Review

# The catalytic oxidation of biomass to new materials focusing on starch, cellulose and lignin

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## Contents

## ABSTRACT

Biomass is a renewable class of materials of growing interest amongst researchers aiming to achieve global sustainability. This review focuses on the homogeneous catalysis of the oxidation of biomass, in particular starch, cellulose and lignin. Often such catalytic reactions lead to depolymerisation of the material as happens in Nature with for example brown rot fungi. This depolymerisation can be desirable or not, and control in industrial applications is thus important to obtain the desired outcome. The two main oxidants in use are $O_2$ and $H_2O_2$ and their use is described as appropriate. Industrial oxidation catalysis is highly significant in the bleaching of cellulose-containing materials due to its high volume application in the paper, pulp and laundry industries. Here, the presence of a ligand on the oxidising metal ion has a significant effect on the catalyst selectivity and stability. In addition to the bleaching of cellulose-containing materials, the oxidation of cellulose, starch, lignin and lignin model compounds are discussed with a focus on generating even more hydrophilic materials which have important applications or materials which may be further modified. Finally developing applications of biomass are described such as new support materials for catalysts, as supports for sensors and nanomaterials for microbial culture.

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## 1. Background

### 1.1. Introduction

Renewable biomass presents tremendous opportunities to produce chemicals as fossil fuels become more expensive due to

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dwindling reserves and political conflict. As a consequence, new methods and materials based on biomass refining are emerging for the chemical industry to use as feedstock [1]. In recent years the concept of developing a biorefinery to produce feedstock for the modern chemical industry has been growing in popularity [2].

The largest material by volume produced in the world every year is ligno-cellulose (typically containing 40–50 wt% cellulose, 10–25 wt% hemicellulose, and 25–40 wt% lignin), which provides strength to trees and plants. The important challenge remains of how to convert ligno-cellulose into a form that can be exploited as a fundamental building block in a wide range of chemical transformations [3].

Starch and cellulose can be used as feedstock for oxygenated materials or could even be reduced to give petroleum-like starting materials. Lignin could be used as a source for aromatic compounds if it can be depolymerised in a controlled fashion. Similarly, in modern materials research natural fibres are studied extensively to form composites as are renewable monomers [4,5]. Polysaccharides such as starch and cellulose, are a potential renewable source of materials particularly for biodegradable polymers [6], wastewater treatment [7] and functional nanomaterials [8]. Lignin has to date found only limited uses but its potential as the only renewable aromatic compound source available in large volumes continues to attract a vast amount of work to make this possible [5].

In addition to their applicability as feedstock for monomers and polymers, and as fibres, many polysaccharides can also be used as a source for renewable nanoparticles. These polysaccharides are naturally found in a semicrystalline state, and aqueous acids can be employed to hydrolyse the amorphous sections of the polymer. Consequentially, the crystalline sections, having dimensions in the nanometre range, are released, resulting in individual monocrystalline nanoparticles [9]. The obtained particles display different shapes depending on the polysaccharide source: platelets for starch and rigid rod-like particles for cellulose and chitin. These nanoparticles are receiving increasing attention because of the abundant availability of the starting material, low cost, renewability, biodegradability, biocompatibility, and non-toxicity [10]. While the use of these nanoparticles has largely focussed on the fabrication of nanocomposites where their function is largely as reinforcement, other uses as functional nanomaterials after surface modification, templating material, and structural material are also emerging [8,9,11].

In recent years, the importance of environmentally benign synthesis has been increasingly recognized and parameters, such as the E-factor [12], atom efficiency [13] and the "12 Principles of Green Chemistry" [14] are often considered as an essential driving force in the quest for sustainable chemical processes. Renewable biomass and solvents are key components in making a process greener as is improved catalytic activity. In addition, if a solvent has to be used, water would represent a best choice. It is cheap, readily available, non-toxic, non-flammable and safe for the environment. Of additional importance to catalysis is that water allows for facile catalyst separation and recycling through a biphasic catalysis process due to its low miscibility with most organic compounds [15]. Additionally, oxidised biomass is frequently isolated via a simple filtration process.

The oxidation of biomass is often performed in water as a medium which is perhaps a less common solvent for chemists [16] and represents a number of challenges when employing coordination compounds as catalysts. In particular, the water will compete as a ligand and functional catalysts based on manganese and iron complexes of common ligands such as polyamines and polyethers often have limited utility because of the thermodynamic sink represented by the mineral forms of these elements [17]. Fortunately, transition metal complexes can be effectively used in water when careful ligand design is employed to improve the stability, particularly under oxidising conditions [18].

In this special issue celebrating the career of Daryle H. Busch, it is appropriate here to highlight the successful work of Busch and co-workers in showing the power of careful ligand design in the realisation of a series of robust transition metal complexes with ultra rigid ethylene cross-bridged tetradentate macrocyclic ligands [19] and cross-bridged pentadentate amine macrocyclic ligands (Fig. 1) [20]. Also the cross-bridged tetradentate macrocyclic complexes have the rare abilities to host stable $Mn^{4+}=O$ and $Mn^{4+}–OH$ functional groups [21]. Compared with other ligands, these cross-bridged macrocycles produce $Mn^{2+}$ complexes having extreme kinetic stability in both acidic and basic media, despite the well-known lability of the high-spin $d^5$ $Mn^{2+}$ ion [22]. The complexes have rich redox chemistries and an industrial partner has demonstrated their excellent catalytic oxidation activity in demanding applications, for example in home-care products [23]. These complexes also catalyse organic oxidations in mixed organic–aqueous media [19c,21a,21b], such as hydrogen abstraction by the mononuclear manganese(IV) complex $[Mn(Me_2EBC)_2(OH)_2]^{2+}$ (EBC = ethylene bridged cyclam = 4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane).

## 1.2. The structures of cellulose, starch and lignin

Cellulose forms the primary component of green plants and of wood. It is the most abundantly available natural material and Nature produces between $10^{10}$ and $10^{11}$ tons of cellulose annually. Cellulose is a linear homopolysaccharide of D-glucopyranose units linked through β-(1,4) linkages [Fig. 2(A)]. The degree of polymerisation of cellulose depends strongly on the plant species but is around 10,000 for wood and 15,000 for cotton. Natural cellulose is a semicrystalline polymer with crystalline sections formed by



M = Mn or Fe    $R^1$, $R^2$ = Me or Bz    X = Cl, $CH_3CN$, $H_2O$
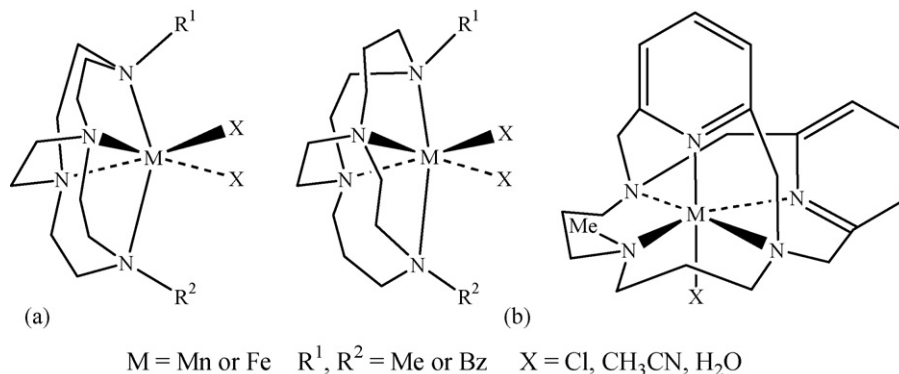
**Fig. 1.** Cross-bridged (a) tetradentate and (b) pentadentate amine macrocyclic complexes of enhanced solution stability used by Busch and coworkers in bleaching experiments [19,20].
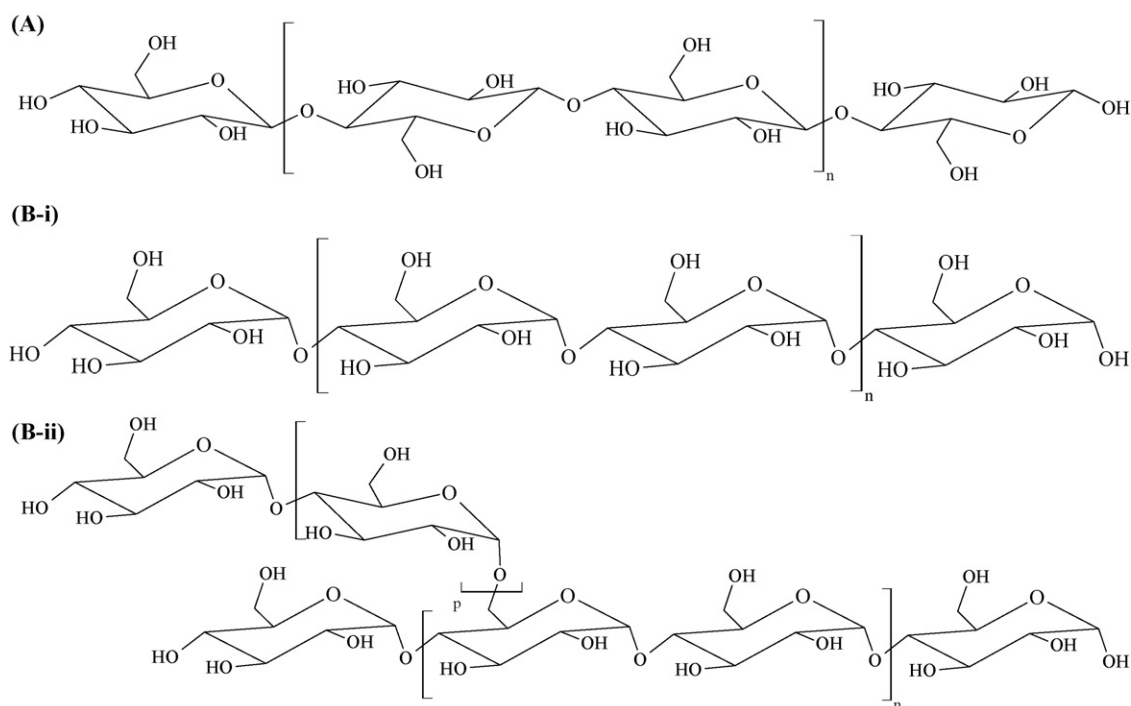
Fig. 2. The structures of (A) cellulose, (B) starch consisting of (i) amylose and (ii) amylopectin as proposed by Nimtz [35].

polymer alignment and held together by strong hydrogen bonding (in-plane) and Van der Waals interactions (between planes). There are 4 different allomorphs for cellulose: cellulose I ($I_\alpha$ and $I_\beta$), cellulose II, cellulose III ($III_I$ and $III_{II}$) and cellulose IV ($IV_I$ and $IV_{II}$), and they can easily be transformed from one form to another by chemical treatment [24]. While cellulose III is thermodynamically the most stable form, it is cellulose I which is most commonly found in Nature. The $I_\alpha$ allomorph is predominant in primitive organisms, while $I_\beta$ is the predominant allomorph in higher plants. $I_\beta$ can also be obtained from $I_\alpha$ by water treatment at 260–280 °C for 15–30 min [25]. Often found in cell-walls accompanying cellulose is hemicellulose, which is a term first used by Schulze [26]. This group of polysaccharides is obtained by extracting materials containing cell-walls with alkali. Hemicelluloses have a random amorphous structure and are comprised of several polysaccharides such as arabinoxylans; $(1 \rightarrow 3)$ and $(1 \rightarrow 4)$-β-glucans, xyloglucans, pectins, and gluco- and galacto-mannans [27].

Starch is a naturally occurring blend of two polymers: amylose and amylopectin. Both are α-D-glucopyranose polymers. For standard starches, the amylose to amylopectin ratio varies from 1:4 to 1:2 [28]. "Amylose-rich" and "waxy" starch varieties are enriched in amylose and amylopectin, respectively. Amylose is a linear homopolysaccharide formed with D-glucopyranose units linked together with α-(1,4) linkages [see Fig. 2(B-i)]. The average degree of polymerisation (DP) of amylose is between 300 and 25,000 and the exact DP depends on the botanical origin of the starch. Amylopectin is a branched homopolysaccharide formed with D-glucopyranose units. The rate of branching is about 4–5% (every 20 units). In each chain, units are linked by α-(1,4) linkages; the side-chains are linked to the main chain thanks to α-(1,6) linkages [See Fig. 2(B-ii)]. The number of glucosyl units is between $10^5$ and $10^9$, but, again, depends on the botanical origin of starch. Starch a is a semicrystalline polymer found in three different allomorphs: the A allomorph is found in cereals, the B allomorph is found in tubers, while the C allomorph is found in legumes, roots, fruits and is actually a combination of both A and B allomorphs [29]. The crystalline sections are formed by alignment of the side-chains of amylopectin alongside the backbone. The crystallinity is thus affected by the amylopectin content and both the extent and length of branching.

