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Immobilized methyltrioxo rhenium (MTO)/H_2O_2 systems for the oxidation of lignin and lignin model compounds

Claudia Crestini,[a,*] Maria Chiara Caponi,[b] Dimitris S. Argyropoulos[c] and Raffaele Saladino[b,*]

[a]*Dipartimento di Scienze e Tecnologie Chimiche Università di Tor Vergata, Via della ricerca Scientifica, 00133, Roma, Italy*
[b]*Dipartimento di Agrobiologia e Agrochimica, Università della Tuscia, Via San Camillo de Lellis, 01100, Viterbo, Italy*
[c]*Forest Biomaterials Laboratory, North Carolina State University Raleigh, NC, USA*

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Abstract—A convenient and efficient application of heterogeneous methylrhenium trioxide (MTO) systems for the selective oxidation of lignin model compounds and lignins is reported. Environmental friendly and low-cost H_2O_2 was used as the oxygen atom donor. Overall, the data presented and discussed in this paper point toward the conclusion that the immobilized heterogeneous catalytic systems based on H_2O_2/and MTO catalysts are able to extensively oxidize both phenolic and non-phenolic, monomeric, and dimeric, lignin model compounds. Condensed diphenylmethane models were found also extensively oxidized. Technical lignins, such as hydrolytic sugar cane lignin (SCL) and red spruce kraft lignin (RSL), displayed oxidative activity with immobilized MTO catalytic systems. After oxidation, these lignins displayed the formation of more soluble lignin fragments with a high degree of degradation as indicated by the lower contents of aliphatic and condensed OH groups, and the higher amounts of carboxylic acid moieties. Our data indicate that immobilized MTO catalytic systems are significant potential candidates for the development of alternative totally chlorine-free delignification processes and environmentally sustainable lignin selective modification reactions.

1. Introduction

In the paper production processes, environmental concerns have prompted us 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 primary 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. The lack of selectivity is due fundamentally 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 a concerted oxygen atom transfer from 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 become 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 oxidation of C–H bonds.[9] Accordingly with this high reactivity, MTO is able to catalyze the oxidation of aromatic derivatives.[10]

Irrespective of the substrate to be oxidized, the reaction proceeds through the formation of a mono-peroxo [$MeRe(O_2)$] (A) and a bis-peroxo [$MeRe(O_2)_2$] complex. These reactive intermediates transfer one oxygen atom to the substrate by a concerted mechanism avoiding the formation of any radical species.[4]

With the aim to design novel delignification and bleaching processes, we recently investigated the reactivity of MTO in the oxidation of lignins and lignin model compounds with H_2O_2 as the primary oxidant.[11]

MTO showed to be a powerful and efficient catalyst for the oxidation of phenolic and non-phenolic lignin model

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* Corresponding authors. Tel.: +39 06 7259 4734; fax: +39 06 7259 4328; e-mail: crestini@uniroma2.it

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compounds representative of the main bonding pattern present within native lignins, affording both side-chain oxidations and aromatic ring cleavage reactions. Diphenylmethane models, that are usually recalcitrant to oxidation, were also found to be extensively degraded mainly via cleavage of their interunit methylene linkages. MTO was also able to catalyze the extensive degradation of selected technical lignins, increasing their degree of solubility and reducing their content in condensed subunits.

The possibility for alternative environmentally sustainable delignification processes requires the use of clean oxidants such as hydrogen peroxide coupled with techniques for the recovery and reuse of the catalysts. From this point of view immobilized catalysts present the advantage of an easy recovery and possibility of reuse and a low environmental impact. In an effort to develop more versatile and environmental friendly heterogeneous catalysts, we described the preparation of novel rhenium compounds of general formula $(polymer)_f(MTO)_g$ (the *f*/*g* quotient expresses the ratio by weight of the two components) by heterogenization of MTO on easily available and low-cost polymeric support, poly(4-vinylpyridine) or polystyrene,[12] applying the 'mediator' concept[13] and the microencapsulation technique.[14]

All the novel MTO compounds were characterized by FT-IR, scanning electron microscopy (SEM), and wide-angle X-ray diffraction (WAXS) analyses.[12] To the best of our knowledge, apart from silica supported MTO complexes,[15] NaY zeolite/MTO supercage system,[16] and a niobia supported MTO compound,[17] no further data are available in the literature about heterogeneous MTO catalysts. These polymer/MTO catalysts have already proved as efficient and selective systems for the epoxidation of simple olefins,[18] and for the oxidation of substituted phenol and anisole derivatives.[19]

