Mild photocatalysed and catalysed green oxidation of lignin: a useful pathway to low-molecular-weight derivatives

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Abstract

Two commercial Ca^{2+} and NH_4^+ lignin derivatives were catalytically oxidised and photooxidised both aerobically and in presence of H_2O_2 (Fenton system), under green conditions (water solution, 20 °C, 1 atm), to obtain fractions with reduced degrees of polymerisation. Analyses of the oxidised solutions were carried out using NMR, MS and UV spectrometry. The catalytic and photocatalytic systems used showed satisfactory conservation of the organic material, except for the Fenton system. Lignins showed some mineralisation when irradiated in the presence of $H_5[PMo_{10}V_2O_{40}]\cdot xH_2O$ (POM-1), $K_5[Ru(H_2O)PW_{11}O_{39}]$ (POM-2), $K_4[SiW_{12}O_{40}]\cdot 8H_2O$ (POM-3) and TiO_2. When the POMs were used as thermal catalysts, POM-3 was almost inactive, while the reactivities of POM-1 and POM-2 under both thermal and photochemical conditions were comparable, revealing little effect of irradiation on the reaction mechanism. The best compromise appears to be the TiO_2 photosystem, which shows low carbon consumption, good preservation of aromatic rings, and greatly reduced mineralisation. Alternatively, POM-1 can be used, and particularly under thermal conditions.

Keywords Lignin; Photocatalysis; Titanium dioxide; Polyoxometalates; Aerobic oxidation; Green chemistry

Introduction

The present concept of 'green chemistry' [1] drives us towards the new uses of residues that are obtained in large amounts from modern industries. On average, lignin constitutes 25% of the plant biomass [2], and it is one of the major derivatives of woody plants and the only aromatic carbon source that is generated in nature [3]. Lignin is a natural, heterogeneous, arylpropanoid polymer, mainly obtained as a waste product in the wood-pulp and sugar-cane milling industries [4]. The use of lignin is becoming more and more attractive for several reasons: (i) independence from the supply and cost of fossil resources; (ii) increases in pulp production without extension of the recovery plant (thus generating a surplus of black liquor); and (iii) readily available in large quantities.

The use of lignin as a biofuel is one solution, while its further conversion for the formation of useful products, e.g. phenols, and/or biodiesel components, would be of added value. In the latter case, a homogeneous mixture of low-molecular-mass products would be desirable, and such a goal can be reached only through looking for innovative procedures for efficient degradation pathways of the isolated lignin. At present, however, there is wide heterogeneity in terms of purity and chemical structure of the lignins [5, 6], and they result from several, often very dissimilar, pretreatment procedures e.g. organosolv, steam explosion, hydrolytic treatments, among others [7]. Moreover, there is a lack of general protocols for the assessment of lignin degradability and its potential for fragmentation reactions.

It is worth noting that the industrial processes that produce second-generation bioethanol by fermentation of cellulose [8, 9] also have important potential as eventual lignin procedures. Lignin has an important physiological role, as it is biosynthesised by plants to provide structural rigidity, to prevent hydrolysis of cellulose, and to protect from external chemical and/or biological attack. Therefore an *ad-hoc* reduction of lignin rigidity through suitable biological or chemical pre-treatments might facilitate enzymatic fragmentation of the cellulose to sugars [10, 11].

Depolymerising lignin is not a new concept, and hydrolysis is probably the first proposed process to find application for the production of short-chain reaction products. Already in 1932, scientists obtained formaldehyde at a considerable yield by hydrolysing lignins in the presence of 12% HCl aqueous solution [12]. Other interesting investigations were performed in the late 1970's by Goldstein and co-workers [13], who obtained phenols and phenolic acids from lignin and bark.

The aliphatic C–C and C–O bonds that characterise the three-dimensional lignin polymers are not particularly sensitive to hydrolytic attack that leads to aromatic derivatives, although the presence of metal catalysts might facilitate the breaking process [14]. Some recent reports have revealed an additional problem linked to the hydrolysis: if the experimental temperature and pressure conditions are not best optimised, repolymerisation processes take place, together with the depolymerisation [15]. Better results in terms of yields of aromatic derivatives (around 20%) can be obtained by

coupling, for example, alkaline hydrolysis with catalytic hydrogenolysis: an oily fraction containing several para-dealkylated monomeric phenol-based compounds has been obtained this way [16].

Oxidation processes under aerobic conditions and in water have been successfully tested with lignin polymers, and they have resulted in mixtures of aromatic aldehydes of great industrial interest. However, the severe operating conditions (150-400 °C, 5-20 bar) are a serious limitation to this proposed technology [17]. Comparable results at lower temperatures and pressures can be obtained by adding a metal catalyst (catalytic wet-air oxidation): for example, black palladium metal supported on γ-alumina effectively converts lignin into aromatic aldehydes [18].