Lignin is the second most abundant, naturally occurring macromolecule following cellulose. It is found as cell-wall component in all vascular plants and in the woody stems of arborescent angiosperms (hardwoods) and gymnosperms (softwoods) and thus coexists with cellulose [30]. As lignin is largely hydrophobic and cellulose is hydrophilic, compatibility is obtained through hemicelluloses, which contains both hydrophilic and hydrophobic sections. The lignin content in woody stems varies between 15 and 40% where it acts as water sealant in the stems and plays an important part in controlling water transport through the cell-wall. It also protects plants against biological attack by hampering enzyme penetration. Finally, lignin also acts as permanent glue, binding cells together in the woody stems, and thus giving the stems their well-known rigidity and impact resistance.

Payen discovered lignin in 1838 during the treatment of wood with nitric acid and alkaline solutions [31]. These treatments yielded an insoluble fraction designated cellulose, and a soluble fraction which he called *incrustant*. This soluble material was later named "lignin" by Schulze [32]. Lignin is generally defined as *polymeric natural products arising from an enzyme-initiated dehydrogenative polymerisation of three primary precursors: trans-coniferyl, trans-sinapyl and trans-p-coumaryl alcohol* [30]. Structures are shown in Fig. 3. Lignin is normally used to address the lignin extracted from wood, while proto-lignin is used for lignin still associated with cells. The enzyme-initiated polymerisation results in bonds of exceptional stability: biphenyl carbon–carbon linkages between aromatic carbons, alkyl–aryl carbon–carbon linkages between an aliphatic and aromatic carbon, and hydrolysis-resistant ether linkages. The only linkage which is relatively weak and hydrolysable is the α-aryl ether bond (identified in Fig. 4). The stable linkages make lignin very resistant against degradation and harsh pulping conditions are therefore needed if one wants to hydrolyse the other, more stable, ether bonds. The plant type determines the relative amounts of the respective precursors and thus
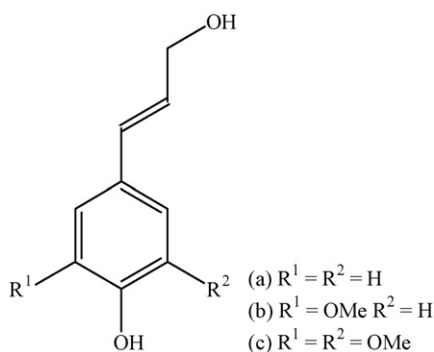
**Fig. 3.** Primary precursors of lignin: (a) *trans-p-*coumaryl alcohol, (b) *trans*-coniferyl alcohol, and (c) *trans*-sinapyl alcohol.

the final structure of lignin. However, due to the similar base structure of the lignin precursors, every lignin molecule consists of sequence of phenyl–propane units. Lignins are divided into two major classes: guaiacyl and guaiacyl–syringyl lignins [33]. The guaiacyl lignins include the majority of gymnosperm lignins, while all angiosperm and herbaceous lignins belong to the guaiacyl–syringyl lignin class [34]. This division is not absolute as different lignins can coexist, even within the same plant. As can be deduced from the class names, guaiacyl lignins only contain *p*-hydroxyphenyl propane (no–OCH$_3$ on the aromatic ring, from trans-p-coumaryl inclusion) and guaiacyl propane units (one–OCH$_3$ group on the aromatic ring from trans-coniferyl), while the guaiacyl-syringyl lignins also contain syringyl propane units (two –OCH$_3$ on the aromatic ring from trans-sinapyl). Fig. 4 represents the structure of beech lignin as proposed by Nimtz [35].

## 1.3. The natural oxidation of biomass

Natural enzymes demonstrate excellent efficiency and exquisite selectivity through the use of several metal ions as at the active sites of cellulose [36] and amylase [37]. Focussing on biomass, Nature degrades wood via an oxidative cleavage with white rot fungi (i.e. through the use of the multinuclear copper laccases) and brown rot fungi (e.g. via the use of iron oxalate complexes). Although the exact mechanisms are still contentious and most likely involve contributions from several species [38]. For instance, the recent genome, transcriptome, and secretome analysis of the wood decay fungus *Postia placenta* supports a unique mechanisms of lignocellulose conversion [39], involving the upregulation during growth on cellulose medium of putative iron reductases, quinone reductase, and structurally divergent oxidases probably leading to the extracellular generation of $Fe^{2+}$ and $H_2O_2$. Furthermore it is intriguing that in brown rot fungi metal-chelating compounds (e.g. oxalate, catecholate and hydroxamate) are observed which have been suggested to complex in particular iron in preference to any potential ligands within the wood itself. The formation of iron chelates further alters the redox chemistry of the iron so that in the presence of $H_2O_2$ the iron chelate complex catalyses Fenton oxidation chemistry involving the production of hydroxyl radicals as the oxidising species and the rapid depolymerisation of cellulose which is a distinguishing feature of brown-rot [40].

Lignin is the largest renewable source of aromatic polymer in Nature but is chemically recalcitrant to breakdown by most organisms because of its complicated heterogeneous structure. White-rot fungi produce a series of extracellular oxidative enzymes that in combination efficiently degrade lignin [41]. The major groups of lignolytic enzymes include lignin peroxidases,
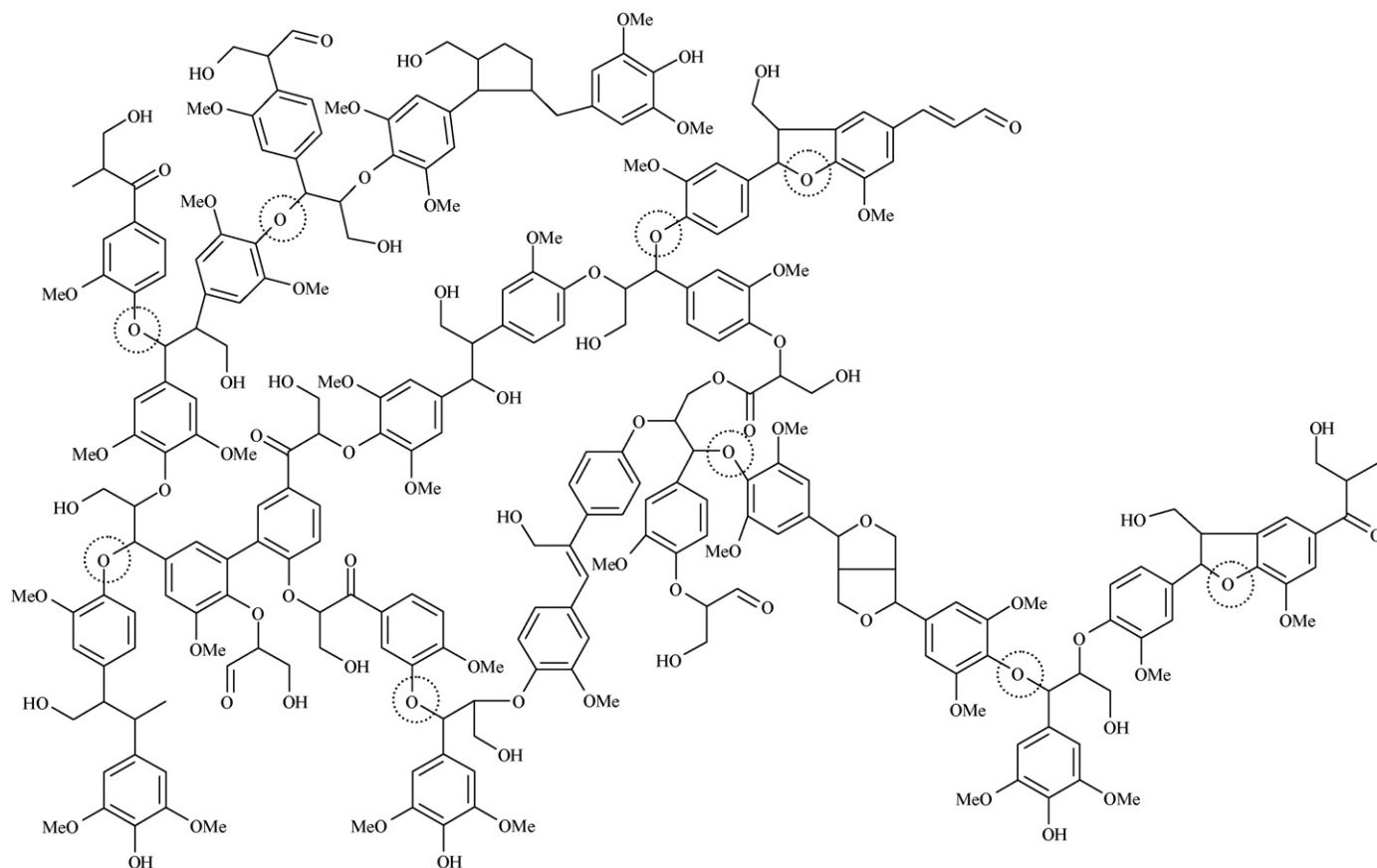


**Fig. 4.** The structure of lignin from Beech as proposed by Nimtz [35]. Examples of the least stable α-aryl ether bonds are identified by the dotted circles.

manganese peroxidases, and laccases. The peroxidases are heme-containing enzymes with catalytic cycles that involve the activation by $H_2O_2$ and substrate reduction of the enzyme intermediates known as compound I and compound II. The formation of compound I is the initial step of the reaction mechanism of plant heme peroxidises [42]. This intermediate stores two oxidising equivalents from $H_2O_2$ as an oxyferryl iron center and a radical, either on the porphyrin ring or on a tryptophan residue [43]. An acid–base mechanism operates in heme peroxidase during the formation of compound I. Furthermore it is now commonly viewed that the conserved distal histidine in the active site of heme peroxidases is the acid–base catalyst that promotes the heterolytic cleavage of $H_2O_2$.

Lignin peroxidases have the unique ability to catalyse oxidative cleavage of C–C bonds and ether (C–O–C) bonds in non-phenolic aromatic substrates of high redox potential. Manganese peroxidises [44] oxidise $Mn^{2+}$ to $Mn^{3+}$, which enables the degradation of phenolic compounds or, in turn, oxidises a second redox mediator, e.g. veratryl alcohol (3,4-dimethoxybenzyl alcohol) or 2-chloro-1,4-dimethoxybenzene, for the breakdown of non-phenolic compounds. Laccases are multi-copper-containing proteins [45] that catalyse the oxidation of phenolic substrates with concomitant reduction of molecular oxygen to water. A physiological role has been suggested for the laccase-catalysed $Mn^{2+}$ oxidation in providing $H_2O_2$ for extracellular oxidation reactions thereby demonstrating a novel type of laccase–MnP cooperation relevant to the biodegradation of lignin [46].

### 1.4. Applications of oxidised cellulose

Oxidised cellulose in various forms has been investigated for use in numerous applications. Since oxidised cellulose is completely bioresorbable and readily degrades under physiological conditions, it is widely used in medical applications such as absorbable hemostatic scaffolding materials [47,48] and as a postsurgical adhesion prevention layer [49], but also as carrier material for agricultural, cosmetic and pharmaceutical applications [50,51]. A blend of oxidised cellulose with vitamin E has been patented for topical hemostatic applications in which it was claimed that oxidised cellulose shows bactericidal effects against a wide range of pathogenic microorganisms [52]. Other bioactive materials such as pain relievers and growth promoters could be included in the wound dressing for additional benefit. Oxidised cellulose fibres have been claimed to be better blood clotting agents than is oxidised regenerated cellulose [53]. Oxidised cellulose is also a safe and effective treatment for moderate tubal hemorrhage during laparoscopic sterilisation of women and for small uterine perforations [54,55]. Osseous regeneration is at least as fast using oxidised cellulose as with collagen, the most widely used material at current, making oxidised cellulose an interesting scaffolding material [47]. While most of these uses are promising, there have also been reports where the use of oxidised cellulose during operation appears to have induced inflammation at the surgical site and even beyond [56].

