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Methyltrioxorhenium: a new catalyst for the activation of hydrogen peroxide to the oxidation of lignin and lignin model compounds

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Abstract—The oxidative degradation of lignin under totally chlorine free conditions is one of the most relevant targets for the design of environmental friendly pulping and bleaching industrial processes. Methyltrioxorhenium was found a powerful and promising catalyst for the oxidation of both phenolic and non-phenolic lignin model compounds by use of hydrogen peroxide as primary oxidant. Three different technical lignins, hydrolytic sugar cane lignin (SCL), red spruce kraft lignin (RSL) and a hardwood organosolvent lignin (OSL), that are representative examples of widely diffused *para*-hydroxyphenyl–guaiacyl, guaiacyl and guaiacyl–syringyl lignins, were also extensively degraded under similar experimental conditions.

1. Introduction

In the paper production processes, environmental concerns prompted to design pulping and bleaching sequences avoiding the use of chlorinated compounds. Totally chlorine free (TCF) processes have been developed, as for example by the use of oxygen, hydrogen peroxide (H_2O_2) and ozone as oxidants.[1] However their major drawback consists in a lack of selectivity in the oxidation of lignin, which leads to the partial degradation of the cellulose contained in pulps, and ultimately in a lower final product yield. This lack of selectivity is mainly due to the formation of radical intermediates, such as hydroxyl radicals that are able to attack both cellulose and lignin.[2] Selective catalytic processes based on the activation of environmental friendly H_2O_2 might solve these problems.

A novel catalyst potentially useful for this purpose is methyltrioxorhenium (VII) ($MeReO_3$, MTO).[3] MTO, in combination with H_2O_2, has became in recent years an important catalyst for a variety of synthetic transformations, such as oxidation of olefins,[4] alkynes,[5] sulfur compounds,[6] phosphines,[7] Bayer–Villiger rearrangement[8] and oxygen insertion into C–H bonds.[9] Accordingly with this high reactivity, MTO is able to catalyze the oxidation of aromatic derivatives.[10] In this latter case the reaction proceeds through the formation of reactive arene epoxide intermediates that further rearrange and are oxidized to corresponding benzoquinones. *para*-Benzoquinones are usually obtained by oxidation of alkyl phenols that lack of substituents on the C-4 position of the aromatic ring. In the presence of bulky substituents, as in the case of cardanols (3-*n*-pentadecyl phenol derivatives), *ortho*-benzoquinones can be obtained in high yields because of steric hindrance to the approach of the catalyst to the aromatic ring.[11] Alkoxyl-substituted benzenes are less reactive than the corresponding phenolic derivatives towards MTO.[12] To date, a concerted mechanism for the oxygen transfer from MTO monoperoxo and diperoxo intermediates by a 'butterfly' transition state is the accepted reaction pathway for MTO, while radical processes have not been reported.[4] To the best of our knowledge, there are no reports in the literature dealing with the use of MTO in the oxidation of polymeric phenolic derivatives like lignin. With the aim to design new catalytic systems for environmental friendly pulping and bleaching processes, we started to study the use of MTO in the oxidative degradation of lignin and lignin model compounds with H_2O_2 as primary oxidant. We selected an array

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of lignin model compounds resembling the main bonding patterns in native and technical lignins and studied their reactivity with MTO. Our attention was next turned to more complex lignin polymers, hydrolytic sugar cane lignin (SCL), red spruce kraft lignin (RSL) and hardwood organosolvent lignin (OSL), that are representative examples of widely diffused *para*-hydroxyphenyl–guaiacyl, guaiacyl and guaiacyl–syringyl lignins. Their oxidation was studied by means of advanced ^{31}P NMR techniques that allow the quantitative determination of all labile OH groups on the polymer—that is, aliphatic, different phenolic OH groups, carboxylic acids—after phosphitylation of the sample.[13,14]

MTO showed to be a powerful and efficient catalyst for the oxidation of phenolic and non-phenolic lignin model compounds affording both side chain oxidations and aromatic ring cleavage reactions. Diphenylmethane models that are usually recalcitrant to oxidation, were also found extensively degraded mainly by cleavage of the interunit bonding. MTO was also able to catalyze the extensive degradation of all technical lignins, increasing their degree of solubility and reducing the content in condensed subunits.

2. Results

2.1. Oxidation of lignin model compounds

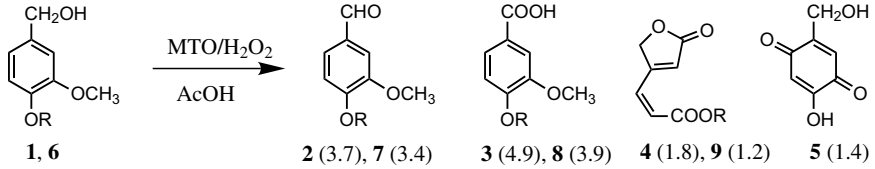
The reactivity of aromatic model compounds resembling the most representative lignin bonding patterns is of pivotal interest in order to rationalize the oxidative behaviour of the polymer. Thus, an array of monomeric and dimeric, phenolic and non-phenolic lignin model compounds was selected in order to clarify the reactivity of lignin subunits with H_2O_2 and MTO as catalyst.

Vanillyl alcohol **1**, veratryl alcohol **6**, 1-(4-hydroxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)propane-1,3-diol **10**, 1-(4-ethoxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)propane-1,3-diol **14**, 1-(4-ethoxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol **23**, 2,2′,3,3′-tetramethoxy-5,5′-dimethyl-diphenyl methane **28** and 2,2′-dihydroxy-3,3′-dimethoxy-5,5′-dimethyl-diphenyl methane **35** were studied as substrates. Reactions were carried out treating the appropriate substrate (1.0 mmol) with H_2O_2 (35% aqueous solution, 1.5 mmol) and MTO (1.0% w/w) in CH_3COOH (5.0 mL) at room temperature during 6.0 h. Acetic acid was selected as solvent because MTO is reported to display in this solvent its maximum catalytic activity.[6] Irrespective from the experimental conditions used for the oxidation, a low mass-balance with respect to isolated products was observed showing an high efficiency for the reaction. In accordance with results previously reported in the literature, the loss of material from the reaction mixture might be due to formation of polar hydrophilic over-oxidation products not recovered by usual work-up procedures.[15]

Reaction products were characterized by means of gas chromatography–mass spectroscopy (GC–MS) analysis after derivatization with bis(trimethylsilyltrifluoroacetamide) (BSTFA) and, when necessary by ^{1}H and ^{13}C NMR determinations. In the absence of the catalyst less than 5% conversion of substrate took place under otherwise identical experimental conditions.