A promising green approach would be the biotransformation of lignin. A Japanese/ Korean study tested the biotransformation of high-molecular-weight lignin under sulphate reducing conditions. Although the transformation yields were relatively low (even conducting the experiments over very long times; e.g. 100 days), the physical parameters of the reaction were certainly less severe (37 °C) [19]. Similarly, white-rot fungi can also degrade lignin, as these fungi produce extracellular enzymes that are associated with ligninolysis, such as lignin peroxidase, manganese peroxidase and laccase [20].

Many studies have applied well-known chemical (hydrolysis, oxidation, reduction), physical (pyrolysis, cracking), and more recently, biological (laccases, peroxidases) transformations to different lignins. However, the issue is far from being resolved: either the experimental conditions are too severe, or alternatively, the yields in the desired products are not satisfactory. In many cases mineralisation occurs, wasting organic carbon that is potentially useful for re-use.

The goal of the present study was to obtain high yields of partially oxidised lignin fractions, through selective oxidation of the alkyl carbons, and at the same time, with preservation of the aromatic rings. Our approach was to apply several advanced oxidation processes that selectively act on the aliphatic carbon moieties and that have been used previously to degrade lignin, even if these are not under particularly green conditions [22-24]. As catalysts, we considered three polyoxometalates (POMs; see Experimental section) under both thermal and photochemical conditions, the Fenton system and titanium dioxide (TiO_2). POMs have been extensively proposed in the past for the delignifying of woody biomass. Many studies have reported applications that use POMs as oxidants under anaerobic conditions, with the subsequent aerobic reoxidation of the reduced POMs [25-28]. The absence of oxygen makes the oxidation more selective *versus* lignin moieties, thus avoiding oxidation of other fibres, such as cellulose. The temperatures, however, remain greater than 100 °C, and these reactions have often been carried out in pressurised autoclave apparatus. Recently, other groups have studied the one-step aerobic reaction in the presence of POMs [29], and sometimes in association with ionic liquids [30], or in a modified solution containing simple alcohols. This last was used to minimise the repolymerisation process, and simultaneously to maximize the yields of simple aromatic derivatives [31]. In our experiments we used a

lower concentration of POMs (3 mM) under extremely mild conditions (room temperature and pressure, and in aqueous solution).

Material and Methods

Materials

The lignin samples used for these investigations were the ammonium (AmLig) and calcium (CaLig) derivatives, and were a kind gift from Burgo Group S.p.A. (Tolmezzo, Italy). They were produced by cooking red pine in a calcium hydrogen sulphite solution. Both of these lignin derivatives are brown powders that are highly soluble in water. Ultra-pure water was produced using a Milli-Q 185 plus purification system that was equipped with a Millipore cartridge. The sorbent sample tubes (Anasorb CSC; 6 mm OD x 70 mm length) were purchased from SKC Inc. They were filled with coconut shell charcoal that was split in two sorbent sections with 100 mg (analytical) and 50 mg (control) sorbent material. Research grade TiO_2 (P-25 Degussa), ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$), hydrogen peroxide (H_2O_2; 35%) and all of the reagents necessary for synthesis of the three POMs were purchased from Aldrich.

Instruments

Nuclear magnetic resonance (NMR) spectra were obtained using a Bruker Avance 300 spectrometer (7.05 Tesla) equipped with a high-resolution multinuclear probe that operated in the range of 30 MHz to 300 MHz. Except for the Fenton system, which required pretreatment with 0.1 M NaOH to precipitate the iron, the proton spectra (^{1}H NMR) of the lignin water solutions were run, without any treatment, in an NMR tube (5 mm) that contained a closed co-axial capillary tube that was filled with a 30 mM 3-trimethylsilyl-2,2'3,3'-tetradeutero propionic acid (sodium salt). Free induction decays (FIDs) were acquired at 22 °C using a pulse sequence (Bruker-made; zgcppr) that suppresses the water signal at 4.7 ppm. The spectral width was -1 ppm to 12 ppm (3894.081 Hz). A 90° excitation pulse and a 1 s relaxation delay were used to collect 64 scans. ^{1}H NMR spectra in $CDCl_3$ solution were acquired using TMS as reference, and the standard pulse sequence (zg) was used. For the carbon NMR spectra (^{13}C NMR), a proton decoupling pulse sequence (zgdc) was used. The spectral width was 0 ppm to 240 ppm (18115.941 Hz), while the 90° excitation pulse and 5 s relaxation delay were used to collect 12,000 scans. For the phosphorus NMR spectra (^{31}P NMR), the simple standard pulse sequence (zg) was used; the spectral width was -40 ppm to 40 ppm (9842.520 Hz), while the 90° excitation pulse and 1 s relaxation delay were used to collect 1,000 scans.