The use of oxidised cellulose in the form of filter sheets and as an ion-exchange column filler resulted in an effective method to remove metal ions from water and aqueous environments [57]. The affinity of oxidised cellulose for metal ions followed the following order: $Cd^{2+}$, $Zn^{2+}$ > $Ni^{2+}$ ≫ $Ca^{2+}$ > $Mg^{2+}$ ≫ $Na^+$. The potential of oxidised cellulose to act as an ion exchange material has been recognized early on with over 500 papers published on this subject in 1971 [58]. The oxidised cellulose materials have been used to purify and fractionate proteins, including enzymes, hemoglobins, hormones serum protein viruses and seed proteins. Oxidised cellulose has also been used in the chromatography of peptides, nucleic acids, nucleotides, amino acids, alkaloids and metallic ions [58].

### 1.5. Applications of oxidised starch

Many chemical oxidations of starch are known, e.g. wet-, semi-dry and dry-oxidation with all of these having been well documented [59]. Recently, the enzyme laccase in combination with 2,2,6,6-tetramethyl piperidinyl-1-oxyl radical (TEMPO) as a mediator has been used to oxidise starch selectively at the primary hydroxyl groups [60]. Oxidised starch (European food additive number E1404) has found significant applications in the food, paper and textile sector. In the food sector, oxidised starch, with or without pregelatinisation, is used as a texturiser in dairy products, batter and coating, as a binder in snacks, batter and confectionary and as a film-former in confectionary [61]. It is especially useful in the production of dry powder for instant preparation powders for puddings, fruit dessert and jelly. The wide appeal of starch in food products is due to its ability to change texture, body, appearance and flavour at the same time [62]. Starch can vary texture from grainy to smooth and from cohesive (gummy or slimy) to gelled. Oxidised starch is a potential replacement for gum Arabic (also known as acacia gum and European food additive number E414) in film forming applications for food applications. An example of this was seen when corn and amaranth starch were oxidised using sodium hypochlorite as oxidant and $MgCl_2$ as catalyst [63]. Oxidised starch (using sodium hypochlorite) is also used in large quantities in the paper and textile industries due to its bright white colour, easy gelatinisation and high solubility. Its use as a coating agent in the paper industry dates from the early part of the 1900s [64]. It is currently used together with other coating agents such as titanium dioxide, calcium carbonate, casein, polyvinyl alcohol, etc [65].

Nearly every kind of starch has been used in textile finishing, but due to the increased cost of oxidising starch, oxidised starch is only used when this cost increase is compensated for by improved performance [64]. For example, high fluidity and stable flow properties allow high solution loading and thus, higher add-on during processing. Its adsorption to the fibre surface results in an elastic film providing protection against the mechanical action of high speed looms. Oxidised starch can also be used as a laundry finish as a liquid or a dry powder [64].

### 1.6. Applications of oxidised lignin

Oxidising lignin to render it more useful is an interesting approach given the well established anti-oxidant properties of lignin [66]. There exist, however, specific lignin-oxidising enzymes that could be used as an alternative to bleach or chemocatalytic oxidation [67]. Oxidised lignin, just like oxidised cellulose and starch, shows a high chelating capability that can be used for heavy metal removal from polluted effluent streams [68]. Enzymatically oxidised lignin [from acetosolv (i.e. from continuous extraction with acetic acid) and ethanol–water extraction processes] exhibits better sequestration of $Cu^{2+}$ than non-oxidised lignin while oxidised ethanol/water extracted lignin was better than oxidised acetosolv lignin [69]. Oxidation of lignin may also render it more dispersible in water, opening up uses as a flocculant, dispersants or binders; currently this is reserved for water-soluble high-sulphur containing lignosuphonates [70]. Selective and controlled oxidation of lignin, however, would be extremely valuable as it is believed to be the only economically viable stream of renewable aromatic compounds for large scale production.

## 2. Cellulose oxidation

The oxidation of cellulose is extremely important [47–58]. The bleaching of cellulose-containing materials is widely used in industry to remove coloured substances and commonly uses hydrogen peroxide or hypochlorites as oxidising media [71]. The use of

hypochlorites produces stoichiometric amounts of chlorides, such that greener, more atom efficient methods are desirable. Various other methods have been investigated. Some of these are hardly greener (e.g. the use of dichromate or hypobromite). In this section, we will describe various studies that have been carried out which use more benign catalysts and reagents to oxidise cellulose.

### 2.1. Bleaching of cellulose-containing materials

Before the use of starch- and cellulose-containing materials in products, e.g. textiles, paper or pulp, the materials are generally bleached and the efficiency of this process is strongly affected by any transition metal ions present [72]. This catalytic oxidation will further yield an increased number of functional groups in addition to the, mainly, hydroxyl groups on the surface of cellulose, i.e. aldehydes and carboxylic acids, which creates opportunities for further functionalisation of the oxidised materials. Consequently the hydrophilic or hydrophobic properties of the material may be significantly altered. There is also the potential for depolymerisation to occur during such bleaching processes leading to weaker fibres. $Mg^{2+}$ ions are believed to protect carbohydrate groups during the bleaching of pulp, and thus it is desirable to retain a proportion of the $Mg^{2+}$ ions that are naturally present [73].

Transition metal catalysts have been extensively studied in the activation of oxidants for the cleaning of laundry and in dishwashers [74]. This bleaching action is mainly directed to destroy unwanted stains on the fabric (i.e. cotton fibres with cellulose as the main component) in order to achieve the intended cleaning effect without oxidative damage of the cellulose. In a second application, the bleaching may be applied to destroy dyes released from a fabric into solution, so as to prevent unwanted dye transfer between fabrics. The bleaching of stains can be considered as a heterogeneous process while the bleaching of migrating dyes is basically a homogeneous oxidation reaction.

Iron and manganese catalysts tend to be the most frequently studied metals in laundry applications due to their acceptable environmental and toxicological properties. It is perhaps unsurprising that Nature too makes widespread use of these metals for its oxidation catalysts. However, in Nature these active sites are present within the protective coating of the rest of the enzyme, while in simple coordination catalysts they are more exposed to the reaction media. Consequently, a frequent failure of catalysts under laundry conditions is due to the poor thermodynamic complex stability resulting in fast decomposition to form iron hydroxides or manganese dioxide under the alkaline conditions. Moreover the oxidative robustness of the ligand under the oxidising conditions is often low. The selectivity of the catalysis is also a key aspect as it is highly desirable to avoid catalysis of Fenton type chemistry that would yield the non-selective but highly reactive hydroxyl radicals. Similarly it is important to limit the catalase activity of any added catalysts with $H_2O_2$ as this is wasteful of the oxidant [75].

Recently, under alkaline conditions hydroxyl radical generation from $H_2O_2$ was determined by a spin-trapping EPR technique with DMPO (5,5-dimethyl-1-pyrroline *N*-oxide) for the series of transition metals $Cr^{3+}$, $Mn^{2+}$, $Fe^{2+}$, $Co^{2+}$, $Ni^{2+}$ and $Cu^{2+}$ [76]. At pH 10, $Cu^{2+}$ was the only metal ion to generate a considerable amount of hydroxyl radicals. It is generally observed that by forming a chelate complex the redox chemistry of a metal ion can be dramatically altered. Consequently, $Fe^{2+}$ and $Cu^{2+}$ in the presence of ethylenediamine tetra-acetic acid, tetrasodium salt ($Na_4EDTA$), sodium iminodisuccinate ($Na_4IDS$), diethylenetriamine pentamethylphosphonic acid, trisodium salt ($Na_3DTPMP$) and *S,S*-ethylenediamine disuccinnic acid, trisodium salt ($Na_3EDDS$) (Fig. 5) were similarly studied. $Cu^{2+}$ complexes with $Na_4EDTA$ and $Na_4IDS$ yielded hydroxyl radicals while the other two chelates inhibited its generation. $Fe^{2+}$ complexes with $Na_4EDTA$, $Na_3DTPMP$
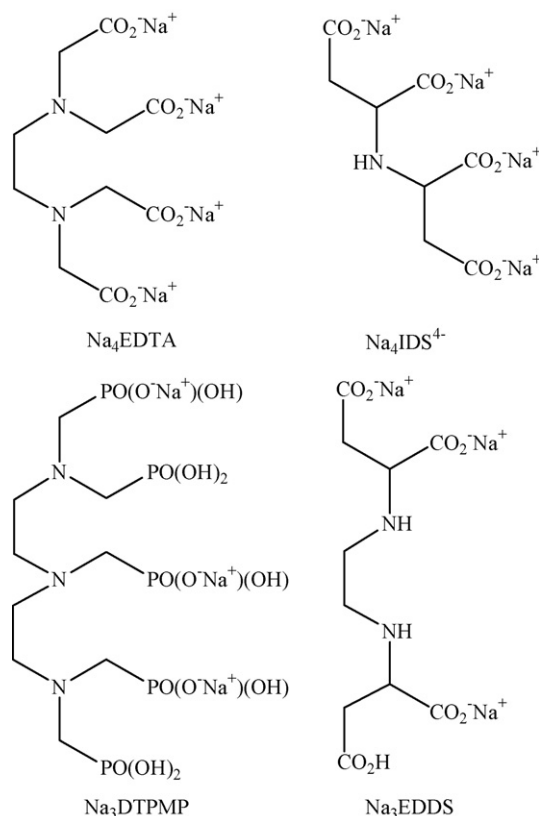
**Fig. 5.** Chelating ligands used in studies on the generation of hydroxyl radicals and the bleaching of cellulose by metal ions and $H_2O_2$.

and $Na_4IDS$ enhance hydroxyl radical generation while complexes with $Na_3EDDS$ do not. Furthermore in model cellulose fabric damage experiments (i.e. using mixed polyester-cotton swatches with $H_2O_2$ at 90 °C) similar results were reported for $Cu^{2+}$ when compared to the generation of hydroxyl radicals. However, experiments with $Fe^{2+}$ gave a similar % weight loss in the absence or presence of a chelating ligand. This latter observation was explained by a difference in the time-scales of the experimental procedure between the homogeneous EPR and the heterogeneous cellulose damage experiments. It is noteworthy in this context that $Fe^{2+}$ is more likely to hydrolyse, oxidise and displays lower stability constants for its complexes compared to $Cu^{2+}$.

The most famous member of this class of bleach catalysts is the dinuclear manganese(IV) complex of 1,4,7-trimethyl-1,4,7-triazacyclononane [77] (i.e. $[Mn_2(\mu\text{-}O)_3(Me_3TACN)_2](PF_6)_2$ in Fig. 6) which is an excellent low temperature catalyst for bleaching and was incorporated into a consumer product. Unfortunately

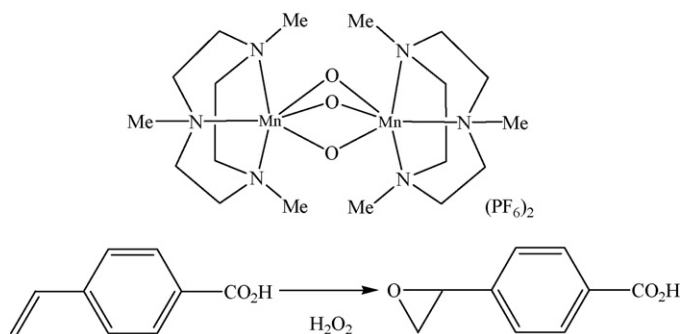**Fig. 6.** The manganese $Me_3TACN$ complex originally used in laundry formulations and one example showing it catalysing an epoxidation.
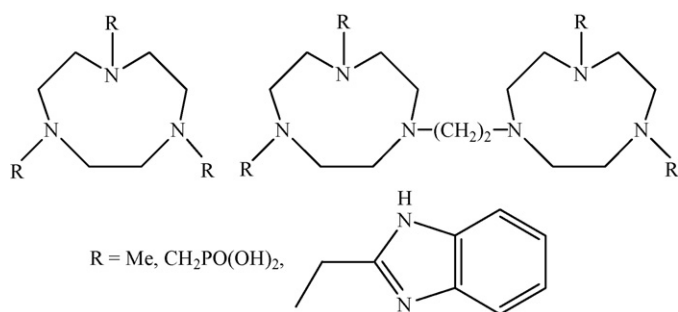
Fig. 7. Derivatives of the macrocyclic ligand triazacyclononane.



