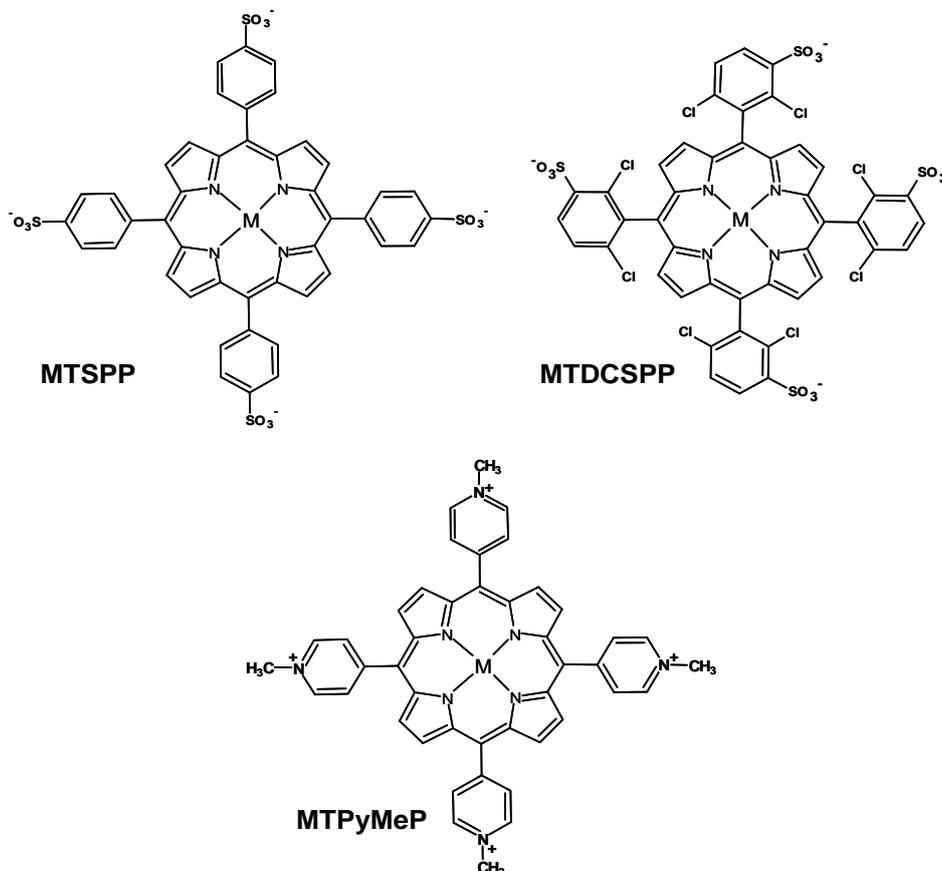Figure 6. Structures of manganese porphyrins used as catalysts in the lignin oxidation (M=Mn, TSPP=*meso*-tetrakis(4-sulphonatophenyl)porphyrin, TDCSPP=*meso*-tetrakis(2,6-dichloro-3-sulphonatophenyl)porphyrin, TPyMeP=*meso*-tetrakis(*N*-methylpyridinio)porphyrin).