UV visible spectra were recorded using a Jenway 6505 UV/Vis system. Before acquisition, the reaction mixtures were diluted 10 times with ultrapure water, directly into the 3 mL high-precision quartz cell (made of Suprasil® quartz; Hellma), and the spectra were then acquired over the wavelength range of 190 nm to 580 nm.

The gas chromatography–mass spectroscopy (GC-MS) apparatus comprised a Thermo Scientific Focus series gas-chromatograph coupled to an ISQ mass-selective detector equipped with a split-splitless injection system (injections made in splitless mode) and an HP5 MS (cross-linked 5% phenyl methyl siloxane) capillary column (15 m length, 0.25 mm diameter, 0.1 μm film thickness) using helium as carrier gas at constant pressure of 50 kPa. The acquisition parameters were: source at 250 °C, transfer line at 250 °C, 3 min of delay acquisition time at the beginning of the analysis, mass range 33 amu to 350 amu, injector temperature 250 °C, initial temperature of the analyses 50 °C (1 min), then 8 °C/min up to 120 °C (kept for 0 min), and 20 °C/min up to 250 °C (kept for 5 min), for a total acquisition time of 20 min.

A photochemical multirays apparatus assembled by Helios Italquartz was used for the photochemical reactions, which contained ten UV lamps of 15 W power each that emit light centred at 254 nm. Open quartz tubes (20 mL) were used to irradiate the aqueous lignin solutions, both under homogeneous and heterogeneous conditions. For the heterogeneous conditions (in the presence of TiO_2), a magnetic stirrer was placed inside the photochemical multirays apparatus.

Methods

Photochemical reactions were carried out using 5 mL or 10 mL of a 2.5% (w/w) aqueous lignin solution that was transferred into several open quartz tubes, each of which was equipped with a magnetic stirrer; these were irradiated together for a maximum of 48-h. The experiments carried out in the presence of TiO_2 were performed by adding TiO_2 powder (1 g/L), while the reactions with POMs were carried out at 3 mM POMs. The POMs used were: $H_5[PMo_{10}V_2O_{40}]\cdot xH_2O$ (POM-1), $K_5[Ru(H_2O)PW_{11}O_{39}]$ (POM-2) and $K_4[SiW_{12}O_{40}]\cdot 8H_2O$ (POM-3). Their synthetic procedures are reported briefly as follow; for further details, see references [32-34].

POM-1: An solution of 30.0 g $NaVO_3$, 3.4 mL 85% H_3PO_4 and 74.0 g MoO_3 in 800 mL of water was refluxed for 8 h. After acidification with 145 mL of concentrated HCl, the product was extracted with 200 mL of ether and purified by recrystallisation from water.

POM-2: Equimolar amounts (0.01 mol) of $K_7[PW_{11}O_{39}]\cdot 15H_2O$ and cis-$[Ru(H_2O)_2(DMSO)_4](BF_4)_2$ were dissolved in water and heated to 40 °C under a nitrogen atmosphere. A red product separated upon addition of methanol, which was recrystallised from the water–methanol. For the synthesis of the two precursors, see references [35,36]

POM-3: A solution of 15 g $Na_2WO_4 \cdot 2H_2O$ and 0.85 mL alkaline (NaOH) Na_2SiO_3 solution (26.5% as SiO_2) in 30 mL of water was heated to close to the boiling point, while 10 mL concentrated HCl were added drop-wise. After cooling and filtering, a further 5 mL of concentrated HCl was added to the clear solution. Diethyl ether solvent extraction allowed separation of the acid, which was dried at 70 °C. The white crystalline product was titrated with KOH to obtain the corresponding salt.

Thermal reactions were carried out in 20 mL test-tubes equipped by magnetic stirrers and left at room temperature for the times necessary in the study (maximum 48 h). The Fenton treatment was carried out by bringing 8.7 mL 2.5% lignin solution to pH 2 with HCl, followed by addition to this acidic solution of 0.5 mL 0.6 M $FeSO_4 \cdot 7H_2O$ and 0.15 mL 35% H_2O_2. The mixtures were stirred at room temperature for 48 h.

The reaction mixtures, together with the control solutions, were then analysed by ESI-MS, UV visible spectrophotometry and NMR (^{1}H, ^{13}C and ^{31}P).

Separation of volatile derivatives from the reaction mixtures (headspace) was carried out by purging the closed tubes with air and trapping the resulting air current on a sorbent sample tube containing coconut-shell charcoal. Desorption steps were performed by adding 1 mL chloroform onto the charcoal sample; the chloroform solutions were then analysed by GC-MS.

The extraction of the low polar fraction from the reaction mixture was carried out by shaking the aqueous solution with 3 mL chloroform; after the separation, the chloroform fraction was analysed by GC-MS.

The CO_2 formed was measured by purging the closed tube with air and trapping the resulting air current in a freshly prepared $Ba(OH)_2$ solution; the CO_2 content was evaluated gravimetrically, by weighting the residual $BaCO_3$.