(a) 5,5,7,12,12,14-hexamethyl-1, 4,8,11-tetraazacyclotetradecane

(b) TAML-type catalysts

R = Me or F

n = 1 for X = H or CONH(CH$_2$)$_2$CO$_2$H

or CONH(CH$_2$)$_2$NMe$_2$

n = 0 for X = CONH(CH$_2$)$_2$NMe$_3^+$

Fig. 8. Macrocyclic bleach catalysts.

the detergent product containing this catalyst was withdrawn from the market [78] after it was alleged that the product yields increased fabric- and dye-damage after repeated washing cycles. The fabric damage occurs due to changes in the cotton fibre structure most likely due to the removal of non-cellulosic materials as well as a decrease in the degree of polymerisation of the cellulose. The catalyst is still applied in various machine-dishwashing products and is responsible for superior removal of tea residues [79]. Research has been reported to limit adverse oxidative degradations but this is difficult to achieve with this type of catalyst (Fig. 7). For example the addition of chelating phosphonic acid pendant groups to improve stability was also accompanied by the dye damage observed for the parent complex [Mn$_2$($\mu$-O)$_3$(Me$_3$TACN)$_2$](PF$_6$)$_2$ [80]. Similarly, manganese complexes of a TACN bearing 1-(benzimidazol-2-ylmethyl) pendant groups have been synthesised [81]. These show improved solution stability compared to the parent TACN complex but also mimic the activity of superoxide dismutase and catalase, in the latter case thereby increasing the decomposition of H$_2$O$_2$ in alkaline solution.

In the oxidation by H$_2$O$_2$ of phenols, chosen as models for the natural phenolic stains in laundry, the precatalyst [Mn$_2$($\mu$-O)$_3$(Me$_3$TACN)$_2$](PF$_6$)$_2$ is first reduced to an EPR-active Mn$^{III}$Mn$^{IV}$ species. Also produced are phenoxy radicals which couple to give bi- and poly-phenols and by further oxidation diphenoquinones. The reduced manganese species is susceptible to the formation of a monomer which is itself oxidised to form a [Mn$^V$(O)(Me$_3$TACN)(biphenol)]$^+$ complex which has been proposed as the active oxidant [82].

The precatalyst [Mn$_2$($\mu$-O)$_3$(Me$_3$TACN)$_2$](PF$_6$)$_2$ is also active in the oxidation of small molecules such as alkenes (Fig. 6) [83]. In these experiments, the dismutation of H$_2$O$_2$ can be controlled by using an appropriate solvent (e.g. acetone) or by applying an additive (e.g. oxalate or ascorbic acid). Addition of trichloroacetic acid or 2,6-dichlorobenzoic acid to [Mn$_2$($\mu$-O)$_3$(Me$_3$TACN)$_2$](PF$_6$)$_2$ and H$_2$O$_2$ yields a selective cis-dihydroxylation versus epoxidation, namely in a 7:1 ratio [84].

Recently, voltammetric measurements at the surface of cotton have been performed after first impregnating the cotton with graphite flakes [85]. Here the complex [Mn$_2$($\mu$-O)$_3$(Me$_3$TACN)$_2$](PF$_6$)$_2$ was absorbed by the cotton and in the presence of H$_2$O$_2$ this catalyst still acts as a catalase model system.

A large selection of complexes has been studied as oxidation catalysts during laundry washing. These comprise macrocycles, salen-, saltren- and terpyridine-type ligands combined with manganese in different oxidation states as the active pre-catalyst (Figs. 1, 8 and 9) [74]. The essentials of the corresponding screening procedures have also been reviewed [86]. Several of the iron complexes of pentadentate amine ligands in Fig. 9 (e.g. N,N,N′,N′-tetrakis(2-pyridylmethyl)ethylenediamine, N-benzyl-N,N′,N′-tris(2-pyridylmethyl)ethylenediamine and N,N-bis(2-pyridylmethyl)-N-bis(2-pyridyl)methylamine) form low spin Fe$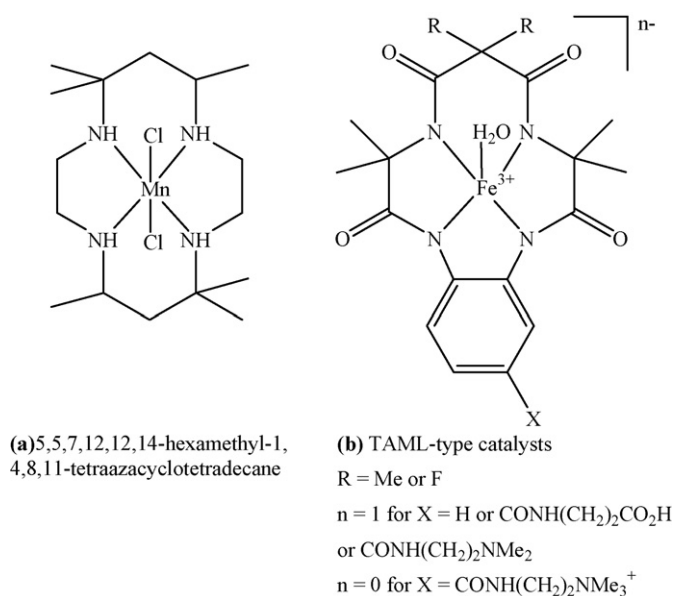^{3+}$-hydroperoxide species analogous to the active form of the anticancer drug bleomycin [87], which functions by oxidatively cleaving the sugar residues of DNA [88]. Recently such complexes have also shown the ability to form an isolable oxoiron(IV) complex with such species also having often been implicated in the catalytic cycles of oxygen-activating non-heme iron enzymes [89]. Several of the iron complexes of pentadentate amine complexes have been patented as catalysts for stain bleaching in the presence of either H$_2$O$_2$ [90] or atmospheric O$_2$ only [91].

Recent studies involved Mn$^{2+}$ bleaching catalysts of meso-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane and racemic-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane ligands (Fig. 8a), in bleaching cotton fabrics stained with tea, coffee, curry, and sugar beet [92]. The catalysts were more active in comparison to the current activator in laundry, i.e. tetraacetyl ethylenediamine (TAED). Also the dye and fabric damage over repeated wash cycles induced by the catalyst was significantly less than with TAED with several different dyes.

Dye-transfer inhibition (DTI) during laundering can be achieved by catalytic bleaching of the migrating dyes in the wash-solution. It is critical here that the rate of the bleaching reaction should be much higher than the rate of dye adsorption onto the acceptor fabric. Furthermore, the stability of the catalyst needs to be high enough to bleach the dyes which are slowly released from coloured fabrics over the whole wash-cycle. For example, iron macrocyclic complexes of the TAML family (Fig. 8b) of oxidatively robust ligands developed by Collins and co-workers, bleach dyes released from fabrics during laundry washing in surfactant-containing media [74b,93]. Similarly the performance of three manganese-salen (Fig. 9) complexes as DTI catalysts have been studied [74e,94]. This showed that a high activity is compatible with a high stability, leading to good DTI properties. Interestingly, with the less stable catalysts, the performance markedly improves by optimising the catalyst and H$_2$O$_2$ concentrations or by formulation within a polymer matrix.

## 2.2. Modification of cellulose

In the preparation of cellulose derivatives, a high solution viscosity is often the decisive quality criterion. Therefore it is important to control the final viscosity of the cellulose derivatives [95]. For example, in the production of carboxymethyl cellulose
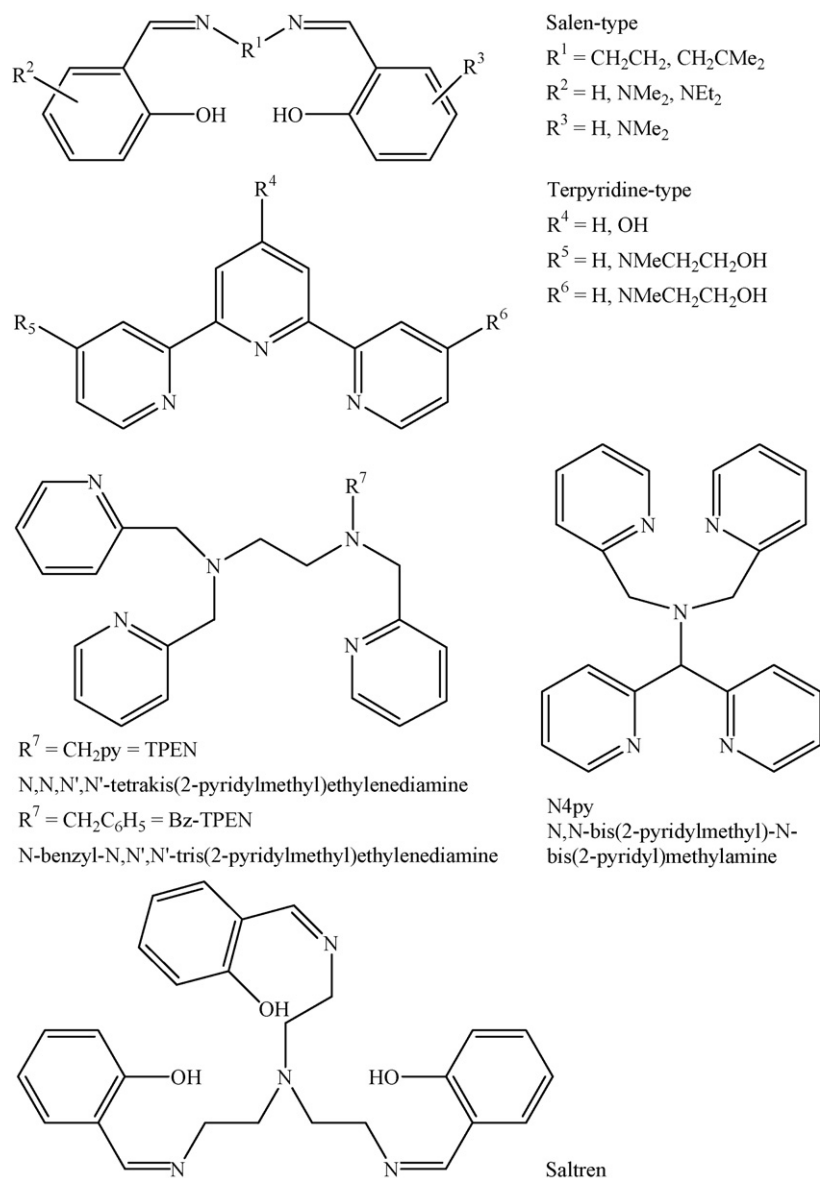
**Salen-type**
$R^1 = CH_2CH_2, CH_2CMe_2$
$R^2 = H, NMe_2, NEt_2$
$R^3 = H, NMe_2$

**Terpyridine-type**
$R^4 = H, OH$
$R^5 = H, NMeCH_2CH_2OH$
$R^6 = H, NMeCH_2CH_2OH$

$R^7 = CH_2py = TPEN$
N,N,N',N'-tetrakis(2-pyridylmethyl)ethylenediamine
$R^7 = CH_2C_6H_5 = Bz$-TPEN
N-benzyl-N,N',N'-tris(2-pyridylmethyl)ethylenediamine

N4py
N,N-bis(2-pyridylmethyl)-N-
bis(2-pyridyl)methylamine

Saltren

**Fig. 9.** Acyclic ligands for complexes targeting laundry applications.

(CMC), controlling the reduction in molecular weight of the cellulose chains is essential. Such a reduction can be achieved by the addition of $Co^{2+}$ ions during the process, which act as a catalyst for an oxidative cleavage reaction. It was shown that it is important for cobalt to be present during the mercerisation stage in order to achieve the desired viscosity [96].