Later, the same research group has immobilised MnTPyMeP (with cationic porphyrin) on the clay montmorillonite, in an effort to mimic the polypeptidic pocket of lignin peroxidase by the clay [21-22]. The new material was found to be an efficient catalyst for the oxidation of different types of lignin model compounds with hydrogen peroxide. After 4 h of reaction at 60 ºC in the presence of MnTPyMeP/clay, 48% of non-phenolic model compound 1(3,4-dimethoxyphenyl)-1-ethanol had reacted. The only recovered oxidation product was the corresponding acetophenone, the product of side-chain oxidation [21]. Phenolic and non-phenolic lignin models, containing β-*O*-4, diphenylmethane or biphenyl-type structures, were also oxidised in the same reaction system. As for example, the β-*O*-4 arylglycerol phenyl ether model compound *4* was treated with the MnTPyMeP/clay/H$_2$O$_2$ catalytic system in dioxane/citrate buffer at 60 ºC to yield products of side-chain oxidation *5*, para-benzoquinone formation *6*, side-chain oxidation and quinone formation *7* and *8*, and products of side-chain cleavage *9* and side-chain cleavage and quinone formation *10* (Figure 7) [23]. Thus, the MnTPyMeP supported on the clay was claimed as an efficient immobilised catalyst for the lignin models oxidation with hydrogen peroxide. Furthermore, the clay was considered to be stable and recyclable [21].
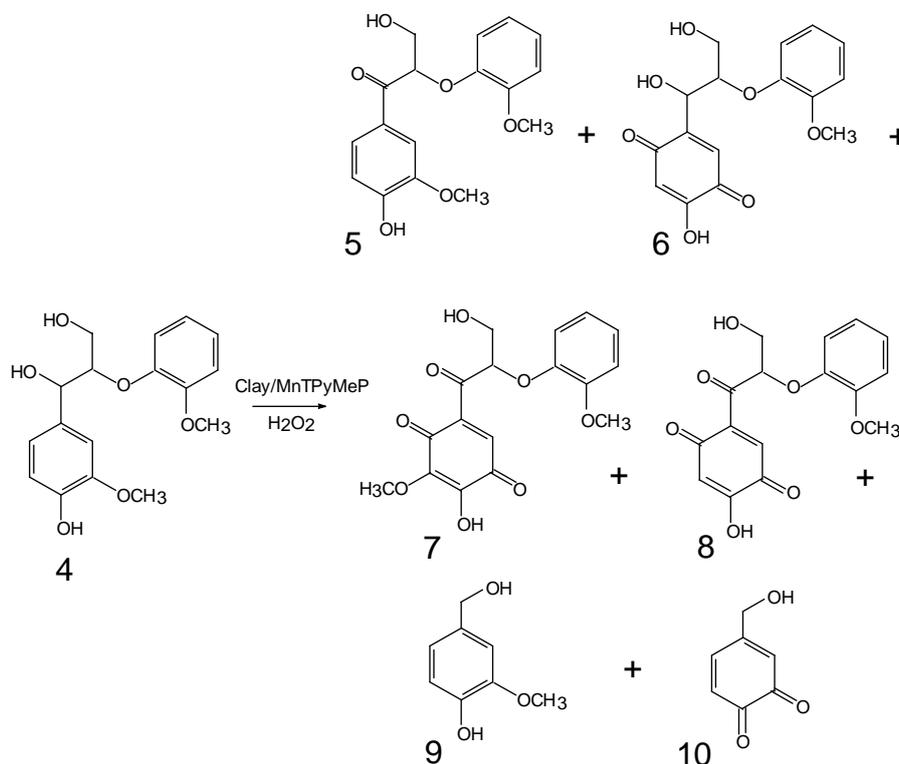
Figure 7. Products obtained from the oxidation of β-*O*-4 arylglycerol phenyl ether model compound with hydrogen peroxide catalysed by MnTPyMeP/clay in a dioxane/citrate buffer mixture at 60 ºC [23].

Recently, the metalloporphyrin MnTSPP has been immobilised in an imidazole-modified silica, which included also a molecular spacer between silica and imidazole long enough to minimize unspecific support/porphyrin interactions. The authors intended to emulate the LiP active site, where the iron (III) is axially coordinated by imidazole-*N* of the proximal histidine. The new material was found to be an active catalyst for the extensive veratryl alcohol oxidation with hydrogen peroxide at 20 ºC affording veratraldehyde and another non-identified major product, the latter of which was suggested to be 2-hydroxymethyl-5-methoxy-1,4-benzoquinone [24].

The manganese porphyrins, MnTSPP, MnTMPS (TMPS=*meso*-tetrakis(3,5-disulphonatomesityl)porphyrin) and MnTDCSPP were used for the lignin models oxidation with potassium monopersulphate (KHSO$_5$) at room temperature [25-32]. These metalloporphyrins were also immobilised onto an ion-exchange resin (cationic Amberlite IRA 900, abbreviated as Amb) or on a cationic polymer derived from 4-vinylpiridine, *i.e.*, poly[4-vinylpyridinium(toluene-4-sulphonate)] cross-linked with 2% of divinylbenzene (abbreviated as PVP). The dimer 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (containing β-*O*-4 linkage) was easily cleaved at the C$_\alpha$-C$_\beta$ bond yielding veratraldehyde and 2-methoxy-1,4-benzoquinone [26, 27, 29, 31, 32]. Substrate conversions in the presence of manganese porphyrins immobilised on solid supports are summarized in Table 1 (results with FeTSPP are presented for comparison). The highest activity was obtained for the MnTSPP immobilised on Amberlite, followed by MnTDCSPP on PVP. In the case of manganese

porphyrins supported on PVP, no addition of proximal nitrogen ligand was required to obtain a high catalytic activity. This fact was explained through the coordination effect of the polymer itself, with the pyridine groups acting as axial ligands to the manganese porphyrin. It has been shown that a few of these supported catalysts could be re-used just by filtration after the reaction (example in Table 1).