Results and Discussion

The elemental compositions of the two lignins used in the present study are reported in Table 1. Lignins absorb UV light with high molar extinction coefficients because of the several methoxylated phenylpropane units of which they are composing (Fig. 1). The effects of UV light irradiation ($\lambda = 254$ nm) were tested in an aqueous solution and in the presence of heterogeneous (TiO_2) or homogeneous photocatalysts (POM-1, POM-2 and POM-3). (see Experimental section). Thermal catalytic systems were also tested: a Fenton system and aerobic oxidation catalysed by each one of the above POMs, selected as a representative vanadophosphomolybdate (POM-1), a d-electron-containing, namely the second-row transition metal cation [Ru(II)], (POM-2), and the widely used photoactive silicotungstate anion (POM-3) [37].

After the irradiation, the 2.5% lignin solutions were a little lighter in colour than initially. In contrast, the Fenton reaction led to complete bleaching of the solution (after the removal of iron), while the thermal oxidation in the presence of POMs did not produce any colour change, at least within 48 h. The latter was the standard reaction time chosen for all experiments, which allowed to satisfactorily follow the course of the reactions, by also complying with the relative stability or photostability of the catalysts. For the phosphorus-contained POMs (POM-1 and POM-2), ^{31}P NMR enabled us to follow the fate of the catalysts during the oxidation reaction of the lignin samples. In all of the experiments carried out in the dark, the ^{31}P NMR signal did not change significantly (-3.1 ppm for POM-1 [38], Supplementary Material Fig. S1; and -10.3 ppm and -10.6 ppm for POM-2 [33], Supplementary Material Fig. S3), while under irradiation, the ^{31}P signal of POM-1 disappeared completely after 2 days of irradiation by being replaced by the phosphate signal (Supplementary Material Fig. S2) clearly indicating extensive photodegradation. POM-2 behaved differently, with no phosphate signal appearing during the photoreactions; however, the two diagnostic peaks at -10.3 ppm and -10.6 ppm (Supplementary Material Fig. S3) changed in intensity, and furthermore, several small signals were detected between -11 ppm and -12 ppm (Supplementary Material Fig. S4), likely due to some structural modifications of the intact POM. POM-3 was tested photochemically in aqueous solution without lignin, and after more than 2 days it still appeared unchanged, as revealed by UV spectroscopy.

A first preliminary analysis of the irradiated solutions was carried out by measuring the weight loss of the lignin. Apart from the Fenton system, the fraction lost during these treatments never exceeded 18% (Table 2, entry 8) thus indicating that, if mineralisation occurred, it was a minor pathway. In contrast, the Fenton treatment consumed 70% to 75% of the whole lignin, thus making efficient recovery of the organic fraction problematic. The residual organic fraction was analysed by GC and GC-MS; after evaporation of the solvent and derivatisation with etherate diazomethane, only short-chain carboxylic and dicarboxylic acids were detected.

In most of the above experiments, the UV profiles and the relative intensities of the diagnostic signals of lignins, at 230 nm (shoulder) and 280 nm (aromatic rings), remained almost unchanged (Fig. 1). The spectra of the irradiated (48 h) samples in the presence of TiO$_2$ (Fig. 2), POM-1 and POM-3 exhibited only minor changes in the intensities of their signals at 280 nm for both lignins; however, in the presence of POM-2, this absorption peak disappeared almost completely (Fig. 3). After the Fenton treatment, the bands relative to the lignin disappeared completely after only 2 h of reaction.

In the thermal catalytic aerobic oxidations by POMs, a significant reduction in the signal at 280 nm was observed only with POM-2, and with no significant differences between the two lignins (Fig. 4). With the exception of the experiments with the Fenton system and the thermal and irradiated POM-2 catalytic system, the 280 nm absorption of the other systems remained unchanged, thus strongly suggesting that the aromatic moieties were largely preserved from

oxidation, which clearly occurred on the aliphatic carbons, as previously reported by Mariano and colleagues in a detailed study on some simple lignin models [39, 40].

The low molecular weight compounds that formed during the oxidation reactions were analysed by GC-MS, for both the chloroform extract of reaction mixtures and the headspace of the reaction tubes, trapped on charcoal (see Experimental section for details). In the POM irradiated solutions, appreciable amounts of vanillin, hydroxyl-methoxy-acetophenone, coniferyl alcohol and coniferyl aldehyde were found (Table 3), by being vanillin and coniferyl aldehyde the most abundant, with maximum values in entries 2-4 and 9-11 of Table 3. The headspace showed the presence of phenol, 2-hydroxybenzyl alcohol and salicylaldehyde, although in very low amounts, thus not interfering in the mass balance of the oxidation reactions (<0.05%). In all GC-MS investigations, however, the extremely volatile compounds were undetectable, since covered by the solvent, and ^{1}H-NMR measurements resulted of great help, clearly indicating the presence of methanol, formic acid, acetic acid, and sometimes, small amounts of C-2 and C-3 alcohols (Fig. 5; for relative amounts of formic and acetic acids, see Table 4). The ^{13}C-NMR spectra were almost unchanged.