The structures of poly(4-vinylpyridine)/MTO and polystyrene/MTO catalysts **I**–**IV** employed, namely poly(4-vinylpyridine) 2% and 25% cross-linked (with divinylbenzene)/MTO (PVP-2%/MTO **I** and PVP-25%/MTO **II**, respectively), poly(4-vinylpyridine-*N*-oxide) 2% cross-linked/MTO (PVPN-2%/MTO **III**), and microencapsulated polystyrene 2% cross-linked/MTO (PS-2%/MTO **IV**), are schematically represented in Figure 1.

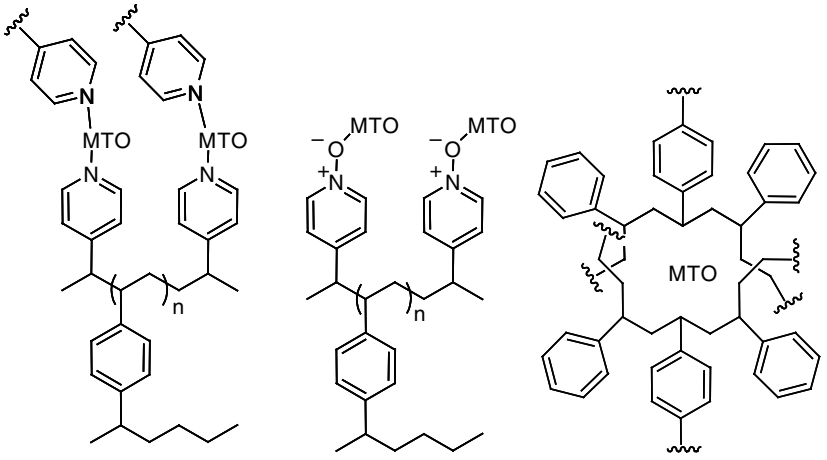
We report here that catalysts **I**–**IV** can be efficiently used for the selective oxidation of lignins and lignin model compounds with H_2O_2 as environmental friendly oxidant.

We selected an array of monomeric and dimeric lignin model compounds resembling the main bonding patterns in native and technical lignins, and studied their reactivity with supported MTO catalysts by characterization of the main oxidation products in the presence of H_2O_2. Our attention was next turned to more complex lignin polymers, hydrolytic sugar cane lignin (SCL) and red spruce kraft lignin (RSL), that are representative examples of widely diffused *para*-hydroxyphenyl-guaiacyl, and guaiacyl lignins. Their oxidation was analyzed 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 kinds of phenolic OH groups, and carboxylic acids—after phosphitylation of the sample.[20,21]

2. Results and discussion

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 behavior of this biopolymer. Thus, an array of monomeric and dimeric, phenolic and non-phenolic lignin model compounds was carefully selected for study in order to clarify the reactivity of the various lignin subunits with H_2O_2 and catalysts **I**–**IV**.



PVP-2%/MTO **I** or PVP-25%/MTO **II**

PVPN-2%/MTO **III**

PS-2%/MTO **IV**

Figure 1. Structure of poly(4-vinylpyridine)/MTO and polystyrene/MTO catalysts **I**–**IV**.

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**, 2,2′-dihydroxy-3,3′-dimethoxy-5,5′-dimethyl-diphenyl methane **19**, and 2,2′,3,3′-tetramethoxy-5,5′-dimethyl-diphenyl methane **26** were studied as substrates.

As a general procedure reactions were carried out by treating the appropriate substrate (1.0 mmol) with H_2O_2 (35% aqueous solution, 1.5 mmol) and supported MTO catalysts enumerated as structures **I–IV** (containing 1.0% w/w of the active MTO oxidizing species) in CH_3COOH (5.0 mL) at room temperature for 6.0 h. Irrespective of the experimental conditions used for the oxidation, a low mass balance (reported in the Tables 1–7) with respect to the isolated products was observed. This was rationalized on the basis of the high efficiency of the reaction. More specifically and in accordance with earlier literature data, the loss of material from the reaction mixture might be due to formation of polar hydrophilic over-oxidation products, not recovered by the usual work-up procedures.[11,22,23]