To help understand the fungal biodegradation of wood, the oxidative degradation with $H_2O_2$ of both hemicellulosic and cellulosic materials has been investigated with $Fe^{3+}$ and the $Fe^{3+}$-complexes with both the catechol ligand 3,4-dihydroxyphenylacetic acid and the hydroxamate ligand deferox-

amine (DFO, Fig. 10) [97]. With hemicelluloses, the $Fe^{3+}$-catechol complex mediated a Fenton reaction that clearly accelerated and increased the degradation of the hemicellulosic materials. While, with the $Fe^{3+}$-hydroxamate an inhibitory effect was seen. The reactivity was related to the reduction of the $Fe^{3+}$ to $Fe^{2+}$ as this species then undergoes a Fenton reaction with the $H_2O_2$ to generate the hydroxyl radicals that are responsible for the degradation observed. That an effect is seen with DFO is interesting, as the X-ray structure of DFO–$Fe^{3+}$ shows that the metal ion is coordinatively saturated within a distorted octahedron and so lacks a free site for reactivity [97b]. With the catechol ligand this reduction was much more
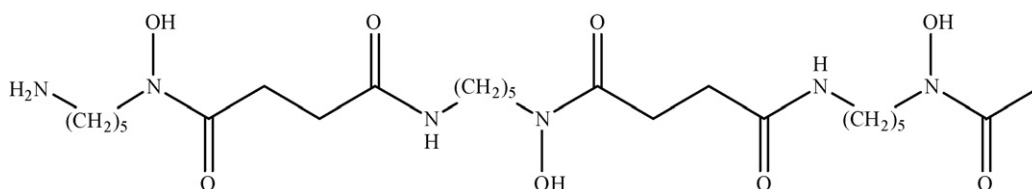


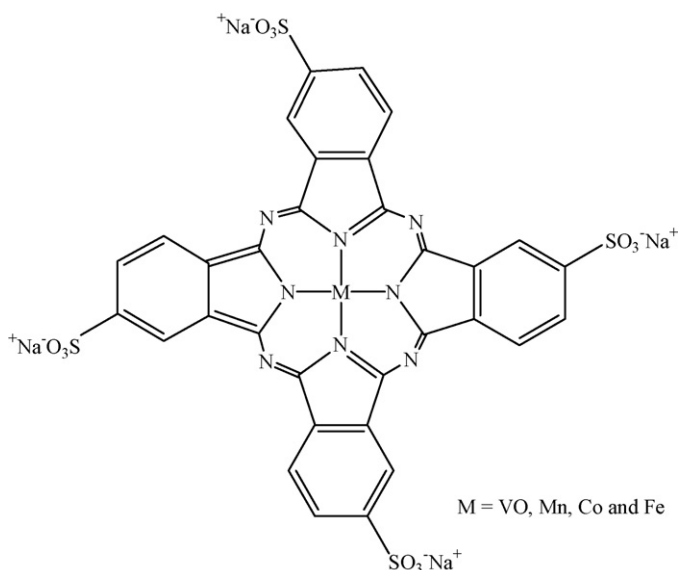**Fig. 10.** The structure of deferoxamine.

**Fig. 11.** A water-soluble iron phthalocyanine catalyst for the oxidation of hydroxyethylcellulose and starch.

efficient. Conversely, in similar experiments with cellulose materials no overall difference in degradation was seen between the $Fe^{3+}$, $Fe^{3+}$–catechol and $Fe^{3+}$–hydroxamate reactions, where the reduction possibly arises due to the release of reducing sugars. However, the catechol-mediated reaction did still accelerate the initial degradation of cellulosic substrates.

Recently, a water-soluble iron phthalocyanine catalyst (M = Fe in Fig. 11) with $H_2O_2$ was shown to oxidise hydroxyethylcellulose (HEC), sodium carboxymethylcellulose (NaCMC), guar gum (GG), and inulin to the extent of 19, 30, 53, 23 carbonyl functions per 100 AGU, respectively [98]. The relatively modest conversion reported and was ascribed to a competing over-oxidation resulting in a depolymerisation of the material.

## 3. Starch oxidation

The paper industry uses oxidised starch widely as a surface sizing agent. Generally the oxidation process uses transition metal catalysts and perchlorates or iodates, which yields large amounts of inorganic waste. Oxidised starch can be formed industrially by TEMPO mediated oxidation with sodium hypochlorite which generates stoichiometric amounts of waste sodium chloride [99]. Alternatively, sodium iodate has been used to form dialdehyde starch but here the high cost of periodate requires its recovery [100]. It would therefore be most beneficial to develop a greener process.

### 3.1. Metal salts

$CuSO_4$ catalyses the air oxidation of potato starch in alkaline solution [101], with carbonyl derivatives being produced in preference to the further oxidation to carboxylates. The catalysing $Cu^{2+}$ ions were not removed from the product by washing with water due to the formation of $Cu^{2+}$ carboxylate complexes. The copper derivatives displayed lower thermal stability than the original starch. Electron micrographs demonstrated that the oxidation process occurred on the surface and not in the granular interior. Similar, surface oxidation of the starch granules was noted in the air oxidation of potato starch in the presence of an $NH_4VO_3$ catalyst [102].

Potato starch has been catalytically oxidised by $H_2O_2$ with $Fe^{2+}$, $Cu^{2+}$ and $WO_4^{2-}$ salts [103]. $Cu^{2+}$ was the most active metal ion, although a combination of $Fe^{2+}$ and $Cu^{2+}$ salts gave the highest carbonyl content of 6.6/100 AGU (anhydroglucose units), while in general the carboxyl content remained low similar to the air oxidation above. The pH influenced the reaction with the highest carbonyl content seen from acid solution and the yields were 90% in alkaline and 99% in acidic solution for the combination of $Fe^{2+}$ and $Cu^{2+}$ salts. It was shown that depolymerisation increased markedly with the degree of oxidation, and the choice of catalyst used, i.e. $Fe^{2+}$ and $Cu^{2+}$ led to the largest decrease. In support of this, rheological measurements showed that with a moderately oxidised starch the storage modulus G′ was high. However, when the degree of oxidation increased and the molecular weight fell, the storage modulus G′ decreased. Additionally, the more the oxidised the starch was, the higher the gelatinisation temperature became.

Maize starch has been oxidised by $H_2O_2$ in either alkaline or acidic solution with an $Fe^{2+}$ catalyst, prior to cationisation with 3-chloro-2-hydroxypropyltrimethyl(ammonium) chloride [104]. At pH 4 the catalyst formed hydroxyl radicals, while at pH 11 the catalyst formed the peroxy anion as the oxidant. At both pH values the catalyst enhanced the number of carboxyl and carbonyl residues in comparison to the uncatalysed reaction. Additionally the samples prepared at pH 11 were more amenable to the subsequent cationisation step. Study of the chemical and rheological properties of the oxidised starch and oxidised–cationised starch materials found properties which make them excellent agents for textile sizing and printing.

As starch is processed, thermal treatments can lead to the formation of radicals that react to alter the material's structure. This is especially true in the presence of metal ions arising from the soil during growth or from catalysts during processing of the starch. Therefore by using EPR spectroscopy this radical generation was studied and this was facilitated by the addition of $Cu^{2+}$ ions as a probe [105]. Clearly the $Cu^{2+}$ ions have several potential binding modes in the starch. The thermal generation of radicals was proposed to arise by cleavage of the carbonyl $RCO–Cu^{2+}$ or carboxylate $RCOO–Cu^{2+}$ bonds in the starch, followed by the reduction of $Cu^{2+}$ to $Cu^+$ ions and formation of transient $RCO^\bullet$ or $RCOO^\bullet$ species. The radical species then abstract a hydrogen atom from the neighbouring carbon atom within the glucose ring where the radical subsequently becomes localised.

### 3.2. Metal complexes

A mixture of $MTO/H_2O_2/LiBr$ (MTO = methyltrioxorhenium) has recently been shown to yield biodegradable oxidised starch super absorbers. This process avoids the highly acidic media previously reported by this same group and so limits depolymerisation of the starch while catalyzing the selective oxidation of the C6 hydroxymethyl group to form a carboxylic acid [106]. Under oxidative conditions using $H_2O_2$, the catalyst mainly exists in three stoichiometric forms: the parent MTO molecule and the 1:1 and 2:1 $H_2O_2$:MTO adducts, known as intermediates A and B in the related literature [107]. Additionally, recent mechanistic studies by Lin and Busch using oxygen-18 labelled probes reported that the deactivation of the catalyst MTO in oxidation reactions using $H_2O_2$ arises by the nucleophilic attack of $HOO^-$ on the parent catalyst rather than by $HO^-$ attack on intermediate A, opening possible strategies to enhanced catalyst stability [108].

Recently, a practical, single step oxidation of starch by $H_2O_2$ was published using water-soluble phthalocyanine complexes [109] (i.e. tetrasulfonatophthalocyanine PcSM, M = VO, Mn, Co and Fe in Fig. 11), to synthesise a series of oxidised starches without producing any inorganic waste [110]. The oxidation was most efficient
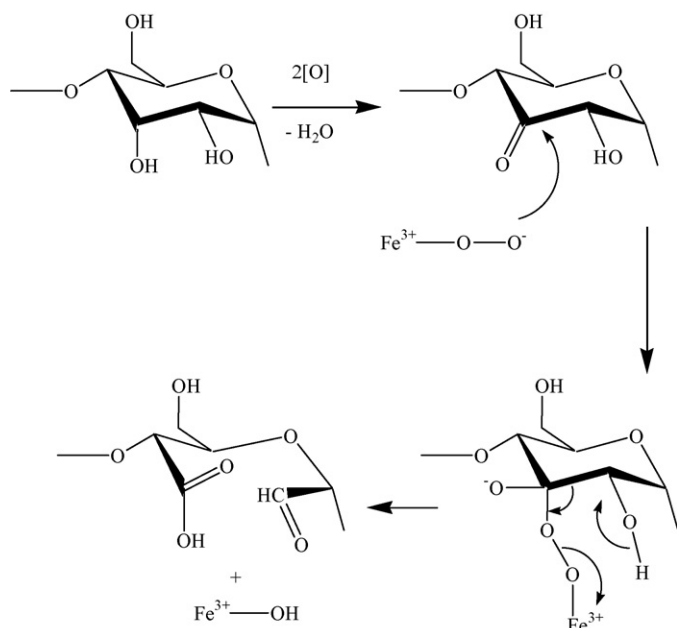
**Fig. 12.** Mechanism of the oxidation of sugars by water-soluble metal phthalocyanines [110a,111].

with the $Fe^{3+}$ catalyst and was best operated in a semi-batch manner with continuous addition of the $H_2O_2$. It was again found to be key that the pH was kept alkaline to avoid any acidic conditions which would lead to depolymerisation of the starch [7]. The catalyst is most active at pH 10, where the $H_2O_2$ was rapidly consumed resulting in a COOH value of 1.6/100 AGU and CO value of 3.0/100 AGU. However, there was an accompanying loss of the solid starch (i.e. yield = 67 wt%) due to both depolymerisation and decomposition. At pH 8.4, more starch was recovered and the formation of carbonyl groups was higher which was ascribed to greater radical formation at this lower pH. The key step in the mechanism was suggested to be related to the mechanism seen previously in the oxidation of chlorinated phenols, namely the nucleophilic peroxo complex $PcSFe^{3+}$–$OO^-$ cleaves the C–C bond bearing hydroxyl groups to form acids via a Grob type fragmentation (Fig. 12) [111]. The oxidation process begins on the surface of the starch particle before this oxidative degradation improves the access of the catalyst to enable oxidation to occur inside the particle.

## 4. Lignin and its model compounds oxidation

As mentioned earlier, lignin offers an enormous potential as a feedstock for renewable aromatic compounds [5,69–71]. In addition, the removal of lignin from ligno-cellulosic fibres (e.g. wood, straw, sisal) is important for textile and paper applications since it discolours the fibres even if present in low quantities. Since lignin is a three-dimensional cross-linked material, lignin removal required breakage of chemical linkages, commonly through oxidation.

### 4.1. Metal salts

$MnO_2$ is found in decayed wood and has been shown in combination with oxalic acid to oxidise the aromatic components in wheat straw [112]. The active catalysts were soluble manganese species that were not identified. The hemicellulose and cellulose components of the straw remained unchanged, while the lignin components were clearly modified. Furthermore, only the phenolic units of lignin were directly oxidised as no structural alteration was

seen with extensively permethylated lignin. This $MnO_2$ and oxalate mixture clearly represents a possible route for fungi to begin the natural degradation of wood.