The simplest lignin model compound studied was vanillyl alcohol **1**. The oxidation of **1** proceeded with >95% conversion of substrate to give products of alkyl side-chain oxidation, vanillin **2** and 4-hydroxy-3-methoxybenzoic acid **3**, the muconolactone **4** and the *para*-benzoquinone derivative **5** (Scheme 1, here and elsewhere products yields are reported in parentheses).

The presence of compounds **2** and **3** are in accordance with data previously reported on the reactivity of simple aromatic hydrocarbons, such as toluene, with H_2O_2 and MTO, in which case the oxidation of the benzylic group was the main observed process. Muconolactone **4** was obtained by an extensive oxidative ring opening of **1** to a muconic acid intermediate (not recovered under our experimental conditions) followed by formation of the lactone moiety. Muconolactone derivatives have been previously recovered as minor products in the oxidative degradation of lignin model compounds.[16] The isolation of the *para*-benzoquinone **5** is in accordance with the known reactivity of methoxybenzenes with MTO.[12] In this latter case, the reaction proceeds by initial oxygen atom insertion on the *para*-position with respect to the methoxy substituent followed by demethylation and formation of the quinone moiety. A similar behaviour was observed in the oxidation of the non-phenolic model compound **6**. Upon treatment with H_2O_2 and MTO a quantitative conversion of substrate was observed (>98%) and products of alkyl side-chain oxidation, 3,4-dimethoxybenzaldehyde **7** and 3,4-

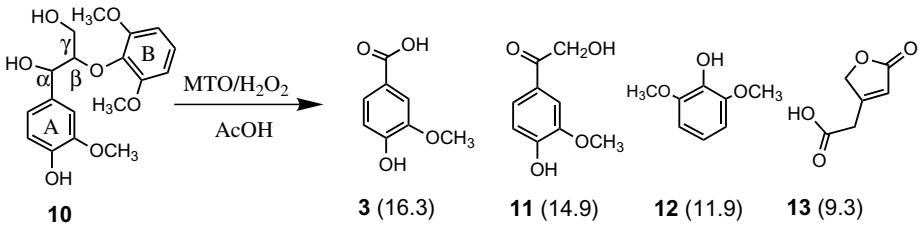


1, **6** **2** (3.7), **7** (3.4) **3** (4.9), **8** (3.9) **4** (1.8), **9** (1.2) **5** (1.4)

1,2,3,4 R=H

6,7,8,9 R=CH_3

Scheme 1.



Scheme 2.

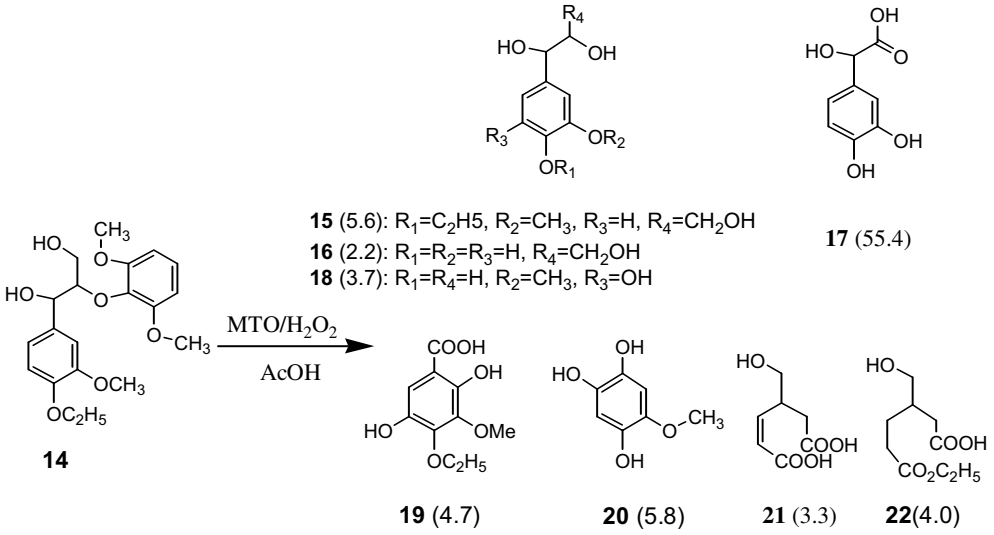
dimethoxybenzoic acid (veratric acid) **8**, and the muconolactone **9** were obtained (Scheme 1).

Our attention was next focused on the oxidation of dimeric lignin model compounds. The β-O-4 dimeric compound **10** represents the most diffuse bonding pattern in hardwood lignins (guaiacyl–syringyl lignins, **GS**-lignins). The oxidation of compound **10** showed an extensive degradation of the substrate (>98% conversion) and a reactivity pattern close to that observed for **1** (Scheme 2).

Low amount of products of alkyl side-chain oxidation and successive cleavage at the α-position, 4-hydroxy-3-methoxybenzoic acid **3**, or at the β-position, the hydroxyketone **11** (deriving from the aromatic A-ring of the substrate) and 2,6-dimethoxyphenol **12** (deriving from the aromatic B-ring of the substrate) were recovered in the reaction mixture. The muconolactone **13** was also recovered in appreciable yield. However, a high molecular weight (>550) compound, probably a trimer or tetramer, that showed in GC–MS a molecular peak fragment corresponding to benzyl alcohol substructure, could not be unambigously identified (see next).

The oxidation of compounds **14** and **23** that are hardwood (guaiacyl–syringyl lignin, **GS**-lignin) and softwood (guayacyl) non-phenolic lignin model compounds, respectively, showed interesting reactivity patterns (Scheme 3). Even if non-phenolic lignin model compounds are usually less reactive than the corresponding phenolic ones,[12] in the presence of MTO a high conversion of substrate was obtained in both cases (>95%). The **GS**-lignin model compound **14** yielded products of alkyl side-chain oxidation and cleavage at the β-position, compound **15**, followed in some cases by dealkylation of the alkyl–aryl ether moieties, as in cathecols **16**–**18**, or by fragmentation at α-position and partial hydroxylation of the aromatic ring, compounds **19** and **20** (Scheme 3).