The ^{1}H-NMR spectra were also used to calculate the R values (Table 5), as the ratios between the areas relative to the regions where the aliphatic and aromatic protons fall. This index provide a useful tool to investigate the relative extend of the degradation i.e. it occur prevalently on aliphatic side chains or on aromatic rings [41]. In both the thermal and photochemical reactions with POM-2, R,s definitely increased, in agreement with the largest sample weight loss observed (Table 2, entries 3 and 8). Thus, degradation was here the most important pathway, with no differences between the thermal and photochemical reactions. Therefore, by taking also into consideration the large quantities of CO_2 formed (Table 2, entries 3 and 8) and the presence of short-chain products, like acetic acid, formic acid (Table 4, entries 3 and 7) and acetone (data not shown), we can conclude that POM-2 triggers faster destruction of the lignin than any other aerobic oxidations considered here.

To better understand the behaviour of POM-2, we tested separately the effects of ruthenium (II) aquo-ion and of the precursor of POM-2 namely $K_7[PW_{11}O_{39}]$. To obtain sufficiently stable Ru (II) ion in water, the well-known Ru(II) complex $Ru(DMSO)_4Cl_2$ was used, which undergoes easy replacement of the DMSO and chloride ligands by H_2O units, as demonstrated in previous reports [42]. In the presence of the aquo Ru^{+2} ion and in absence of irradiation, both of the lignins showed a slightly increase in the R value, while the UV and ^{1}H NMR spectra remained unchanged; also the lignin solutions containing $K_7[PW_{11}O_{39}]$, kept for two days at room temperature and in the dark, remained unchanged, indicating a very low catalytic effect. The irradiation of the lignins in the presence of Ru(II) lead to a moderate degradation of the aromatic fraction (as monitored by 280 UV absorption), with a concomitant increase in the R value (6.0 and 5.7 for CaLig and AmLig, respectively) and conservation of the ^{1}H NMR spectral pattern; the presence of $K_7[PW_{11}O_{39}]$ under irradiation lead to the destruction of the aromatic rings, by UV and ^{1}H-NMR evidences, whereas R values increased to 6.4 and 5.9

(for CaLig and AmLig, respectively), with a noticeable production of short-chain derivatives (e.g. methanol, formic acid). From a comparison of the data obtained with POM-2 and "naked" ruthenium, it can be concluded that the caged ruthenium/POM complex results into an enhancement of the catalytic activity only in the dark, whereas under irradiation the reaction pathways are essentially the same, likely indicating the same redox mechanism. Moreover, these results confirmed that to degrade aromatic organic pollutants ruthenium acts as a monoelectronic catalyst, as previously reported on several occasions [43].

With POM-3, the differences between the thermal and photochemical pathways were much more significant, even if the weight losses were always very low, with CO_2 formed under the detection limit and the 280 nm bands substantially preserved, at least in comparison with the other POMs. In contrast, the R values were preserved only in the thermal reactions, while they were considerably enhanced in the photochemical reactions, thus pointing to a critical role of UV light, as shown in previous investigations [44]: under our experimental conditions, the photoreaction was addressed particularly towards transformations of the aromatic moieties, leading to the formation of monomers, like vanillin and coniferyl aldehyde, without noticeable mineralisation.

The R values for POM-1, for both thermal and photochemical experiments, are particularly difficult to interpret, as they increased slightly, and in some cases, surprisingly, they decreased, even if the weight losses of the samples were always low (around 10%) and the mineralisation to CO_2 was in the range of 1% to 2 % (Table 2, entries 2 and 7). Significant amounts of acetic acid and formic acid were detected, especially during the photochemical reactions (Table 4, entries 2 and 6). It is important to note that acetic acid and formic acid are volatile substrates (noting also that the solutions were in acidic medium), and as the values reported in Table 2 come from a solvent-evaporation step at reduced pressure, they do not take these compounds into consideration. Considering also the negligible decrease in the 280-nm band in the UV Vis spectra and the moderate quantity of aromatic monomers (see Table 3), we can conclude that the oxidation involved both aliphatic side chains and aromatic rings at a comparable ratio.

In the presence of TiO_2, the ΔR was about one unit, and it only became important during the second day of irradiation (Table 5, entries 1 and 9). The weight losses of the samples were low in both cases (9% and 1%, for AmLig and CaLig, respectively), in agreement to the negligible mineralization, not greater than 1% (as CO_2 content), while formic acid formation was significant, particularly for CaLig. We can conclude here that the formic acid and other volatile products were indeed adsorbed onto the TiO_2 during the evaporation step of the solvent (which was necessary to weight the samples at the end of the reactions). The 280 nm band was largely preserved (by about 60%), indicating that the aromatic rings were only partially oxidised, although mineralisation was kept to relatively low levels. It is worth mention that the aromatic monomers were formed in low amounts. These findings support the concept that the aromatic rings are

not particularly subjected to oxidation, and during their rearrangements, the detachment of aromatic moieties leading to the carbonyl and alcoholic aromatic monomers are not the preferred reaction pathway.