All reaction products were characterized by gas-chromatography coupled to mass-spectroscopy (GC–MS) analyses after derivatization with bis(trimethylsilyltrifluoroacetamide) (BSTFA) and, when necessary, by ^1H and ^{13}C NMR spectroscopies. Notably, during our control measurements which were carried out in the absence of the catalyst, less than 5% conversion of substrate took place, under otherwise identical experimental conditions. Similar oxidations carried out in the presence of MTO are reported as references.[11]

The simplest lignin model compound selected for this investigation was vanillyl alcohol **1**. The oxidation of **1** by immobilized catalyst systems **I–III** proceeded with high conversion of substrate affording products of alkyl side-chain oxidation, vanillin **2** and 4-hydroxy-3-methoxybenzoic acid **3**, the muconolactone **4**, and the *para*-benzoquinone derivative **5** (see Scheme 1 and Table 1). In all cases products **2** and **3** were obtained in significantly higher yields (Scheme 1). Catalysts **I–III** showed a reactivity comparable to that of homogeneous MTO: **II** and **III** yielded a quantitative conversion of the substrate, while a 75% conversion was found with **I** (Table 1) irrespective of the catalyst used in the transformation. The data suggest a common reaction pathway. The efficient oxidation of **1**, under relatively mild experimental conditions, may be attributed to both the retained reactivity of the mono-peroxo and the bis-peroxo rhenium intermediates[24] in the presence of the polymeric supports, and to the lack of a kinetic barrier of the substrate to approach the supported rhenium complex.

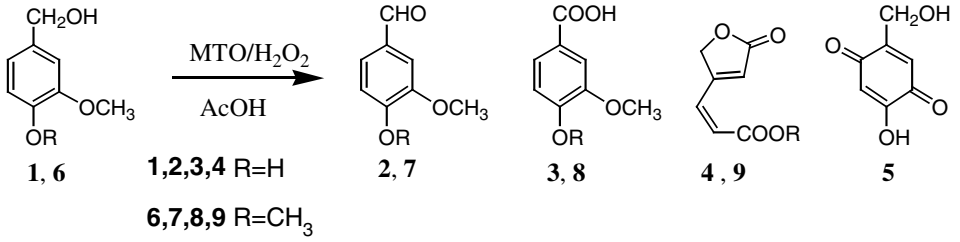
The formation of compounds **2** and **3** is in accordance with data previously reported on the reactivity of simple aromatic hydrocarbons, with H_2O_2 and MTO, in which case the oxidation of the benzylic group was the main observed process.[11] Muconolactone **4** was most likely obtained via an extensive oxidative ring opening of **1** to a muconic acid intermediate (not recovered under our experimental conditions) followed by formation of the lactone moiety, probably catalyzed by MTO, which is known to possess Lewis and Brönsted acidic character. Muconolactone derivatives have been previously recovered as minor products in the oxidative degradation of lignin model compounds.[25] Finally, the isolation of *para*-benzoquinone **5** is in accordance with the known reactivity of methoxybenzenes with MTO.[18]

The fact that the mass balance measured for heterogeneous oxidations (Table 1) was significantly higher than that obtained with homogeneous MTO was very revealing. This most likely suggests that in the presence of immobilized catalysts further oxidation reactions, yielding to polar hydrophilic or polymeric products, are significantly reduced.[11]

Table 1. Oxidation of vanillyl alcohol **1** and veratryl alcohol **6** with H_2O_2 and catalysts **I–III**

Catalyst	Conversion of **1** (%)	Product yield				Mass balance	Conversion of **6** (%)	Product yield			Mass balance
		2	**3**	**4**	**5**			**7**	**8**	**9**	
MTO[a]	98	3.7	4.9	1.8	1.4	16	98	3.4	3.9	1.2	12
I	78	8.8	3.3	4.3	4.2	45	70	6.7	2.6	2.3	45
II	98	11.0	13.0	6.9	7.9	44	98	7.8	21.0	5.9	39
III	98	14.2	18.9	5.5	4.5	49	86	12.5	12.1	4.5	44

[a] Homogeneous conditions.



Scheme 1.