On the basis of the reactivity showed by MTO in the oxidation of anisole derivatives,[6] it is reasonable to suggest that the *para*-benzohydroquinone **20** can be formed by initial oxidation of the aromatic ring to a reactive arene oxide. Successive acidic rearrangement of this intermediate to a γ-hydroxy cyclohexadiene, followed by hydrolytic C-α side-chain degradation, dealkylation and hydroxylation on the activated *para*-position (with respect to the methoxy substituent) afforded **20**. Supporting evidence for this hypothesis is provided by previously reported results on the oxidation of β-O-4 non-phenolic lignin model compounds with dimethyldioxirane (DMD). DMD is a stoichiometric oxidant characterized by a butterfly diperoxo like transition state similar to that observed for MTO peroxo intermediates in the oxidation of arenes.[17] In this latter case a *para*-benzohydroquinone derivative,



Scheme 3.

2-methoxy-1,4-dihydroxy benzene, similar to **20**, was recovered in the reaction mixture.[18] Reactive cyclohexadienyl intermediates were identified by electrospray ionization mass spectrometry during the biomimetic one-electron oxidations of β-O-4 non-phenolic lignin model compounds with heteropolyanion $[PMo_7V_5O_{40}]^{-8}$.[19] It is interesting to note that **20** was previously obtained by reaction of vanillin with the UV-alkaline peroxide system. In this latter case, the addition of the hydroperoxide anion by a Dakin transformation was suggested as a plausible reaction pathway.[20] Compound **19** is probably an over-oxidized derivative of initially formed 4-ethoxy-3-methoxybenzaldehyde. Benzaldehyde derivatives such as 3-methoxy-4-hydroxybenzaldehyde (vanillin) and 3,4-dimethoxybenzaldehyde (veratraldehyde) are typical products of biomimetic degradation of β-O-4 phenolic and non-phenolic lignin model compounds with porphyrins resembling the active site of lignin peroxidases and manganese dependent peroxidases.[21]

Products of alkyl side-chain oxidation and aromatic ring cleavage, the muconic acid derivatives **21** and **22**, were also recovered in the reaction mixture. Compound **22** that shows apparently a reduced structure, was probably obtained by an internal redox process. Signals referring to reduced lignin subunits were previously observed in the ^{1}H and ^{13}C NMR spectra of extensively oxidized lignins.[22] In a similar way, the oxidation of compound **23** afforded products of alkyl side-chain oxidation and cleavage at the α- and β-positions deriving both from the A-aromatic ring of substrate, products **24**, **26** and **27**, or from the B-aromatic ring, compound **25** (Scheme 4).

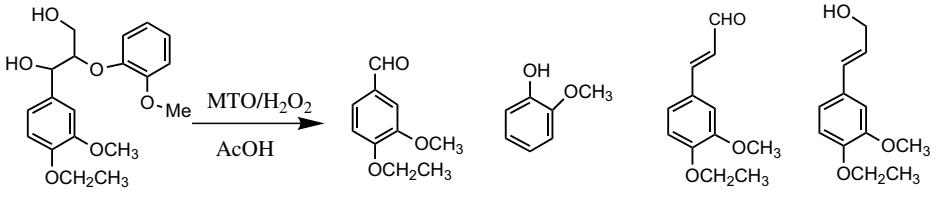
In this latter case, the occurrence of acid-catalyzed (acidolytic) cleavage of β-O-4 linkages due to the acidity of MTO was concluded on the basis of the presence of 2-methoxyphenol **25** as a typical acidolysis product. Compound **25** was probably obtained by formation of a benzyl cation followed by β-hydrogen elimination and hydrolytic cleavage. The effective formation of a benzyl cation under acidolytic cleavage of β-O-4 lignin model compounds was previously detected by means of ESI/MS analysis.[23]

In the case of compound **26** and **27**, the alkyl side-chain was found dehydrated in accord with the acidic Lewis and Brönsted character of MTO.[4] In analogy with the oxidation of **10** reported above, a high molecular weight (>550) compound that showed in GC–MS a molecular peak fragment corresponding to 4-ethoxy-3-methoxy benzyl alcohol substructure, was recovered.

In order to further investigate the structure of the high molecular weight products produced during the oxidation of β-O-4 lignin model compounds, the LC–MS analysis of the high molecular weight product from model **14** was performed. The molecular ion peak M = 618 showed a value corresponding to twice the molecular weight of substrate with loss of a water molecule. In accordance with the GC–MS molecular ion fragmentation, and since MTO is considered to catalyze oxidation with H_2O_2 without formation of radical species, this tetramer was tentatively identified as a product of nucleophilic addition of one of the free hydroxy groups on the side-chain of **14** on the benzylic cation derived by acidolysis of a second molecule of substrate. This hypothesis is in accord with the above reported presence of other products from the acidolytic pathway.

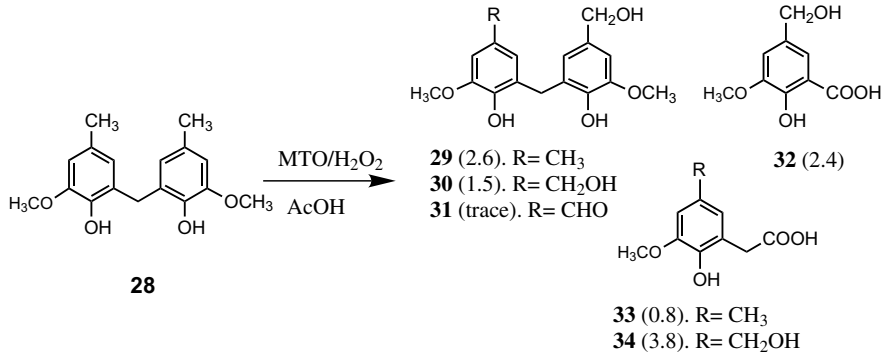
Diphenylmethane subunits are formed during lignin pulping processes, their amounts varies upon the specific wood species and pulping procedure used.[24] Diphenylmethanes present in lignin show high recalcitrance to oxidation and their efficient degradation requires severe reaction conditions in bleaching processes.[18] In order to study the reactivity of such lignin subunits towards the H_2O_2/MTO system two diphenylmethane lignin model compounds **28** and **35** were oxidized. The oxidation of **28** performed under previously described experimental conditions gave products showing a different degree of oxidation at the benzylic positions, compounds **29**, **30** and **31**, alkyl side-chain oxidation and cleavage of the diphenylmethane bridge, compound **32**, or deriving from the oxidative cleavage of one of the aromatic ring as showed by the presence of a two carbon atom alkyl side-chain, compounds **33** and **34** (Scheme 5).