2.2. Manganese Porphyrins in the Lignin Oxidation

Only a few reports have been published regarding the application of manganese porphyrins for the lignin oxidation. Oxidation of residual kraft lignin was carried out using the water soluble metalloporphyrins, MnTDCSPP and MnTPyMeP, with hydrogen peroxide in buffered aqueous medium at 50 ºC. The structural modifications induced on the polymer were evaluated by ^{31}P NMR spectroscopy [19]. It was found a decrease of aliphatic OH groups, showing the occurrence of side-chain reactions, with the simultaneous increase of COOH units. The very high increase of COOH groups observed should indicate also the occurrence of aromatic ring cleavage. No significant condensation reactions occurred during the manganese porphyrins-catalysed oxidations of residual lignin. This contrasts to the behaviour of the iron porphyrin, FeTDCSPP, where a substantial increase of condensed substructures was detected. MnTPyMeP was shown to be the best catalyst, confirming the results also observed in the oxidation of lignin model compounds [19].

MnTPyMeP/clay/H_2O_2/HBT catalytic system has been proposed for the kraft lignins oxidation by Crestini and co-workers [23]. In this system, 1-hydroxybenzotriazole (HBT) acts as a diffusible low molecular weight redox mediator. The redox mediator is oxidised by the metalloporphyrin (in its oxidised form) and then diffuses out of the clay matrix to lignin and oxidises the substrate. In this way, the difficulties in the approach of the solid lignin (or pulp) to the porphyrin metal centre when using the MnTPyMeP/clay/H_2O_2 system for the lignin oxidation could be possibly overcome by adding the redox mediator.

Table 1. Conversion of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol with KHSO$_5$ catalysed by metalloporphyrins [26, 27, 29, 31] [a]

Catalyst	Equiv. number of 4-*tert*-butylpyridine *vs.* catalyst	Substrate conversion for a reaction time of one min (%)
FeTSPP-Amb[b]	0	63
MnTSPP-Amb[c]	100	100
MnTSPP-PVP[c]	0	60
MnTDCSPP-Amb[c]	100	59
MnTDCSPP-PVP[c]	0	76
MnTMPS-Amb[c]	100	46
MnTMPS-PVP[c]	0	61 (55)[d]

[a] All the reactions were performed at room temperature. A molar ratio of 10% of catalyst *vs.* substrate was used in all cases.

[b] The reactions were performed in 1:3 acetonitrile/pH 3 buffer mixtures.

[c] The reactions were performed in 1:3 acetonitrile/pH 6 buffer mixtures.

[d] After the re-use of the supported catalyst: third run.

In another report, MnTSPP was used as catalyst for the oxygen bleaching of softwood kraft pulps [33]. The kappa number of the pulp was reduced from 29.2 to 4.5, while the intrinsic viscosity dropped from 34.7 to 12.2 mPa s after 0.5 h treatment at 100 ºC with 1 M KOH and under 0.8 MPa of oxygen pressure. In a blank experiment (without catalyst) the kappa number was reduced to 5.4 and the final viscosity of the pulp was 6.6 mPa s.

3. MANGANESE COMPLEXES WITH TRIAZACYCLONONANE LIGANDS AND HETEROCYCLIC AMINES IN THE LIGNIN MODELS/LIGNIN OXIDATION CATALYSIS