Conclusion

At present, it is difficult to state unambiguously what (photo)catalytic system is the best one to obtain a selective cleavage of aliphatic C-C bonds, without appreciable losses of organic material and with preservation of the aromatic rings, though some conclusion can be done.

The Fenton system is certainly inappropriate, as it degrades the organic matter almost completely, mainly to CO_2, with 20% to 25% residual essentially containing only short-chain carboxylic derivatives.

The photoreactions with POM-3 exhibit the most significant increase in the ratio between aliphatic and aromatic carbons (the R value $\geq$ 1.4), POM-2 and TiO_2 showed a less pronounced increase ($\Delta R \approx 1$) while POM-1 is the photocatalyst with the best conservation of the initial R value. On the other hand, POM-2 shows the most marked quenching of the 280 nm band and leads to the largest consumption of the organic carbon for both the lignins tested. Comparing the thermal with the photochemical reactions, it is evident that the POMs are less selective when used as photocatalysts, as an important mineralisation step often takes place. However, when they were used as thermal catalysts, in the case of POM-3, no appreciable bleaching of the solution was seen, together with an unmodified R value, which indicates an oxidative power that is not satisfactory for purpose. POM-1 and POM-2 behave similarly both in the thermal and in the photochemical reactions, which indicates a negligible effect of irradiation on the reaction mechanism (it should be noted that, to the best of our knowledge, $K_5[Ru(H_2O)PW_{11}O_{39}]$ (POM-2) has never been used as a photocatalyst). Another important finding to be considered is the scarce photostability of POM-1 and POM-2 catalysts, for which a re-use is unlikely to be effective; however, POM-1 can be successfully used under dark aerobic conditions to obtain lignin fractions of lower molecular weight.

TiO_2 photooxidation probably represents the best compromise, with a relatively moderate increase in the R value, a low amount of carbon-loss fraction and a good preservation of the 280 nm absorption band; this heterogeneous catalyst can be recovered easily from the reaction mixture.

If we consider the additional purpose, i.e. the selective production of monomeric aromatic derivatives from lignin, the best results are obtained with POM-2 and POM-3 catalysts under irradiation, which lead, especially in the presence of POM-2, to large amounts of vanillin and coniferyl aldehyde, even if extended mineralisation also takes place and, more important, the catalyst does not appear fully intact after 48 h reaction. For the POM-3/ UV system, we believe

that the intended optimisation of the oxidative procedure, e.g. the addition of methanol to avoid the repolymerisation process, might enhance the yields of aromatics that will be attractive for industrial applications.

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Table 1. Elemental compositions of the two lignins obtained from the dried samples at 105 °C for 2 h.

Lignin	Element (%)				
	C[a]	H[a]	N[a]	S[b]	Ca[c]
AmLig	44.82	5.51	3.66	7.67	--
CaLig	44.25	5.22	0.05	5.97	3.76

[a] By CHN analysis;

[b] Obtained gravimetrically by HNO_3/ H_2O_2 microwave mineralization, and subsequent precipitation with $BaSO_4$;

[c] By ICP analysis

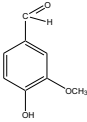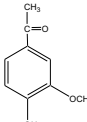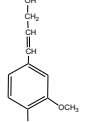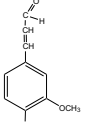**Table 2.** Residual levels of the lignins and the CO_2 formed after 48 h of thermal or photochemical reactions. The experiments were conducted at room temperature and in aqueous solution, with weighing of the entire solute before and after the treatments. The % of CO_2 is related to the total carbon content.

Entry	Lignin	Catalyst	Thermal reaction		Photoreaction (254 nm)	
			Residual levels (%)	CO_2 (%)[a]	Residual levels (%)	CO_2 (%)[a]
1	AmLig	TiO_2	--	--	91	0.8
2	AmLig	POM-1	90	1.5	92	2.1
3	AmLig	POM-2	90	7.0	86	11.2
4	AmLig	POM-3	97	< 0.5	101	< 0.5
5	AmLig	Fenton	28	n.a.	--	--
6	CaLig	TiO_2	--	--	99	< 0.5
7	CaLig	POM-1	92	1.1	88	2.3
8	CaLig	POM-2	91	5.5	82	12.3
9	CaLig	POM-3	99	< 0.5	95	< 0.5
10	CaLig	Fenton	25	n.a.	--	--

[a] : 0.5% is the detection limit of the method used to evaluate $BaCO_3$
n.a., not available

Table 3. The aromatic derivatives detected by chloroform extraction of reaction mixture; the vanillin contents of blank solutions were 6 mg/L for AmLig, and 12 mg/L for CaLig; mg/L units refer to the aqueous lignin solutions.