The presence in the reaction mixture of compounds **32**–**34** is noteworthy. In fact, on the basis of these data, it is possible to suggest that MTO can effectively catalyze the oxidative degradation of lignin containing high amount of recalcitrant diphenylmethane subunits by decreasing their reticulation grade. When the non-phenolic diphenylmethane lignin model compound **35** was submitted to oxidation under the same experimental conditions several products of side-chain oxidation to benzyl alcohol **36** and **37**, aldehyde and carboxylic acid, compound **38**, were detected. Moreover, products of demethylation at the alkyl–aryl ether moieties, **39**, **40** and **41**, and deriving from the oxidative cleavage of one of the aromatic rings, compound **42**, were also found (Scheme 6, prod-

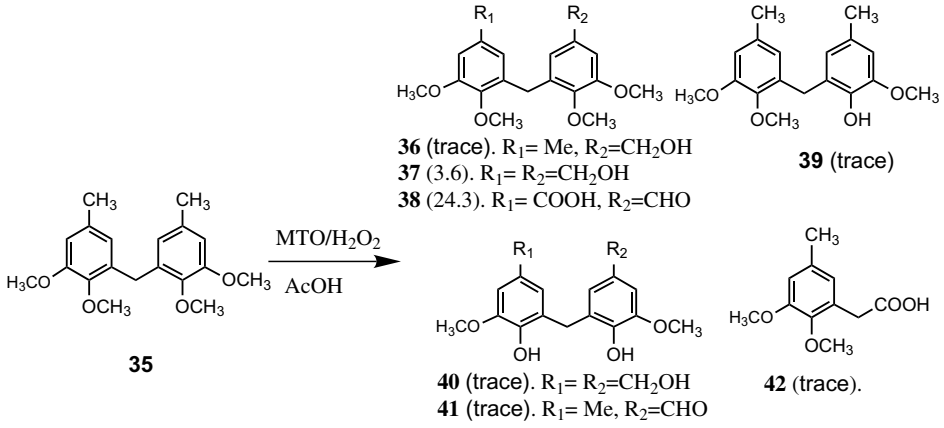


23 **24** (3.4) **25** (24.4) **26** (5.8) **27** (7.3)

Scheme 4.



Scheme 5.



Scheme 6.

ucts yields are reported in parentheses). It is interesting to note that the methyl ester of **42** (not shown) was previously recovered in low amount after the ozonation of **35**. In accordance with the reactivity showed by MTO, this derivative was formed by initial oxidative ring opening of one of the aromatic rings to give the corresponding muconic acid derivative followed by a stepwise oxidative degradation.[25]

Products of oxidation of the activated benzylic position and oxidative cleavage of one of the aromatic moieties were recently observed in the treatment of phenolic and non-phenolic diphenylmethane lignin model compounds with polyoxometalate[26] and by hydrogen peroxide biomimetic oxidation with manganese and iron porphyrins.[27] In this latter case, the site of oxidation was determined by the distribution of the electronic density on the aromatic ring, which was in turn modulated by the electronic effect of the substituents.

From the data above reported it is possible to conclude that the catalytic system H_2O_2/MTO is able to extensively oxidize monomeric and dimeric, phenolic and non-phenolic, lignin model compounds. In all the cases studied the cleavage of the alkyl side-chain, or both alkyl side-chain oxidation and aromatic ring cleavage were operative processes. Recalcitrant diphenylmethane units were also efficiently degraded.

2.2. Oxidation of lignins

Once clarified the reactivity of MTO towards lignin model compounds, our attention was focused on the oxidation of the lignin polymer. Technical lignins are samples of lignin recovered after pulping processes. As such they are chemically modified and contain significative amounts of condensed subunits heavily recalcitrant to further oxidation treatments. In order to verify the ability of MTO to degrade the complex phenolic polymeric structures present during bleaching processes, we selected three different technical lignins, from hydrolytic, kraft and organosolvent processes, respectively.

More specifically, a hydrolytic sugar cane lignin (SCL), a red spruce kraft lignin (RSL) and a hardwood organosolvent lignin (OSL) were selected as representative examples of *p*-hydroxyphenyl–guaiacyl, guaiacyl and guaiacyl–syringyl lignins.

The lignins were submitted to oxidation with H_2O_2 and MTO as catalyst. After recovery, the samples were derivatized with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane in the presence of a known amount of cholesterol as internal standard.[13,14] In Table 1 the amounts of the different labile OH groups expressed as millimole per gram of lignin as measured by ^{31}P NMR of phosphytilated samples are reported. Since

Table 1. MTO/H_2O_2 oxidative degradation of lignins analyzed by ^{31}P NMR

Sample/treatment	Aliphatic OH (mmol/g)	Condensed/syringyl OH (mmol/g)	Guaiacyl OH (mmol/g)	*p*-Hydroxy phenyl OH (mmol/g)	COOH (mmol/g)
SCL/CH_3COOH	1.7	0.82	0.50	0.560	0.807
SCL/CH_3COOH, H_2O_2, MTO	0.921	0.29	0.354	0.548	1.26
OSL/CH_3COOH	1.052	1.822	0.755	—	0.367
OSL/CH_3COOH, H_2O_2, MTO	0.904	0.984	0.606	—	0.535
RSL/CH_3COOH	1.587	0.713	0.278	—	0.882
RSL/CH_3COOH, H_2O_2, MTO	0.528	0.289	0.173	—	1.504

Data are reported as millimoles of each functional group per gram of lignin; RSL: red spruce kraft lignin MW 28,000; SCL: sugar cane hydrolysis lignin; OSL: Organosolvent hardwood lignin (50% maple, 35% birch, 15% aspen).