Several papers can be found in the scientific literature on the use of binuclear manganese complexes containing the organic ligands 1,2-bis(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethane (Me$_4$dtne) and 1,4,7-trimethyl-1,4,7-triazacyclononane (Me$_3$tacn) (Figure 8), as catalysts for the lignin models oxidation with hydrogen peroxide and, mostly, for the lignin oxidation in kraft pulps (delignification/bleaching) [34-43]. With the catalyst [Mn^{IV}(μ-O)$_3$Mn^{IV}L](ClO$_4$)$_2$, L= Me$_4$dtne (*11*, structure in Figure 8-B), the non-phenolic lignin model compounds, 1-(3,4-dimethoxy-phenyl)ethanol, 1-(3,4-dimethoxy-phenyl)-1-propene and *E*-1,2-diphenylethene were readily oxidised to a significant extent (50%, 90% and 40% yields after 10 min reaction at 60 ºC) by hydrogen peroxide [35]. A reaction mechanism was proposed for the 1-(3,4-dimethoxy-phenyl)ethanol oxidation catalysed by [L'Mn^{IV}(μ-O)$_3$Mn^{IV}L'](ClO$_4$)$_2$, L'= Me$_3$tacn (*12*, structure in Figure 8-C), in which hydroxyl radicals are assumed to participate in the substrate oxidation [36]. However, other authors questioned this proposal, taking into account that no hydroxyl radicals have been detected by EPR [43]. Other dimanganese complexes of general formulae, [Mn^{III}$_2$(μ-OCH$_3$)(μ-CH$_3$COO)L]$^{3+}$ (H$_3$L= 1,5-bis[(2-hydroxy-5-X-benzyl)(2-pyridylmethyl)amino] pentan-3-ol, X = H, OCH$_3$ or Br), were found to be active for the 2,6-dimethoxyphenol oxidation with hydrogen peroxide at room temperature affording 3,3',5,5' tetramethoxydiphenoquinone [44].

As mentioned, in the context of lignin oxidation catalysis, most of the studies concerning the use of manganese complexes with triazacyclononane ligands have been directed to the kraft pulp delignification/bleaching, *i.e.*, to the lignin oxidation in lignocellulosic pulps. The first report on the use of manganese-triazacyclononane complexes for the delignification/bleaching of kraft pulps was presented by Patt [34]. The author reported the bleaching of softwood pulps with hydrogen peroxide catalysed by [Mn^{IV}Mn^{III}(μ-O)$_2$(μ-CH$_3$COO)L](ClO$_4$)$_2$, L= Me$_4$dtne (*13*, structure in Figure 8-A). The new developed bleaching system showed high efficiency and selectivity for the degradation of residual lignin at 50-60 ºC (as compared to 90 ºC in conventional hydrogen peroxide bleaching). Furthermore, it was demonstrated that very small loads of manganese catalyst (10-30 ppm on pulp weight) enhance delignification at a considerable level [34]. In a typical peroxide stage run at 60 ºC for 80 min, the kappa number of a softwood pulp was reduced from 7.5 to 3.2, and the brightness increased from 37% ISO to 75% ISO in the presence of 30 ppm of catalyst. Without the catalyst addition, a kappa number of 5.5 and a brightness of 58% ISO were obtained. However, it was found that the catalyst decomposed under the conditions of the

peroxide bleaching experiment (pH of about 11). In addition, the filtrate from the peroxide/catalyst stage did not show catalytic activity when re-used [39,40].

Figure 8. Structures of binuclear manganese complexes with Me$_4$dtne (A and B) and Me$_3$tacn (C) used for the lignin oxidation with hydrogen peroxide (Me$_4$dtne=1,2-bis(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethane, Me$_3$tacn=1,4,7-trimethyl-1,4,7-triazacyclononane).

The complex *11* was also found to catalyse the delignification of a softwood kraft pulp with hydrogen peroxide. The kappa number of the original pulp decreased from 31.6 to 16.8 (a decrease of 46%) and the GE brightness increased from 24.2 to 44.7, while the intrinsic viscosity had a drop of 30.2 to 20.1 mPa s in the *11*-catalysed reaction at 80 ºC [38]. The analogous manganese complex *12* was also evaluated for the pulp delignification [42]. Firstly, this complex was considered to be less effective than catalyst *11* for the bleaching of pulps with hydrogen peroxide [40]. However, later it was shown to be more active catalyst for the delignification than the complex *11* [42]. Moreover, in the same work, it was found that the residual lignins resulting from the bleaching catalysed by *11* at 80 ºC were less degraded than the corresponding lignins from the bleaching catalysed by *12* at both 60 and 80 ºC [42]. The different concentrations of catalyst, NaOH and H$_2$O$_2$ employed in the bleaching experiments by different research groups could be responsible for the apparent contradictory results regarding the comparison of the catalytic activity of compounds *11* and *12*.