A mixture of $Co(CH_3CO_2)_2/Mn(CH_3CO_2)_2/HBr$ in acetic acid can oxidise the lignin model compound 3,4-dimethoxytoluene to its corresponding benzaldehyde [113]. This process is unusual for several reasons, namely the rate of $O_2$ reacting with the substrate is bi-phasic, i.e. two maxima in the rate of reaction are seen. In the first phase, all of the 3,4-dimethoxytoluene is converted to intermediates, but very little to the carboxylic acid. During the second maximum of activity, virtually all the intermediates are converted to the carboxylic acid. In addition, the rate of CO and $CO_2$ formation is considerably higher during the second phase and as a by-product methyl 3,4-dimethoxybenzoate is also formed.

A closely related process with five different lignin samples, from wood and bagasse, involved their oxidation in air with a $Co(CH_3CO_2)_2/Mn(CH_3CO_2)_2/Zr(CH_3CO_2)_4/HBr$ mixture in acetic acid [114]. The aim was to harvest valuable aromatic compounds from the lignin as could be seen in a future biorefinery and eighteen products were identified via gas chromatography–mass spectrometry with an overall conversion of 10.9 wt% of the lignin. The most valuable compounds were 4-hydroxybenzaldehyde, 4-hydroxy-benzoic acid, 4-hydroxy-3-methoxybenzaldehyde (vanillin), 4-hydroxy-3-methoxybenzoic acid (vanillic acid), 4-hydroxy-3,5-dimethoxybenzaldehyde (syringaldehyde) and 4-hydroxy-3,5-dimethoxybenzoic acid (syringic acid). Studies with model substrates (i.e. 4-hydroxybenzaldehyde, 3-methoxy-4-acetoxy-benzaldehyde, 4-methoxytoluene, 3-methoxy-4-hydroxytoluene and 3-methoxy-4-acetoxytoluene) showed firstly that the presence of the phenolic functionality on an aromatic ring does inhibit the rate of reaction but that the alkyl group on the ring still oxidises to the carboxylic acid. Secondly, that the acetylation of the phenols occurs at a reasonable rate in acetic acid and that the alkyl group of these acetylated phenols readily oxidise. Therefore a two-step acetylation/oxidation to the carboxylic acid is a feasible route to recovering valuable aromatic compounds.

### 4.2. Metal complexes

Methyltrioxorhenium catalyses the oxidation by $H_2O_2$ of both phenolic and non-phenolic lignin model compounds (e.g. vanillyl alcohol, veratryl alcohol, 1-(4-hydroxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)propane-1,3-diol) [115]. Furthermore three lignins, hydrolytic sugar cane lignin (SCL), red spruce kraft lignin (RSL) and a hardwood organosolvent lignin (OSL) were extensively degraded under similar conditions. Related catalytic activity was retained when the catalyst was supported on a polymeric support, e.g. poly(4-vinyl pyridine), poly(4-vinyl pyridine-N-oxide) or within polystyrene, to allow ease of recovery of the expensive catalyst [116].

A large series of ligands (Fig. 13 shows typical examples) have been screened to prepare $Cu^{2+}$ catalysts *in situ* for the oxidation of lignin model compounds, in particular veratryl alcohol to its corresponding aldehyde [117]. The oxidations proceed under alkaline conditions with $O_2$ as the oxidant, with the authors aiming to develop a process for the $O_2$ bleaching of pulp. It was found that the most active catalysts were formed from diimine type ligands, i.e. dimethylglyoxime, 1,10-phenanthroline and 2,2′-bipyridine. In later studies using 1,10-phenanthroline, the catalysis was proposed to be initiated by the reduction of $[Cu(phen)(OH)_2]$ by the veratryl alcohol with subsequent reoxidation of the catalyst by $O_2$, as verified by UV/vis and EPR studies. Unfortunately this catalyst also depolymerises the model carbohydrate dextran showing inadequate selectivity for application in pulp bleaching [118]. If a solution of the catalyst was left to stand then crystals
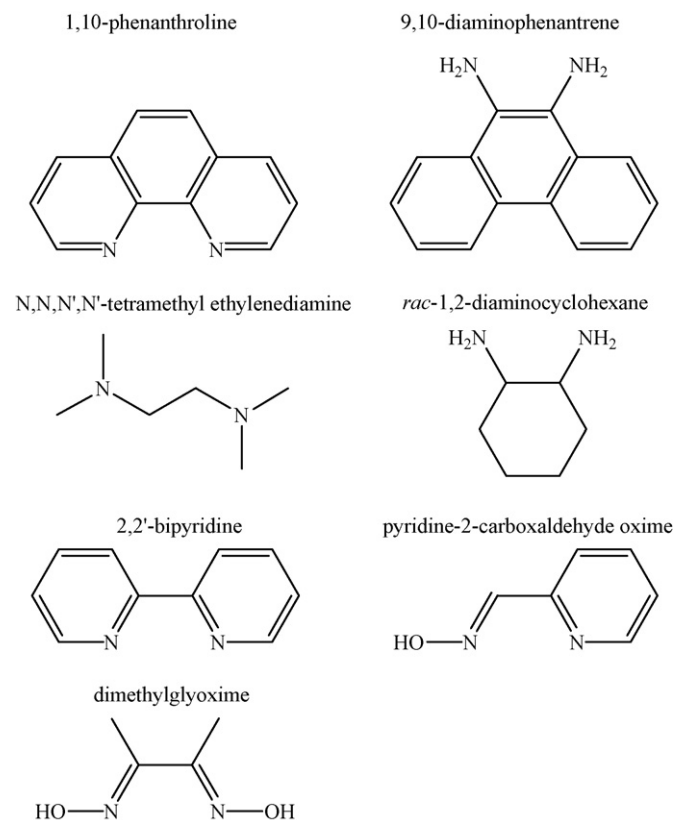
**Fig. 13.** Ligands used *in situ* to generate catalysts for the oxidation of model substrates for lignin.

of [Cu(phen)$_2$CO$_3$].7H$_2$O were isolated supporting the view that several species will be present in the solution.

2,2′-Bipyridine and modified 2,2′-bipyridines were similarly further studied with the substituents on the bipyridine rings having a large effect on the catalytic oxidation. Namely the Cu-complexes of the 4,4′- and 5,5′-substituted bipyridine ligands were highly active in the oxidation of veratryl alcohol. The 4,4′-disubstituted bipyridines showed that electron donating methyl and methoxy substituents enhance the oxidation activity of Cu-bipyridine. The most effective Cu-complexes also catalysed the oxidation of 2,2′-biphenol and again the oxidative depolymerisation of the carbohydrate dextran. The performance of Cu-2,2′-bipyridines in O$_2$ delignification of softwood pulp was in accordance with the model compound studies; the catalysts lowered the lignin content of the pulp, but they also tended to attack the cellulose fibres. According to the oxidation experiments, the complex distribution calculations and the UV-vis studies, the structure of the most active species was proposed to be [Cu(2,2′-bipyridine)$_2$OH]$^+$ [119].

In the presence of TEMPO the Cu-complexes of either 1,10-phenanthroline or 2,2′-bipyridine form even more efficient catalysts for the oxidation of veratryl alcohol by O$_2$ [120]. For example under the same conditions, adding TEMPO to the phenanthroline catalyst increases the conversion from 44% to 90%.

The Cu$^{2+}$ catalysts formed with either N,N,N′,N′-tetramethyl-ethylenediamine (TMEDA), *rac*-1,2-diaminocyclohexane (DACH) or 9,10-diaminophenanthrene (DAPHEN) similarly oxidise veratryl alcohol as above [121]. Low conversions are noted with Cu$^{2+}$-(TMEDA) and Cu$^{2+}$-(DACH) catalysed reactions, with the most active catalyst being the poorly soluble Cu(DAPHEN). The catalytic precursor in Cu$^{2+}$-(TMEDA) catalysed reactions is proposed to be the binuclear hydroxyl bridged complex [(TMEDA)Cu-μ-(OH)$_2$-Cu(TMEDA)]$^{2+}$. The main reason for the deactivation of these catalysts was the reactivity of the ligands under the reaction con-

ditions. With TMEDA and DACH it was shown that this occurred by an imine condensation with the veratryl aldehyde as the oxidation reaction progressed. However, the DAPHEN ligand was observed to mainly decompose by a dimerisation process.

The *in situ* generated [Cu$^{II}$(pyridine-2-carboxaldehyde oxime)$_2$] complex also catalyses selective oxidation of veratryl alcohol but with a reduced activity compared to the bipyridine or phenanthroline complexes [122]. Under alkaline conditions, the catalyst is suggested to have both oxime groups deprotonated. However, the complex that crystallises from the catalytic solution reveals a square pyramidal geometry established by two protonated pyridine-2-carboxaldehyde oxime ligands and sulfate as a counter anion. This again shows that these solutions of Cu$^{2+}$ with simple chelate ligands contain a mixture of Cu$^{2+}$ complexes.

Oxygen-prebleached kraft pulp (OKP) was bleached with H$_2$O$_2$ under alkaline conditions using a Cu$^{2+}$ complex formed with either 2,2′-dipyridylamine (dpa) or 4-aminopyridine (4-ap) [123]. The selectivity for delignification, expressed by kappa number/viscosity was increased 12-fold and 2.6-fold by the coordination with dpa and 4-ap, respectively. ESR showed that the coordination suppressed the production of hydroxyl radicals by 57% for dpa and 47% for 4-ap. This finding suggests the involvement of a more selective hydroperoxo complex of Cu$^{2+}$ in this oxidation process.

Several cobalt catalysts (Fig. 14) namely Co(salen), Co(α-CH$_3$salen) [α-CH$_3$salen = N,N′-bis(α-methylsalicylidene)ethylenediamine], Co(4-OHsalen) [4-OHsalen = N,N′-bis(4-hydroxosalicylidene)ethylenediamine], Co(sulfosalen), Co(acacen) [acacen = N,N′-bis(acetylacetone)ethylenediamine)] and Co(*N*-Me-salpr) [*N*-Me-salpr = bis(salicylideniminato-3-propyl)methylamine] were compared in the O$_2$-oxidation of veratryl alcohol in alkaline solution [124]. The oxidation is selective for the benzylic position
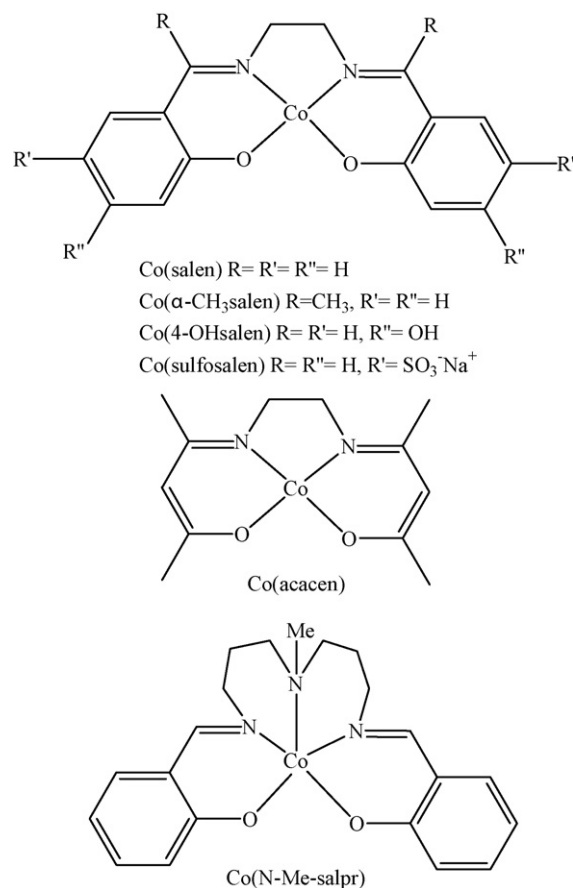


**Fig. 14.** Cobalt catalysts studied in the oxidation of model substrates for lignin.
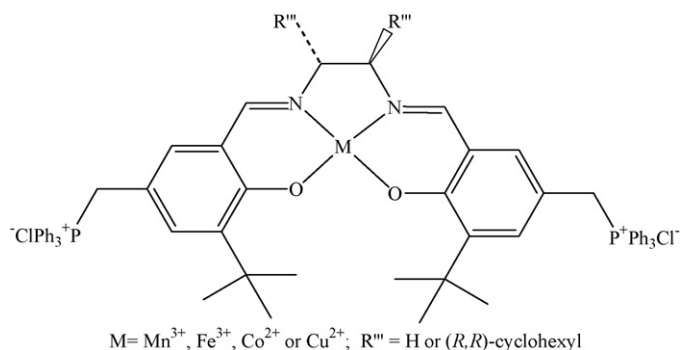
**Fig. 15.** Bulky water-soluble salen catalysts.

as veratryl aldehyde was the sole product. The unsubstituted Co(salen) was the most active and so was studied in most detail. Both the pH and temperature were found to be key with the reaction continuing for up to 72 h if the pH is kept at 12.5 and the optimum temperature is between 80 and 90 °C. Decomposition of the catalyst is seen at higher pH or higher temperatures. Reactivity increases linearly with increased $O_2$ pressure and the catalytic activity is further improved by increasing the catalyst:substrate ratio, e.g. the highest turnover number of 330 was seen with a ratio of 1:5950 (where the turn over number = moles of veratryl aldehyde produced per mole of complex). During the oxidation an insoluble red precipitate was noted which was ascribed to a bimetallic Co(salen) species.