the oxidations were carried out in glacial acetic acid, the occurrence of acidolytic side processes should be considered.[28] For this reason data about reference experiments carried out treating the samples with acetic acid are also reported in Table 1. The oxidative treatments induced an appreciable decrease in the content of aliphatic OH groups (43%, 14% and 67% reduction in SCL, OSL and RSL, respectively), thus indicating the occurrence of side-chain oxidation reactions. Syringyl OH units in OSL were found to be reduced of 46%. All the lignins showed guaiacyl OH groups reduction after MTO catalyzed oxidation, while *para*-hydroxyphenyl (*p*-OH) groups in SCL were only slightly modified. Besides the general decrease of guaiacyl units, a reduction of the condensed units by 67% and 60% in SCL and RSL, respectively, was observed. All the lignin samples displayed an increase in COOH content after MTO/H_2O_2 treatment. The modifications occurred on the lignin samples are in accord with the above reported reactivity of model compounds. The decrease of aliphatic OH groups is indicative of side-chain oxidation processes. The decrease of non-condensed phenolic groups could be explained either by aromatic ring cleavage or by oxidative coupling reactions. However, the decrease of condensed OH groups is noteworthy since it indicates that coupling processes—that result in more condensed and insoluble structures—are not operative to a significative extent.[29] Furthermore the reactions of side-chain and aromatic ring cleavage yield the formation of carboxylic acid groups. This reaction pathway is confirmed by the increase of COOH content after MTO catalyzed oxidation of all the lignin samples studied.

3. Conclusions

MTO was an efficient catalyst for the H_2O_2 oxidation of lignin model compounds. Its reactivity towards monomeric and dimeric, phenolic and non-phenolic lignin model compounds is displayed at the level of the alkyl side-chain with oxidation and fragmentation reactions and at the level of the aromatic moieties by hydroxylation, demethylation and oxidative ring-opening cleavage reactions. The efficiency of MTO was also high towards recalcitrant condensed lignin models such as phenolic and non-phenolic diphenylmethanes. In this latter case, both alkyl side-chain oxidation and cleavage of the diphenylmethane bridge and of the aromatic ring were observed.

Experiments performed on technical lignins, hydrolytic sugar cane lignin (SCL), red spruce kraft lignin (RSL) and hardwood organosolvent lignin (OSL), showed that MTO is highly efficient also in the oxidative degradation of complex polymeric substrates, yielding to the formation of more soluble lignins fragments with a high degree of degradation as indicated by low contents in aliphatic and condensed OH groups and high amounts of carboxylic acid moieties.

These data indicate MTO as an interesting candidate for the development of alternative totally chlorine free (TCF) delignification processes. Further work is therefore in progress in order to exploit further on the reactivity of lignin and lignin model compounds with heterogeneous MTO catalysts.

4. Experimental

^1H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on a Bruker AM 400, or Bruker 200 spectrometer. Mass Spectroscopy (MS) was performed with a GC Shimadzu GC-17A and a mass-selective detector QP 6000. All solvents were ACS reagent grade and were redistilled and dried according to standard procedures. Chromatographic purifications were performed on columns packed with Merck silica gel 60, 230–400 mesh for flash technique. Thin layer chromatography was carried out using Merck platten Kieselgel 60 F254. Lignin samples were purchased from Aldrich and used without further purification. Quantitative ^{31}P NMR spectra were obtained using methods identical to those described by Argyropoulos et al. The chemical shifts were referenced to phosphoric acid. LC–MS analyses were performed by means of a TSQ Quantum Ultra AM Thermo Finnigan instrument.

4.1. Starting materials

Lignin model compounds 1-(4-hydroxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)-3-hydroxypropanol **10**, 1-(4-ethoxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)propane-1,3-diol **14**, 1-(4-ethoxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol **23**, 2,2′-methylenebis(6-methoxy-4-methylphenol) **28**, 1,1′-methylenebis(2,3-dimethoxy-5-methylbenzene) **35** were synthesized according to literature procedures.[30,31]

4.2. Typical procedure for the oxidation of lignin model compounds

The model compounds (1.0 mmol) to be oxidized and H_2O_2 (1.5 mmol, 35% water solution) were added to a solution of the catalyst (1.0% w/w) in CH_3COOH (5 mL), and the mixtures were stirred at room temperature. At the end of the reaction the catalyst was filtered off and the solvent was evaporated under reduced pressure. The residues were dissolved in 20 μL of pyridine in the presence of 3,4-dimethoxytoluene as an internal standard for GC–MS analysis. The mixture were than derivatized with bis-trimetylsilyl trifluoroacetamide (BSTFA) and analyzed.

Gas chromatography and gas chromatography–mass spectrometry of the reaction products were performed using a DB1 column (30 m × 0.25 mm and 0.25 mm film thickness), and an isothermal temperature profile of 100 °C for the first two minutes, followed by a 20 °C/min temperature gradient to 300 °C and finally an isothermal period at 300 °C for 10 min. The injector temperature was 280 °C. Chromatography grade helium was used as the carrier gas.

The identification of vanillin **2**, 2,6-dimethoxyphenol **12**, 4-ethoxy-3-methoxybenzaldehyde **24**, (2*E*)-3-(4-ethoxy-3-methoxyphenyl)aceylaldehyde **25** was carried out by comparison with sample of authentic products. 2-hydroxy-5-(hydroxymethyl)benzo-1,4-quinone **5**, 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)ethanone **11**, (5-oxo-2,5-dihydrofuran-3-yl)acetic acid **13**, 5-methoxybenzene-1,2,4-triol **20**, (2*E*)-3-(4-ethoxy-3-methoxyphenyl)-acrylaldehyde **26**, (2*E*)-3-(4-ethoxy-3-methoxyphenyl)-prop-2-en-1-ol **27**, [3-(2,3-dimethoxy-5-methylbenzyl)-4,5-dimethoxyphenyl]methanol **36**, 4-(hydroxymethyl)-2-[5-(hydroxymethyl)-2,3-dimethoxybenzyl]-6-methoxyphenol **37**, 3-(5-formyl-2,3-dimethoxybenzyl)-4,5-dimethoxybenzoic acid **38**, 2-(2,3-dimethoxy-5-methylbenzyl)-6-methoxy-4-methylphenol **39** were assigned by comparison with the GC–MS fragmentation spectra of original compounds.[16,32,33]