On the other hand, the kraft pulp bleaching during 2 h at room temperature (pH 9) catalysed by [Mn$^{III}_2$(μ-OCH$_3$)(μ-CH$_3$COO)L]$^{3+}$, H$_3$L= 1,5-bis[(2-hydroxy-5-H-benzyl)(2-pyridylmethyl)amino] pentan-3-ol) revealed a kappa number decrease from 15.6 to 13.1 (without catalyst the kappa number decreased from 15.6 to 14.1). In addition, no appreciable damage of cellulose fibres was observed [44]. These results cannot be directly compared to those obtained with the other manganese complexes with triazacyclononane ligands since different temperatures were employed (room temperature *vs.* 50-80 ºC).

A binuclear manganese complex [Mn^{III}Mn^{IV}(μ-O)$_2$(TPA)$_2$]$^{3+}$, TPA=tris(2-methylpyridyl)amine, has also been used for the pulp delignification/bleaching [45-47]. The

complex enhanced the delignification of chemical pulps with hydrogen peroxide while keeping the depolymerisation of cellulose low, when used at acidic pH values. In fact, during 3 h reaction at 80 ºC and at a pH of 3.5 the kappa number of a kraft pulp decreased from 20 to about 4. In the same experimental conditions but with no catalyst, the kappa number of the treated pulp was of only 14 [46]. However, the amount of catalyst used in the bleaching experiments was very high (about 10% on pulp weight) limiting its practical application. Based on electrochemical and kinetic studies [46-48] it was proposed a mechanism including an electron transfer from the lignin to $[(TPA)Mn^{III}(\mu-O)_2Mn^{IV}(TPA)]^{3+}$ complex, originating $[(TPA)Mn^{II}O-HOMn^{III}(TPA)]^{2+}$, being the initial complex regenerated with hydrogen peroxide in a second step. The authors argued that diffusion of the manganese complex from the solution into the pulp fibres could be the limiting step in the delignification process [47].

4. DELIGNIFICATION WITH MANGANESE-SUBSTITUTED POLYOXOMETALATES

Since the mid-nineties, the polyoxometalates (POM) [49,50] have been extensively used for the delignification of kraft pulps. A large number of these species, including manganese and vanadium-containing POM were considered [13]. In particular, a few Mn(III)-substituted polyoxotungstates, namely $[SiW_{11}Mn^{III}(H_2O)O_{39}]^{5-}$ ($SiW_{11}Mn^{III}$), with the Keggin-type structure, and the sandwich-type polyoxotungstate $[(PW_9O_{34})_2Mn^{III}_3Mn^{II}(H_2O)_2]^{7-}$ (Figure 9) have proven to be effective and highly selective for the oxygen delignification of hardwood kraft pulps [51-53]. However, it was found that these POMs were presented at the end of the delignification experiments mostly in the reduced form [51,53] which limits their re-use, unless a second stage is applied for the POM re-oxidation. Moreover, it was found that $SiW_{11}Mn^{III}$ under O_2 is able to oxidise phenolic structures but not non-phenolic [51].

(A)   (B)
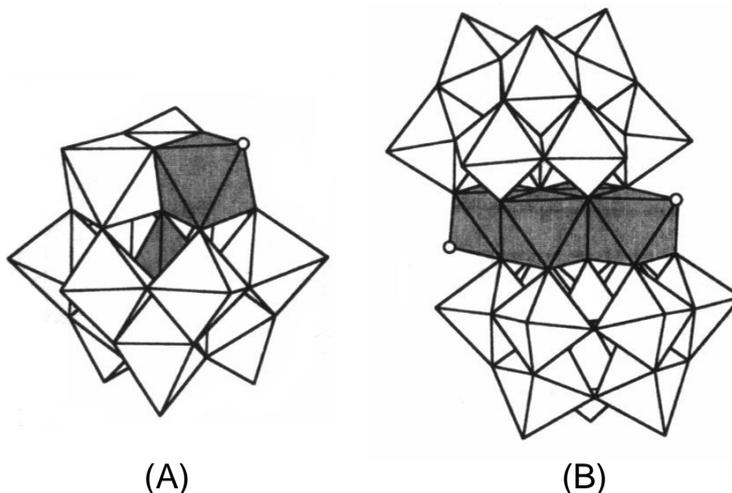
Figure 9. Polyhedral structures of manganese-substituted polyoxometalates used for the oxygen delignification of lignocellulosic pulps: α-$[SiM_{11}Mn^{III}(H_2O)O_{39}]^{5-}$ (A) and $[(PW_9O_{34})_2Mn^{III}_3Mn^{II}(H_2O)_2]^{7-}$ (B).