In a separate study [125], the decomposition of the Co(sulfosalen) catalyst occurs via hydrolysis of the imine bond and was independent of the formation of the veratryl aldehyde unlike the Cu amine systems discussed earlier [121]. The decomposition of Co(sulfosalen) increased with increasing pH and was higher in the absence of oxygen. Additionally with the Co(sulfosalen) catalyst the generation of $H_2O_2$ strongly effects the oxidation of the lignin compounds and especially the depolymerisation of dextran [126]. However, adding phenylglyoxylic acid eliminated the effect of the generated $H_2O_2$ to enhance the selectivity for the delignification reactions.

The complexes of MnCl(salen) and Co(salen) were compared with related bulky water-soluble salen-type complexes (Fig. 15) in the oxidation of phenolic lignin model compounds in aqueous water–dioxane solutions (pH 3–10) [127]. Oxygen was used with the $Co^{2+}$ catalysts while $H_2O_2$ was employed with all the $Mn^{3+}$ catalysts. Here the simple salen complexes reacted much slower than the bulky complexes. The bulky $Mn^{3+}$ catalysts oligomerise coniferyl alcohol, i.e. 3-(4-hydroxy-3-methoxyphenyl)-2-propen-1-ol in a similar reaction time as the enzyme horseradish peroxidase (HRP). The $Mn^{3+}$ and $Co^{2+}$ catalysts yielded different one-electron products, i.e. oligomers versus dimers, suggesting a different substrate to catalyst interaction in the oxidative coupling. As seen earlier with Co(salen) [124], the oxidation of veratryl alcohol yielded veratryl aldehyde showing again that the complexes can catalyse two-electron oxidations depending on the bulk of the substrate.

The oxidation by $H_2O_2$ of the lignin model compounds, 1-(3,4-dimethoxyphenyl)ethanol, 1-(3,4-dimethoxyphenyl)-1-propene and E-1,2-diphenylethene has been compared for the catalysts $[Mn_2(\mu\text{-O})_3(Me_3TACN)_2](PF_6)_2$ (Fig. 6) and an analogue where the macrocyclic ligands are joined $[(Me_4DTNE)Mn_2(\mu\text{-O})_3](ClO_4)_2$ ($Me_4DTNE = 1,2\text{-bis}(4,7\text{-dimethyl-1,4,7-triazacyclonon-1-}$yl)ethane, Fig. 7) [128]. With $[Mn_2(\mu\text{-O})_3(Me_3TACN)_2](PF_6)_2$ the oxidation decreases above 60 °C, where the cause for this is again most likely to be due to decomposition of the catalyst as was seen earlier in its use with laundry. For example this

catalyst forms various species in solution, namely below pH 9.5 mononuclear manganese(IV) species seem to dominate the catalytic activity while at higher pH dinuclear species seem to dominate [74c,129]. Furthermore, when the two catalysts are compared, $[Mn_2(\mu\text{-O})_3(Me_3TACN)_2](PF_6)_2$ is more effective in the oxidation of 1-(3,4-dimethoxyphenyl)ethanol and 1-(3,4-dimethoxyphenyl)-1-propene but not E-1,2-diphenylethene.

The two $Mn^{4+}$ catalysts above were further studied in the bleaching of Pine Kraft-anthraquinone pulp with $H_2O_2$ under alkaline conditions at 80 °C for 2 h [130]. Afterwards the bleached pulp was hydrolysed with cellulase to allow analysis of the insoluble and soluble residual lignins. For both catalysts, the degradation of the residual lignin increased upon increasing the temperature from 60 to 80 °C. Thus, the findings of the catalysed delignification seem to differ from those observed in the oxidation of the model compounds catalysed by $[Mn_2(\mu\text{-O})_3(Me_3TACN)_2](PF_6)_2$ when the reaction temperature was increased above 60 °C. In addition, the resulting residual lignins in the $[(Me_4DTNE)Mn_2(\mu\text{-O})_3](ClO_4)_2$ catalysed bleaching at 80 °C are less degraded than the corresponding lignins from the $[Mn_2(\mu\text{-O})_3(Me_3TACN)_2](PF_6)_2$ catalysed bleaching. A possible explanation is that above 60 °C decomposition of the $[Mn_2(\mu\text{-O})_3(Me_3TACN)_2](PF_6)_2$ leads to some $MnO_2$ forming in solution and that this actually degrades the lignin as was discussed earlier [112].

The iron–TAML catalysts (Fig. 8b) of Collins and co-workers activate $H_2O_2$ in the bleaching of wood pulp [74b]. These iron–TAML catalysts give 60–75% delignification and at 50 °C the selectivity is competitive with the chlorine dioxide bleaching process.

The oxidation by $H_2O_2$ of lignin model compounds and lignin with several water-soluble anionic and cationic iron and manganese porphyrins (Fig. 16) has been explored [131]. The manganese porphyrins were found more effective in degrading lignin and its model compounds than were the related iron porphyrin. The most active catalyst was the cationic meso-tetra(N-methyl-pyridino)porphyrin-Mn(III) pentaacetate $[TPyMePMn](CH_3CO_2)_5$. Different reactivity was apparent with the manganese porphyrins, i.e. no significant condensation reactions occurred, compared with the iron porphyrin where a substantial increase of condensed structures was detected. This finding points to the formation of hydroxy radicals only with the iron porphyrin. The most active catalyst $[TPyMePMn](CH_3CO_2)_5$ was further studied in lignin oxidation when supported on the clay montmorillonite [132]. As now both the lignin substrate and the catalyst are insoluble in aqueous solution it was necessary for a redox mediator, e.g. veratryl alcohol or 1-hydroxybenzotriazole, to be employed to avoid any kinetic problems. The clay supported catalyst is a stable, recyclable, and efficient catalyst for the oxidation of lignin.

5,10,15,20-Tetrakis(4-sulfonato-phenyl)porphyrin-Mn(III) when supported on an imidazole-bearing silica showed a good ability to catalyse veratryl alcohol oxidation with $H_2O_2$ [133]. On a related theme, tetrakis(pentafluorophenyl)porphyrin-iron(III) chloride when supported on pyridyl-functionalized cross-linked poly(vinyl alcohol) was studied for catalytic oxidations by $H_2O_2$ [134]. Interestingly a dramatic enhancement was seen with the addition of $Mn^{2+}$ at neutral pH. Similarly, as was described in the example above, the $Mn^{2+}/Mn^{3+}$ acts as a redox mediator shuttling between the insoluble catalyst and the insoluble lignin.

Wood fibres can be modified for packaging applications by grafting synthetic polymers onto the cellulose backbone via a radical process. Therefore recently the radicalisation of several unbleached lignocellulosic fibres was studied using a Co(salen) catalyst with $O_2$ and discussed relative to similar studies with the enzyme laccase [135]. EPR spectroscopy identified that the amount of phenoxy cobalt radicals within the fibres was determined by the degree of swelling caused by the solvent, i.e. methanol causes more swelling than chloroform. The concentration of phenoxy radicals was 10
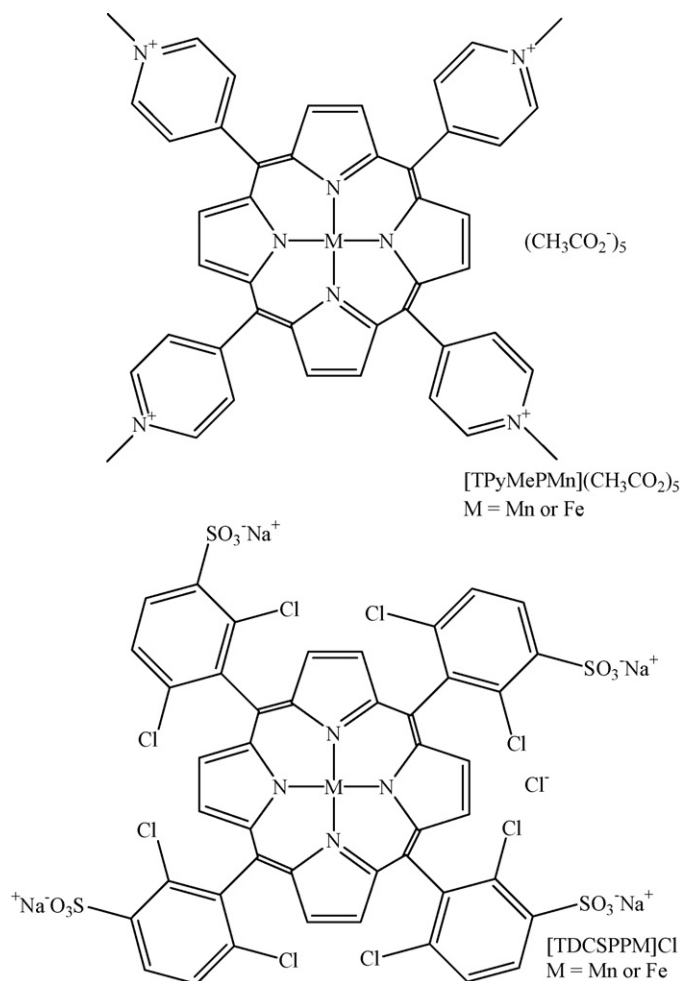
**Fig. 16.** Water-soluble catalysts of *meso*-tetra(N-methylpyridino)porphyrin and *meso*-tetra(2,6-dichloro-3-sulphonatophenyl)porphyrin.

times higher than that seen from similar oxidative processes catalysed by laccase. The fibres were also analysed before and after the radicalisation by scanning electron microscopy (SEM). The results show that under oxidative treatment chemothermomechanical (CTMP) pulps do not undergo morphology changes at the surface, while thermomechanical (TMP) pulps suffer heavy surface damage. Subsequently, a similar oxidation of TMP fibres was compared for either [Co(salen)] in methanol or [Co(sulphosalen)] in water [136]. Here the fibre integrity was highest after the process in water.

## 5. Developing areas—routes to new materials and applications

As cellulose is a hydrophilic bio-polymer, it was used to support the water-soluble catalyst $Pd(OAc)_2/5TPPTS$ [TPPTS = $P(m-C_6H_4SO_3Na)_3$] [137]. This formed a new heterogeneous catalyst for the Trost Tsuji allylic alkylation reaction of (E)-cinnamyl ethyl carbonate and morpholine in benzonitrile. Interestingly the activity of this catalyst depends upon its water content and the presence of this water in the reaction mixture failed to cause any unwanted leaching of the palladium catalyst. It was thought, however, that the catalytic reaction was hindered by the uncontrolled agglomeration of the particles under some reaction conditions. This aggregation was reduced by the addition of the surfactant cetyltrimethyl(ammonium) bromide but unfortunately this led to an increased leaching of the $Pd^{2+}$. In the context of this review, it

would be informative to see in the future whether using oxidised cellulose would reduce this leaching by providing more sites for coordination of the $Pd^{2+}$.