4-Hydroxy-3-methoxybenzoic acid **3**, (2*Z*)-3-(5-oxo-2,5-dihydrofuran-3-yl)acrylic acid **4**, 3,4-dimethoxybenzaldehyde **7**, 3,4-dimethoxybenzoic acid **8**, methyl (2*Z*)-3-(5-oxo-2,5-dihydrofuran-3-yl)acrylate (muconolactone derivative) **9**, 1-(4-ethoxy-3-methoxyphenyl)propane-1,2,3-triol **15**, (4-hydroxy-3-methoxyphenyl)(hydroxy)acetic acid **17**, 5-(1,2-dihydroxyethyl)-3-methoxybenzene-1,2-diol **18**, 5-methoxybenzene-1,2,4-triol **20**, 2-[2-hydroxy-5-(hydroxymethyl)-3-methoxybenzyl]-6-methoxy-4-methylphenol **29**, 2,2′-methylenebis[4-(hydroxymethyl)-6-methoxyphenol] **30**, 2-hydroxy-5-(hydroxymethyl)-3-methoxybenzoic acid **32**, (2-hydroxy-3-methoxy-5-methylphenyl)acetic acid **33** and [2-hydroxy-5-(hydroxymethyl)-3-methoxyphenyl]acetic acid **34**, were recovered in appreciable amount after flash chromatography of the respective crude and characterized by ^{1}H NMR and ^{13}C NMR analyses (see next).

1-(3,4-Dihydroxyphenyl)propane-1,2,3-triol **16**, 4-ethoxy-2,5-dihydroxy-3-methoxybenzoic acid **19**, (2*Z*)-4-(hydroxymethyl)hex-2-enedioic acid **21**, 6-ethoxy-3-(hydroxymethyl)-6-oxohexanoic acid **22**, 4-hydroxy-3-[2-hydroxy-5-(hydroxymethyl)-3-methoxybenzyl]-5-methoxybenzaldehyde **31**, 4-(hydroxymethyl)-2-[5-(hydroxymethyl)-2,3-dimethoxybenzyl]-6-methoxyphenol **40**, 3-(2,3-dimethoxy-5-methylbenzyl)-4-hydroxy-5-methoxybenzaldehyde **41** and (2,3-dimethoxy-5-methylphenyl)acetic acid **42** were identified on the basis of the fragmentation spectra. The fragmentation patterns are shown in Table 2.

Selected data for compounds **3**, **4**, **7**, **8**, **9**, **15**, **17**, **18**, **19**, **20**, **26**, **27**, **29**, **30**, **32**, **33** and **34**.

4.2.1. 4-Hydroxy-3-methoxybenzoic acid (3). δ_H ($CDCl_3$ + DMSO-d_6): 7.50 (2H, m, PhH), 6.80 (1H, m, PhH), 3.80 (3H, s, OCH_3). δ_C ($CDCl_3$): 166.6 (CO), 150.4 (C), 146.5 (C), 123.9 (CH), 121.3 (C), 114.3 (CH), 111.7 (CH), 51.7 (CH_3); *m*/*z* (EI) 168 (M^+).

4.2.2. (2*Z*)-3-(5-Oxo-2,5-dihydrofuran-3-yl)acrylic acid (4). Characterized as methyl ester. δ_H ($CDCl_3$): 6.75 (dd, 1H, J = 12.4 Hz, J = 2 Hz, CH), 6.30 (m, 1H, HCO), 6.12 (d, 1H, J = 12.4 Hz, CH), 5.25 (m, 2H, CH_2OOC), 3.78 (s, 3H, CH_3COO) *m*/*z* (EI) 168 (M^+).

4.2.3. 3,4-Dimethoxybenzaldehyde (7). δ_H ($CDCl_3$): 9.86 (1H, s, CHO), 6.90–7.42 (3H, m, PhH), 3.86 (3H, s, OCH_3), 3.82 (3H, s, OCH_3). δ_C ($CDCl_3$): 190.4 (CO), 134.3 (C), 149.1 (C), 129.7 (C), 126.5 (CH), 110.4 (CH), 108.4 (CH), 55.7 (CH_3), 55.5 (CH_3); *m*/*z* (EI) 166 (M^+).

4.2.4. 3,4-Dimethoxybenzoic acid (8). δ_H ($CDCl_3$ + DMSO-d_6): 7.60–6.80 (3H, m, PhH), 3.80 (3H, s, OCH_3), 3.78 (3H, s, OCH_3). δ_C ($CDCl_3$ + DMSO-d_6): 167.1 (CO), 151.7 (C), 147.8 (C), 124.5 (CH), 111.7 (CH), 110.4 (CH), 111.7 (CH), 54.3 (CH_3), 54.1 (CH_3); *m*/*z* (EI) 182 (M^+).

4.2.5. Methyl (2*Z*)-3-(5-oxo-2,5-dihydrofuran-3-yl)acrylate (9). δ_H ($CDCl_3$): 6.75 (dd, 1H, J = 12.4 Hz, J = 2 Hz, CH), 6.30 (m, 1H, HCO), 6.12 (d, 1H, J = 12.4 Hz, CH), 5.25 (m, 2H, CH_2OOC), 3.78 (s, 3H, CH_3COO) *m*/*z* (EI) 168 (M^+).

4.2.6. 1-(4-Ethoxy-3-methoxyphenyl)propane-1,2,3-triol (15). δ_H ($CDCl_3$ + DMSO-d_6): 6.50–7.0 (3H, m, PhH), 4.50 (1H, m, CH), 4.10–4.20 (2H, m, OCH_2), 3.80 (3H, s, OCH_3), 3.62 (1H, m, CHOH), 3.30–3.50 (2H, m, CH_2OH), 1.40–1.50 (3H, m, CH_3). δ_C ($CDCl_3$ + DMSO-d_6): 149.89 (C), 148.78 (C), 134.64 (C), 118.35 (CH), 113.59 (CH), 110.06 (CH), 76.51 (CH), 74.79 (CH), 64.40 (CH_2), 63.7 (CH_2), 55.8 (CH_3), 14.90 (CH_3); *m*/*z* (EI) 242 (M^+).

4.2.7. (3,4-Dihydroxyphenyl)(hydroxy)acetic acid (17). δ_H ($CDCl_3$ + DMSO-d_6): 6.50–7.0 (3H, m, PhH), 5.0 (1H, s, CH). δ_C ($CDCl_3$ + DMSO-d_6): 176.46 (C=O), 145.70 (C), 143.30 (C), 131.60 (C), 120.90 (CH), 117.40 (CH), 115.80 (CH), 71.56 (CH); *m*/*z* (EI) 185 (M^+).