Entry	Lignin	Catalytic system	(mg/L)	(mg/L)	(mg/L)	(mg/L)
1	AmLig	UV/TiO$_2$	15	2	2	10
2	AmLig	UV/POM-1	50	3	3	31
3	AmLig	UV/POM-2	71	1	4	45
4	AmLig	UV/POM-3	105	9	4	65
5	AmLig	POM-1	46	1	0	0
6	AmLig	POM-2	6	1	0	0
7	AmLig	POM-3	15	2	0	2
8	CaLig	UV/TiO$_2$	6	2	7	5
9	CaLig	UV/POM-1	76	5	5	36
10	CaLig	UV/POM-2	133	12	8	65
11	CaLig	UV/POM-3	125	11	5	68
12	CaLig	POM-1	67	2	0	0
13	CaLig	POM-2	12	1	0	0
14	CaLig	POM-3	12	1	0	0

Table 4. Acetic acid and formic acid levels detected by ^{1}H-NMR, after 48 h of reaction.

Entry	Lignin	Catalyst	Thermal reactions		Photoreactions (254 nm)	
			CH$_3$COOH (mg/L)	HCOOH (mg/L)	CH$_3$COOH (mg/L)	HCOOH (mg/L)
1	AmLig	TiO$_2$	--	--	109	455
2	AmLig	POM-1	25	194	45	320
3	AmLig	POM-2	81	134	56	43
4	AmLig	POM-3	62	0	46	141
5	CaLig	TiO$_2$	--	--	82	677
6	CaLig	POM-1	82	92	74	793
7	CaLig	POM-2	51	6	38	204
8	CaLig	POM-3	71	18	46	376

Table 5. Ratio (**R** value) between the relative areas of the aliphatic and aromatic protons in the ^{1}H-NMR spectra. Experiments were carried out at room temperature and in aqueous solution.

Entry	Lignin	Catalytic system	R value		
			0 h	**24 h**	**48 h**
1	AmLig	UV / TiO$_2$	4.57	4.40	5.54
2	AmLig	UV / POM-1	4.65	--[a]	5.20
3	AmLig	UV / POM-2	4.65	--[a]	5.68
4	AmLig	UV / POM-3	4.65	--[a]	6.04
5	AmLig	POM-1	4.57	4.53	4.86
6	AmLig	POM-2	4.57	5.94	5.79
7	AmLig	POM-3	4.57	4.89	4.92
8	AmLig	Fenton	4.57	∞[b]	--
9	CaLig	UV / TiO$_2$	4.92	5.06	5.91
10	CaLig	UV / POM-1	4.85	4.71	5.02
11	CaLig	UV / POM-2	4.85	5.46	5.80
12	CaLig	UV / POM-3	4.85	6.30	6.80
13	CaLig	POM-1	4.92	4.55	4.34
14	CaLig	POM-2	4.92	5.65	5.55
15	CaLig	POM-3	4.92	4.89	5.10
16	CaLig	Fenton	4.92	∞[b]	--

[a] data not available;
[b] the total area of the aromatic protons (the denominator of the ratio) was 0

Figure captions

Figure 1. UV-vis spectrum of AmLig in aqueous solution.

Figure 2. UV-Vis spectra of CaLig in aqueous solution. Arrow: before (top trace), and after 24 h (middle trace) and 48 h (bottom trace) of UV irradiation at 254 nm in the presence of TiO_2

Figure 3. Normalised absorbance at 280 nm from UV Vis spectra following 48 h of UV irradiation at 254 nm (t0 before irradiation), as indicated.

Figure 4. Normalised absorbance at 280 nm from UV Vis spectra following 48 h of thermal catalytic aerobic oxidation (t0 before thermal oxidation), as indicated.