Table 2. Results of eucalyptus kraft pulp delignification catalysed
by SiW$_{11}$Mn or SiW$_{11}$V and laccase [55]^a

System	Kappa number	Viscosity (cm^3 g^{-1})	Delignification (%)[b]	Viscosity loss (%)
Kraft pulp (control)	12.3	1185	---	---
		POM = SiW$_{11}$Mn^{III}		
POM	9.5	1130	23	5
POM-L	8.9	1080	28	9
POM-L-POM	6.9	1075	44	9
POM-L-POM-L-POM	6.0	1020	52	14
POM-L (30 ºC)-POM	7.1	1065	42	10
POM-L (60 ºC)-POM	7.5	1065	39	10
		POM = SiW$_{11}$V^{V}		
POM	9.0	1055	26	11
POM-L	8.2	1035	33	13
POM-L-POM	6.9	1005	44	15
POM-L (60 ºC)-POM	6.2	935	50	21

^{a} consistency = 6%; POM stage: 110 ºC, 2 h, $p°(O_2)$ = 0.6 MPa, [POM] = 3.6 mmol L^{-1}, pH 4.5; Laccase
    stage: 45 ºC, 4 h, $p°(O_2)$ = 0.3 MPa, laccase 380 U L^{-1}.
^{b} Estimated as the decrease of kappa number.

To overcome this limitation an alterative multi-stage process was developed in which the pulp is treated with SiW$_{11}$Mn^{III} at high temperature (100-110 ºC) in a first stage, followed by the POM re-oxidation with laccase at moderate temperatures (30-60 ºC) in a separate stage [54-55]. The application of this multi-stage process brought delignifications around 50% when applied to SiW$_{11}$Mn^{III}. Comparison was also made with the parent vanadium-substituted POM, [SiW$_{11}$V^{V}O$_{40}$]$^{5-}$ (SiW$_{11}$V^{V}). When compared to SiW$_{11}$V^{V}, SiW$_{11}$Mn^{III} was found to be more selective, while SiW$_{11}$V^{V} was more effective in the oxidative delignification (Table 2) [55]. Remarkably, no indications of degradation of the Keggin structure were found under the experimental conditions used.

Another approach consisted in using versatile peroxidase (VP), a Mn-peroxidase analogous, for the oxidation of the reduced form of SiW$_{11}$Mn. The enzyme in the presence of hydrogen peroxide easily oxidises SiW$_{11}$Mn^{II} to SiW$_{11}$Mn^{III} at 20 ºC. The delignification filtrate containing the re-oxidised POM can then be used in a second delignification stage. The substitution of the first ClO$_2$ stage by a POM–VP–POM$_{reox}$ treatment in a conventional elemental chlorine-free (ECF) bleaching sequence allowed 50% ClO$_2$ saving without decreasing the pulp strength properties. Hence, the continuous reutilization of SiW$_{11}$Mn^{III} in a two-reactor system may be implemented in the future [56].

5. OTHER SYSTEMS FOR THE LIGNIN OXIDATION

A Mn(II) acetate/Co(II) acetate (5:1 mol/mol) mixture was found to catalyse the oxidation of non-phenolic lignin model compound with peracetic acid under moderate

conditions (50 ºC) [57]. Several lignin model compounds representing arylglycerol β-aryl ether and 1,2-diarylpropane linkages were also oxidised in the presence of Mn(II) and Co(II) acetates at 170 ºC in 80% acetic acid. In particular, 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-propane-1,3-diol was degraded almost completely via C_α-C_β bond cleavage under aerobic conditions [58]. Other studies reported the use of Mn(II) acetate together with Co(II) acetate and HBr for the aerobic oxidation of organosolv lignins in acetic acid [59,60]. Lignins from wood and bagasse were also oxidised in air using Mn(II) acetate/Co(II) acetate/Zr(IV) acetate/HBr catalyst in acetic acid. Approximately 11% of the lignin was converted to aromatic products such as vanillin, vanillic acid, syringaldehyde and syringic acid [61].