Table 2. Mass spectrometric data of compounds **9**, **11**–**42**

Product	Derivative[a]	MS (*m*/*z*) data (%)
9	—	168 (M+, 12), 136 (100), 124 (53)
11	–$Si(CH_3)_3$	254 (M+, 28), 212 (68), 197 (32), 182 (100), 73 (93)
12	—	154 (M+, 100), 139 (55), 93 (41), 96 (32), 65 (30), 111 (30)
13	–$Si(CH_3)_3$	214 (M+, 52), 213 (100), 169 (95), 139 (91), 111 (86), 75 (62), 73 (48)
15	3 × –$Si(CH_3)_3$	458 (M+, 2), 328 (6), 313 (75), 145 (31), 132 (28), 117 (81), 73 (100)
16	3 × –$Si(CH_3)_3$	416 (M+, 8), 401 (2), 329 (18), 328 (100), 160 (24), 73 (45)
17	4 × –$Si(CH_3)_3$	472 (M+, 8), 430 (100), 207 (12), 165 (70), 73 (68)
18	3 × –$Si(CH_3)_3$	416 (M+, 8), 318 (100), 262 (63), 160 (32), 73 (43)
19	3 × –$Si(CH_3)_3$	444 (M+, 3), 357 (12), 356 (100), 284 (2), 262 (58), 73 (46)
20	–$Si(CH_3)_3$	228 (M+, 4), 215 (19), 213 (100),169 (72), 139 (63), 11 (51), 73 (22)
21	2 × –$Si(CH_3)_3$	318 (M+, 3), 245 (14), 147 (100), 73 (76)
22	2 × –$Si(CH_3)_3$	348 (M+, 2), 275 (21), 147 (32), 111 (68), 73 (100)
24	—	180 (M+, 37), 151 (100), 109 (17), 95 (10), 81 (20), 65 (25)
25	—	124 (M+, 74), 109 (100), 81 (75), 77 (4), 65 (7)
26	—	206 (M+, 23), 191 (26), 176 (35), 161 (100), 147 (53)
27	–$Si(CH_3)_3$	280 (M+, 6), 206 (24), 103 (18), 73 (100)
29	2 × –$Si(CH_3)_3$	448 (M+, 3), 313 (78), 299 (49), 207 (43), 132 (48), 117 (83), 75 (98), 73 (100)
30	2 × –$Si(CH_3)_3$	464 (M+, 4), 282 (8), 207 (100), 85 (61), 73 (98)
31	3 × –$Si(CH_3)_3$	534 (M+, 2), 516 (8), 309 (17), 287 (24), 197 (85), 147 (52), 73 (100)
32	2 × –$Si(CH_3)_3$	356 (M+, 12), 341 (23), 309 (18), 207 (100), 132 (31), 117 (61), 75 (88), 73 (81)
33	2 × –$Si(CH_3)_3$	340 (M+, 8), 339 (22), 309 (24), 147 (38), 117 (32), 75 (54), 73 (100)
34	3 × –$Si(CH_3)_3$	414 (M+, 36), 413 (100), 309 (38), 251 (46), 207 (75), 73 (79)
36	–$Si(CH_3)_3$	404 (M+, 12), 351 (6), 347 (8), 207 (43), 73 (100)
37	2 × –$Si(CH_3)_3$	492 (M+, 21), 462 (16), 207 (100), 73 (87)
38	–$Si(CH_3)_3$	432 (M+, 12), 431 (38), 401 (8),281 (6), 207 (100), 96 (16), 73 (43)
39	–$Si(CH_3)_3$	374 (M+, 92), 344 (100), 313 (20), 193 (36), 162 (28), 151 (32), 73 (81)
40	2 × –$Si(CH_3)_3$	464 (M+, 12), 404 (9), 207 (100), 73 (68)
41	2 × –$Si(CH_3)_3$	446 (M+, 2), 431 (46), 207 (100), 73 (49)
42	–$Si(CH_3)_3$	282 (M+, 38), 252 (12), 223 (18), 208 (43), 193 (21), 73 (100)

[a] Underivatized; number of –$Si(CH_3)_3$ per molecule: trimethylsilylated with *N*,*O*-bis(trimethylsilyl)-acetamide.

4.2.8. 5-(1,2-Dihydroxyethyl)-3-methoxybenzene-1,2-diol (18). δ_H ($CDCl_3$ + DMSO-d_6): 6.70–6.40 (2H, m, PhH), 4.90–4.65 (1H, m, CH), 3.81 (3H, s, OCH_3), 3.70–3.50 (2H, m, CH_2). δ_C ($CDCl_3$ + DMSO-d_6): 145.3 (C), 149.7 (C), 133.8 (C), 131.3 (C), 110.01 (CH), 105.3 (CH), 76.7 (CH), 68.1 (CH_2), 56.2 (CH_3); for mass spectrum (EI) see Table 2.

4.2.9. 4-Ethoxy-2,5-dihydroxy-3-methoxybenzoic acid (19). δ_H ($CDCl_3$ + DMSO-d_6): 7.67 (1H, broad s, OH), 6.72 (1H, s, PhH), 4.40–4.20 (2H, m, OCH_2), 3.83 (3H, s, OCH_3), 1.50–1.40 (3H, m, CH_3). δ_C ($CDCl_3$ + DMSO-d_6): 167.7 (CO), 151.6 (C), 150.7 (C), 135.4 (C), 134.5 (C), 112.6 (C), 107.7 (CH), 64.5 (OCH_2), 60.9 (CH_3), 14.8 (CH_3); for mass spectrum (EI) see Table 2.

4.2.10. 4-Methoxybenzene-1,2,3,5-tetrol (20). δ_H ($CDCl_3$ + DMSO-d_6): 6.30–6.50 (2H, m, PhH), 3.9 (3H, s, OCH_3). δ_C ($CDCl_3$ + DMSO-d_6): 144.30 (C), 142.43 (C), 141.64 (C), 89.34 (CH), 84.31 (CH), 56.09 (CH_3); *m*/*z* (EI) 156 (M^+).