Figure 5. ^{1}H-NMR spectra of the CaLig with TiO_2 at 0, 24 and 48 h of irradiation. All NMR acquisitions were carried out in aqueous solution using a pulse sequence that suppressed the water signal at 4.7 ppm; a co-axial closed capillary containing 30 mM D_2O solution of 3-thrimethylsilyl-2,2',3,3'-tetradeutero sodium proprionate was placed inside the NMR tube.
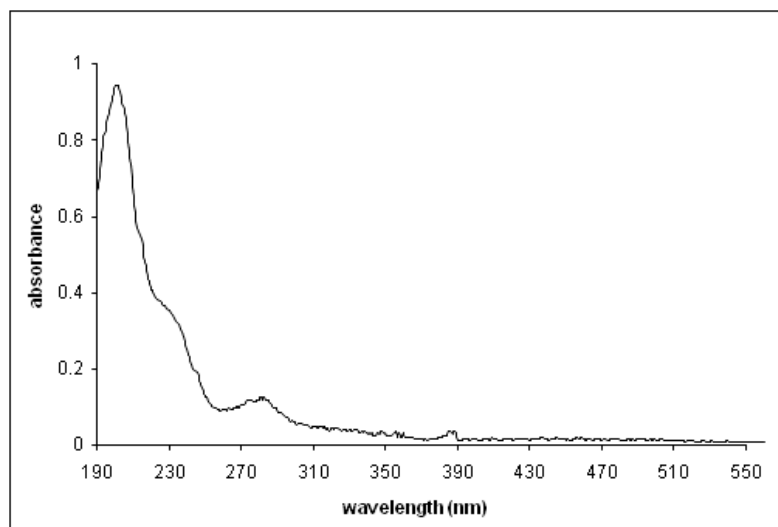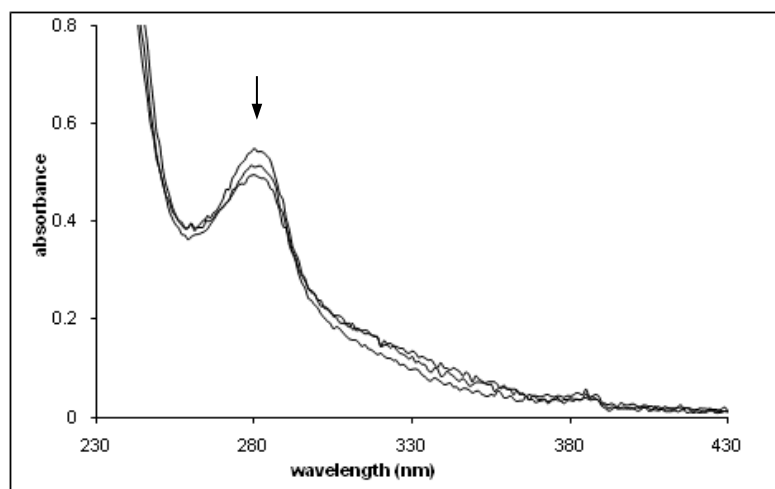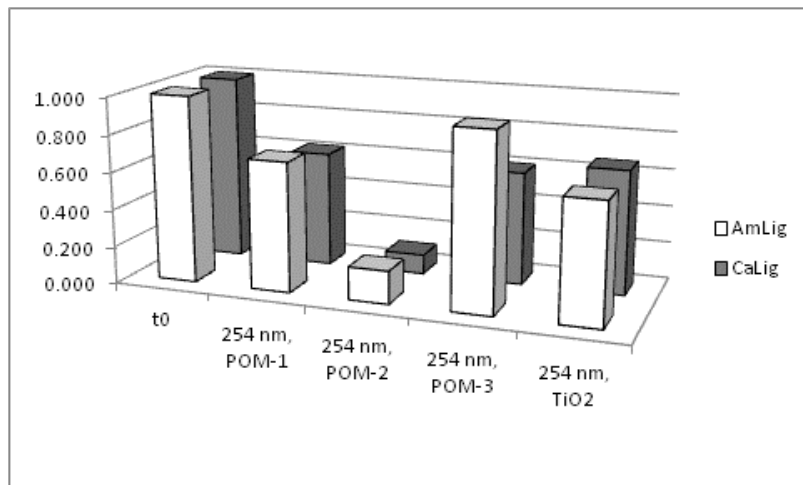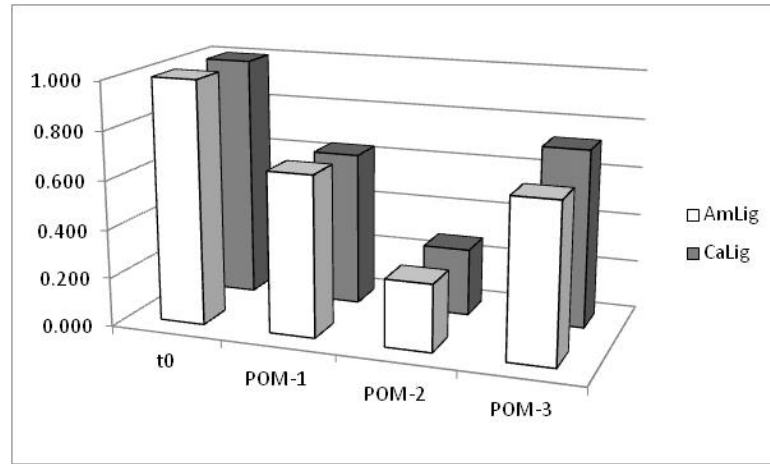
Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

t = 48 h

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0   ppm

t = 24 h

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0   ppm

t = 0 h

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0   ppm