In the last five years a great attention has been paid to the use of ionic liquids in the lignin oxidation/depolymerisation, since some of them are excellent solvents for the dissolution of lignin (for instance, according to [62], 500 g of lignin can dissolve in 1 Kg of 1,3-dimethylimidazolium methylsulphate and 1-butyl-3-methylimidazolium trifluoromethanesulphonate after 24 h incubation at 90 ºC). The dissolution of lignin in ionic liquids together with the use of appropriate catalysts will certainly help to functionalize the polymer and to obtain products of high value. Concerning the use of manganese, veratryl alcohol oxidation to veratraldehyde with oxygen in EMIM DEP (1-ethyl-3-methylimidazolium diethyl phosphate) was observed when catalysed by simple Mn salts such as $Mn(NO_3)_2$ and $Mn(CH_3COO)_2$ (conversions of up to 30% at 80 ºC) [63]. In another study, $Mn(NO_3)_2$ was found to be a very effective catalyst for the aerobic oxidation of an organosolv-beech lignin in $[EMIM](CF_3SO_3)$ (1-ethyl-3-methylimidazolium trifluoromethanesulphonate). At a temperature of 100 ºC, more than 50% of the initial lignin could be converted into low molecular weight products such as vanillin, vanillic acid, syringaldehyde, syringol, and 2,6-dimethoxybenzoquinone, which were further extracted with organic solvents [62]. Interestingly, 2,6-dimethoxybenzoquinone could be isolated as a pure substance in 11.5 wt% overall yield by a simple extraction/crystallization process when the reaction was carried out using 20% w(catalyst)/w(lignin). In order to implement in industrial practice the use of ionic liquids as solvents for the lignin oxidation, efficient methods for the recovery of both the ionic liquids and catalysts should be found.

CONCLUSION

In this book chapter, the results of numerous research works about the oxidation of lignin and lignin model compounds catalysed by manganese complexes are reviewed. Manganese porphyrins, mimicking specific enzymes involved in the biological delignification (LiP and Mn-P), have proven to be very active catalysts for the oxidation at moderate temperatures of several lignin model compounds (including phenolic and non-phenolic structures) with hydrogen peroxide or with $KHSO_5$. Some interesting results on the use of manganese porphyrins for the kraft lignin oxidation with hydrogen peroxide have been reported as well. However, the main drawback of porphyrins is their high cost, and, often, their oxidative degradation under the experimental conditions applied. Several researchers have immobilised metalloporphyrins on clays, on imidazole-modified silica and on other supports. This

approach would be most helpful if applied, for instance, for the kraft lignin oxidation in ionic liquids.

Manganese complexes with triazacyclononane ligands and heterocyclic amines, such as $[Mn^{IV}(\mu\text{-}O)_3Mn^{IV}L](ClO_4)_2$, L= Me_4dtne, $[L'Mn^{IV}(\mu\text{-}O)_3Mn^{IV}L'](ClO_4)_2$, L'= Me_3tacn and $[Mn^{III}Mn^{IV}(\mu\text{-}O)_2(TPA)_2]^{3+}$, were found to catalyse the lignin oxidation with hydrogen peroxide in lignocellulosic kraft pulps. Similar to manganese porphyrins, they can oxidise non-phenolic lignin model compounds. However, the relatively high cost of these complexes and the degradation of the triazacyclononane ligands with hydrogen peroxide under alkaline conditions limit their application for the lignin oxidation.

Manganese-substituted polyoxometalate, $SiW_{11}Mn^{III}$, which is a more robust species than the other complexes mentioned above, was found to be a highly selective catalyst for the oxygen delignification. It can be re-oxidised with enzymes (such as laccase or versatile peroxidase), thus enabling its re-use. The main drawback is that it can hardly oxidise non-phenolic structures.

On the other hand, interesting results were reported for the lignin oxidation in acetic acid using Mn(II) acetate and Co(II) acetate. Valuable products such as vanillin, vanillic acid, syringaldehyde and syringic acid were obtained. Finally, the high solubility of lignin (and other lignocellulosic materials) in ionic liquids, recently claimed, will make easier to accomplish the lignin oxidation reactions. The new systems for the lignin oxidation, employing ionic liquids, will certainly play an important role in the future research on the lignin valorisation to high value-added products.

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