4.2.11. (2*E*)-3-(4-Ethoxy-3-methoxyphenyl)acrylaldehyde (26). δ_H ($CDCl_3$ + DMSO-d_6): 9.61 (1H, s, CHO), 7.38–7.34 (1H, m, CH), 7.03 (1H, m, PhH), 6.94 (1H, s, PhH), 6.93 (1H, m, PhH), 6.60–6.56 (1H, m, CH), 4.10–4.07 (2H, m, CH_2), 3.87 (3H, s, CH_3), 1.44–1.40 (3H, m, CH_3). δ_C ($CDCl_3$ + DMSO-d_6): 193.41 (CO), 152.63 (CH), 150.96 (C), 148.86 (C), 128.56 (C), 127.17 (CH), 123.04 (CH), 112.82 (CH), 110.25 (CH), 64.40 (CH_2), 55.73 (CH_3), 14.73 (CH_3); for mass spectrum (EI) see Table 2.

4.2.12. (2*E*)-3-(4-Ethoxy-3-methoxyphenyl)prop-2-en-1-ol (27). δ_H ($CDCl_3$ + DMSO-d_6): 6.91 (1H, s, PhH), 6.85–6.79 (2H, m, 2PhH), 6.54–6.49 (1H, m, CH), 6.30–6.24 (1H, m, CH), 4.83 (1H, s, OH), 4.20 (2H, m, CH_2), 4.10–4.05 (2H, m, CH_2), 3.87 (3H, s, OCH_3), 1.42 (3H, m, CH_3). δ_C ($CDCl_3$ + DMSO-d_6): 149.89 (C), 148.57 (C), 131.28 (C), 130.11 (CH), 128.64 (CH), 119.18 (CH), 112.23 (CH), 109.73 (CH), 64.40 (CH_2), 62.84 (CH_2), 55.73 (CH_3), 14.73 (CH_3); for mass spectrum (EI) see Table 2.

4.2.13. 2-[2-Hydroxy-5-(hydroxymethyl)-3-methoxybenzyl]-6-methoxy-4-methylphenol (29). δ_H ($CDCl_3$): 7.06 (1H, m, PhH), 6.97 (1H, m, PhH), 6.77 (1H, m, PhH), 6.63 (1H, m, PhH), 4.87 (2H, broad s, OH), 4.65 (2H, s, CH_2), 3.91 (2H, s, CH_2), 3.79 (3H, s, OCH_3), 3.76 (3H, s, OCH_3), 2.31 (3H, s, CH_3). δ_C ($CDCl_3$): 148.7 (C), 146.8 (C), 145.4 (C), 142.8 (C), 138.1 (C), 134.2 (C), 126.3 (C), 125.1 (C), 124.0 (CH), 122.3 (CH), 110.9 (CH), 109.1 (CH), 63.6 (CH_2), 56.21 (CH_3), 26.9 (CH_2), 20.9 (CH_3); for mass spectrum (EI) see Table 2.

4.2.14. 2,2′-Methylenebis[4-(hydroxymethyl)-6-methoxyphenol] (30). δ_H ($CDCl_3$): 7.05 (2H, m, PhH), 6.77 (2H, m, PhH), 4.64 (4H, s, $2CH_2$), 4.40 (2H, broad s, OH),

3.91 (2H, s, CH_2), 3.79 (6H, s, $2CH_3$). δ_C ($CDCl_3$): 147.7 (C), 145.4 (C), 139.8 (C), 126.3 (C), 122.4 (CH), 110.9 (CH), 63.6 (CH_2), 56.2 (CH_3), 26.9 (CH_2); for mass spectrum (EI) see Table 2.

4.2.15. 2-Hydroxy-5-(hydroxymethyl)-3-methoxybenzoic acid (32). δ_H ($CDCl_3$ + DMSO-d_6): 7.6–7.31 (5H, m, 2PhH + 3OH), 4.75 (2H, s, OCH_2), 3.92 (3H, s, OCH_3). δ_C ($CDCl_3$ + DMSO-d_6): 169.8 (CO), 155.7 (C), 144.7 (C), 137.5 (C), 122.01 (CH), 112.94 (CH), 63.8 (CH_2), 56.0 (CH_3); for mass spectrum (EI) see Table 2.

4.2.16. 2-(Hydroxy-3-methoxy-5-methylphenyl) acetic acid (33). δ_H ($CDCl_3$ + DMSO-d_6): 8.64 (1H, broad s, OH), 6.96 (1H, s, PhH), 6.60 (1H, s, PhH), 3.76 (3H, s, OCH_3), 3.69 (sH, s, CH_2), 2.31 (3H, s, CH_3). δ_C ($CDCl_3$ + DMSO-d_6): 177.8 (CO), 147.6 (C), 141.2 (C), 133.1 (C), 125.8 (C), 121.3 (CH), 110.9 (CH), 56.2 (CH_3), 36.6 (CH_2), 21.5 (CH_3); for mass spectrum (EI) see Table 2.

4.2.17. [2-Hydroxy-5-(hydroxymethyl)-3-methoxyphenyl] acetic acid (34). δ_H ($CDCl_3$ + DMSO-d_6): 7.5–6.6 (3H, m, 2PhH + OH), 4.6–4.4 (2H, m, CH), 3.79 (3H, s, OCH_3), 3.66 (2H, s, CH_2). δ_C ($CDCl_3$ + DMSO-d_6): 177.8 (CO), 146.5 (C), 143.5 (C), 138.7 (C), 122.2 (C), 118.9 (CH), 111.2 (CH), 63.6 (CH_2), 56.2 (CH_3), 36.6 (CH_2); for mass spectrum (EI) see Table 2.

4.3. Oxidation of lignin. General procedure

Oxidations of hydrolytic sugar cane lignin (SCL), red spruce kraft lignin (RSL) and hardwood organosolvent lignin (OSL) were carried out in acetic acid (5 mL), in the presence of 100 mg of lignin, 1.0 mg of MTO (1% w/w) and 500 μL of H_2O_2 (35% water solution). After 24 h the reaction mixtures were evaporated, washed with water, centrifuged and freeze-dried.

4.4. Quantitative ^{31}P NMR

Derivatization of the lignin samples with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane were performed as previously described. Samples of lignin (30 mg) accurately weighed, were dissolved in a solvent mixture composed of pyridine and deuterated chloroform, 1.6:1 v/v ratio (0.5 mL). The phospholane (100 μL) was then added, followed by the internal standard and the relaxation reagent solution (100 μL each). The ^{31}P NMR data reported in this effort are averages of three phosphitylation experiments followed by quantitative ^{31}P NMR acquisitions. The maximum standard deviation of the reported data was 2×10^{-2} mmol/g, while the maximum standard error was 1×10^{-2} mmol/g.

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