Waste newsprint paper has recently been functionalised with *p*-aminobenzoic acid to yield a sorption active gel [138]. Waste paper was chosen over cellulose as the former is more amorphous and accessible to such functionalisation. This gel selectively and efficiently recovers $Au^{3+}$, $Pd^{2+}$ and $Pt^{2+}$ over other coexisting metal ions such as $Cu^{2+}$, $Ni^{2+}$, $Zn^{2+}$ and $Fe^{3+}$ from hydrochloric acid solution. With $Au^{3+}$ a reduction occurred to elemental gold which then aggregated. The gel was regenerated by using a mixture of thiourea and HCl. Naturally, in the context of this review it would be interesting here to further study whether bleaching the waste paper rather than washing with NaOH would improve the metal uptake by providing additional sites for the complexation of metal ions as is discussed later with starch materials.

Optical sensors for $Hg^{2+}$ have been developed on a cellulose support by incorporating a probe molecule, 1-(2-pyridylazo)-2-naphthol or cis-dithiocyanatobis-(2,2′-bipyridine-4,4′-dicarbo xylic acid)-4,4′-tridecyl-2,2′-bipyridineruthenium(II) [139]. The sensors were produced by the codissolution of cellulose and the probe in the ionic liquid 1-butyl-3-methylimidazolium chloride (BMImCl) prior to casting into a thin film. The ionic liquid is then simply removed by washing with water to form strips. These strips exhibit a proportionate (1:1) response to $Hg^{2+}$ in water and may be easily regenerated by further washing with water.

Similarly, calix[4]arenes were immobilized in a cellulose-based film for either the removal or detection of $NO_x$ gases [140]. Again the ionic liquid BMImCl was used to co-dissolve cellulose and the calix[4]arenes before casting into a film. If these films are exposed directly to $NO_x$ gas then a rapid calixarene–$NO^+$ complexation occurs with an accompanying colour change. Depending on the desired application (i.e. sensing or storage), the $NO_x$ complexation can be quickly or slowly reversed with humidity.

Porous plates made of nanofibrous crystalline cellulose have been synthesised as a support for microbial cultures [141]. For example the growth of the microorganisms *Escherichia coli*, *Bacillus subtilis*, and *Saccharomyces cerevisiae* was similar on the cellulose plate or a traditional agar plate. The cellulose plates were shown by microscopy to be stable under harsh conditions and so were used to culture the thermophile *Thermus thermophilus* at 80 °C. This demonstrates that these cellulose plates have some advantages over agar- and gellan gum-derived media, including both versatility and stability.

Starch was firstly modified by a telomerisation reaction with butadiene prior to it being successfully used as a solid support for a chiral pyridine-bis(oxazoline) (Pybox) ligand. Subsequent reaction with $[RuCl_2(p$-Cymene)]_2$ under an ethylene atmosphere yielded a ruthenium Pybox catalyst for the cyclopropanation reaction of styrene with ethyl diazoacetate. The supported catalyst exhibited lower activity and selectivity than the unsupported complex but higher than silica immobilised catalysts. It was demonstrated that the yield, diastereoisomeric excess and enantiomeric excess remained constant over three runs [142]. This report firstly suggests the use of biomass as solid supports in organometallic catalysis reactions and secondly in the context of this review it could be envisaged that by using oxidised biomass additional substrate directing groups could be included to further improve the selectivity.

Dialdehyde starch (DAS) (Fig. 17) with various degrees of oxidation has been used to synthesis a number of complexes of its dioxime (DASOX) [143], starch dialdehyde dithiosemicarbazone (DASTSC) [144] and starch dialdehyde aminothiazole (DASAT) [145]. In complexation between DASTSC and the metal ions $Ca^{2+}$, $Cd^{2+}$, $Co^{2+}$, $Cu^{2+}$, $Fe^{2+}$, $Mg^{2+}$, $Mn^{2+}$, $Ni^{2+}$, $Pb^{2+}$, and $Zn^{2+}$, the imino nitrogens and the sulphur atoms are proposed as the chelating
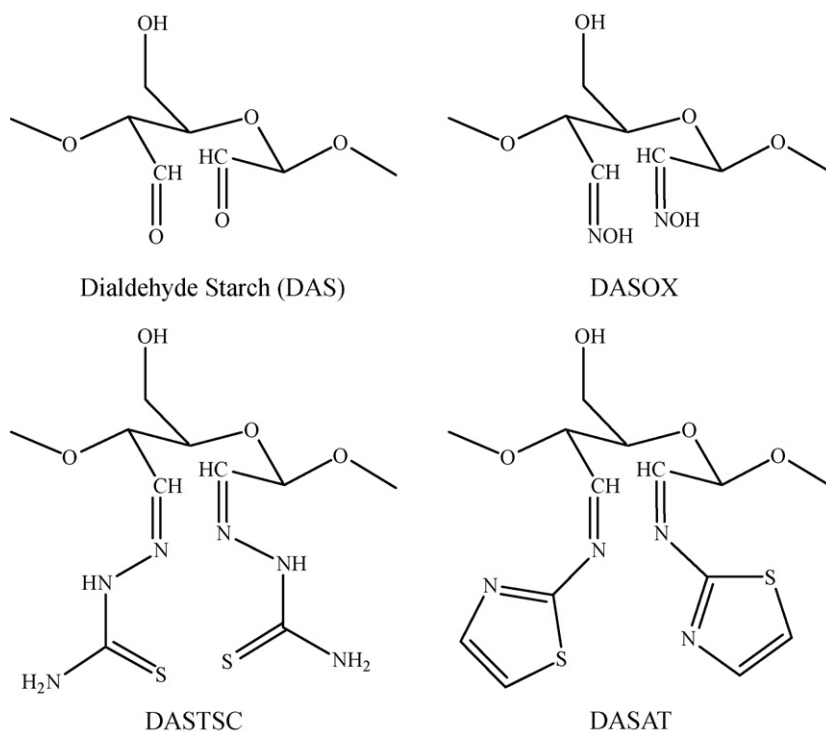
Fig. 17. Modified dialdehyde starch for studies on the adsorption of metal ions (only the oxidised unit of the starch polymer is shown).

sites for the metal ions. Similarly with DASOX the dioxime was again coordinated to the same series of metal ions [143]; e.g. $Cu^{2+}$ and $Fe^{2+}$ were the most strongly bound to DASOX while $Mn^{2+}$ and $Zn^{2+}$ were the most weakly bound ions. The authors proposed these findings suggest applications for either the DASTSC or the DASOX materials in the temporary immobilisation of heavy metal ions in the remediation of contaminated soil.

Starch dialdehyde aminothiazole (DASAT) was synthesised with different degrees of substitution (DS = 0.29, 0.46 and 0.78) to assess the adsorption of $Cu^{2+}$ ions from water [145]. The adsorption capacity was optimum between pH 6 and 7 and increases with the increasing degree of substitution of the DASAT. The optimum adsorption time is 120 min and the adsorption is greatest at the highest temperature studied of 60 °C. In light of the earlier discussion in this review of the metal catalysed oxidation of starch, functionalisation of starch with imino ligands needs to be undertaken cautiously to avoid forming complexes that will activate oxygen and catalyse the oxidative depolymerisation of the starch.

After first cross-linking cornstarch with epichlorohydrin, it was oxidised with $H_2O_2$ and a $CuSO_4$ catalyst [146]. Subsequent studies with this material for the removal of $Ca^{2+}$ ions from water showed the adsorption efficiency increased proportionally with both the carboxyl content and the concentration of starch material in the water. Ionisation of the carboxyl groups in starch was necessary for the effective removal of the $Ca^{2+}$ ions. When the pH was below 4, the starch was no longer an effective sequestering agent and so by lowering the pH to 2 the material was easily regenerated.

With use of the biodegradable compounds oxidised starch, hydroxyapatite and deacetylated chitosan a new biodegradable bone wax substitute was developed with the potential to also act as a bone filling material [147]. The hydroxyapatite particles were adapted in a layer-to-layer process involving the oxidised starch and deacetylated chitosan. In water, the different particles are linked by Schiff base reactions between the aldehyde groups of the oxidised starch and the amino groups of the deacetylated chitosan. The lack of cytotoxicity of this new composite was assessed in vitro

by seeding the surface with MC3T3 mouse fibroblasts. It was then seen by fluorescence spectroscopy that the cells proliferated well on the surface showing good biocompatibility.

Dialdehyde starch (DAS) when dispersed in aqueous solution shows activity in antiviral tests against three non-envelop viruses, namely two bacterial viruses MS2 and PRD1, and one human virus Poliovirus [148]. The antiviral activity was appreciably enhanced with a longer exposure time, reaching a maximum of seven orders of magnitude reductions against MS2 and PRD1, and four-order reduction against Poliovirus. The antiviral activity of DAS was pH-dependent, showing higher activity in acidic or alkaline media compared to neutral pH. The ability of DAS to be dispersed in water is critical, as simple granular suspensions by comparison demonstrated a reduced activity. Similarly this dispersion allows the easy casting of films onto surfaces, which the authors suggested advocates applications in the formation of antimicrobial surfaces.

The drug deferoxamine (DFO, Fig. 10) as its mesylate derivative is effective in iron chelation therapy but it often needs prolonged daily infusions, which in turn can result in poor compliance by patients [149]. Therefore DFO was conjugated to starch to form a high-molecular-weight iron chelator, which shows a prolonged vascular retention and is biocompatible. In trials drug-related adverse events were limited to four urticarial reactions (i.e. skin rashes), none necessitating termination of the trial. The starch–DFO conjugate safely produced clinically significant urinary iron excretion over 1 week. Consequently, treatment with starch–DFO by a weekly dose could help treat iron balance in poorly compliant patients.

Lignin materials have been reviewed as sorbents for a range of pollutants including metals, surfactants, dyes, pesticides and phenols [150]. In particular, the surface charge characteristics and functional group present in lignins, especially kraft lignin, are suitable for metal sorption. Sorption of $Cu^{2+}$ and $Cd^{2+}$ improved with increasing pH and decreasing ionic strength. It was suggested that additional pretreatment and surface modifications (e.g. increased oxidation to provide more carboxylic acids on the surface) of

these biosorbents might further improve metal sorption ability and develop their application to the treatment of metal-containing water or wastewater [151]. Similarly, lignocellulosic biosorbents have been modified with iron species from acid mine drainage and studied in the subsequent removal of phosphorus from water [152].

Recently, the higher absorption of hydrophobic organic contaminants (HOCs) (e.g. pyrene, phenanthrene and naphthalene) by lignins in comparison to chitins and celluloses has been discussed [153]. Therefore the presence of lignins will reduce both the mobility and bioavailability of HOCs in soil, sediment organic matter or waste material. Interestingly, once the alkyl and aromatic domains of lignin are concealed by nearby polar groups formed via oxidation with $NaIO_4$, the absorption of HOCs is lowered. Furthermore, coating both chitins and celluloses with lignin improves their absorption of HOCs. These studies point to chemical properties, such as functionality, polarity and structure, jointly controlling the absorption of HOCs in biopolymers.

## 6. Conclusions

This review has discussed examples of catalytic oxidations which have been applied to different types of biomass often to achieve quite different goals. For instance, the oxidation of the surface of biomass compared to the oxidation of stains on the surface of the biomass. Often researchers have studied firstly the catalysts with model small molecules under homogeneous conditions, before using the catalysts with actual biomass where the substrate is naturally more variable and often less soluble. Common challenges have been identified with respect to using catalysts in water, catalyst decomposition, selectivity, competing depolymerisation of the biomass, etc. Clear progress has been made but if materials based on biomass are to replace the current petrochemical derived materials then there is still much more work to be done. One obvious aspect is that the cost of the catalysts needs to be lower or recycling strategies need to be introduced. Additionally the highly efficient oxygenase catalysts employed by Nature often contain more than one metal ion, while the bulk of the research reviewed herein has involved monomeric metallic complexes. Similarly, Nature often uses several catalysts (i.e. enzymes) together to transform biomass while chemists currently tend to only use one catalyst at a time. The potential applications of biomaterials are varied and at an early stage of replacing more traditional polymers. Although compared to traditional polymers, biomaterials do generally display the added advantages of biocompatibility and biodegradability. However, further tuning of catalytic oxidation processes will greatly advance this while also enabling the realisation of many new materials and applications.

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