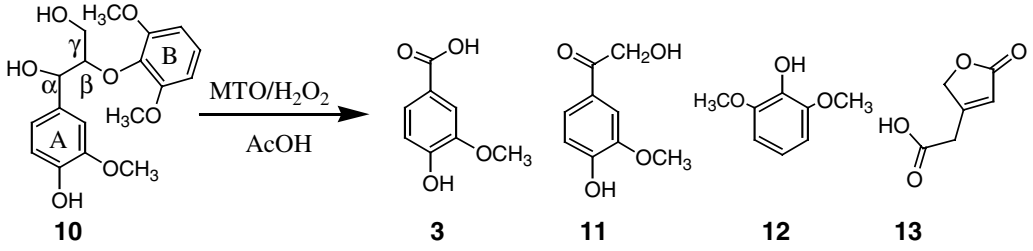
A similar behavior was observed in the oxidation of veratryl alcohol **6**, a non-phenolic lignin model compound. Upon treatment with H_2O_2 and MTO catalysts **I**–**III**, products of alkyl side-chain oxidation, 3,4-dimethoxybenzaldehyde **7** and 3,4-dimethoxybenzoic acid **8**, and the muconolactone **9** were obtained (Scheme 1). The conversion amounts ranged from 70% with catalyst **I** to >98% with catalyst **II** (Table 1) and were thus found comparable to MTO (>98% conversion). Once again the highest mass balances were obtained for reactions carried out with supported catalysts.

Our attention was next focused on the oxidation of dimeric lignin model compounds. The β-O-4 dimeric compound **10** represents the most abundant bonding pattern in softwood and hardwood lignins (guaiacyl, **G** and guaiacyl-syringyl-lignins, **GS**-lignins, respectively). The oxidation of compound **10** resulted in an extensive degradation of the substrate (>98% conversion with MTO and comparable conversions were obtained with catalysts **I**–**IV**) and showed a reactivity pattern close to that observed for **1** (Scheme 2 and Table 2).

It is interesting to note that the oxidation of **10** yielded almost exclusively fragmentation products along the β-O-4 bond linking the two aromatic moieties together. Furthermore, Cα oxidation products were abundant as evidenced by the presence of 4-hydroxy-3-methoxybenzoic acid **3** and the hydroxyketone **11**. The same products are also indicative of alkyl side-chain oxidation with **11** deriving from the aromatic A-ring of the substrate and 2,6-dimethoxyphenol **12** deriving from the aromatic B-ring of the substrate. The muconolactone **13** was also recovered in appreciable yield. However, a high molecular weight (>550) compound, probably a trimer or tetramer, that was apparent in GC–MS possessing a molecular peak fragment corresponding to benzyl alcohol substructure, could not be unambiguously identified.[11]

The oxidation of compound **14** that is a softwood (guaiacyl) non-phenolic lignin model compound afforded products of alkyl side-chain oxidation and cleavage at the α- and β-positions deriving both from the A-aromatic ring of substrate, **15**, **17**, and **18**, or from the B-aromatic ring, compound **16** (Scheme 3 and Table 3).

The mass balance for the oxidations of **10** and **14** with hydrogen peroxide catalyzed by compounds **I**–**IV** was found higher than in the presence of homogeneous MTO . These data are in accord with a reduced reactivity and increased selectivity due to the immobilization

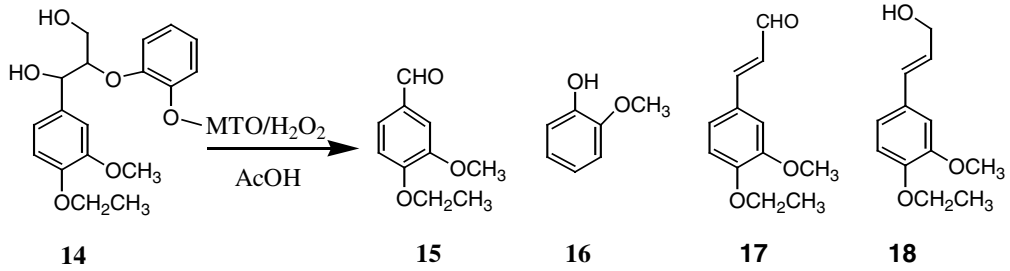


Scheme 2.

Table 2. Oxidation of 1-(4-hydroxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)-3-hydroxypropanol **10** with H_2O_2 and catalysts **I**–**IV**

Catalyst	Conversion (%)	Product yield (%)				Mass balance (%)
		3	**11**	**12**	**13**	
MTO[a]	98	16.3	14.9	11.9	9.3	50
I	75	9.8	4.2	23.4	12.4	71
II	98	17.2	13.2	26.3	19.5	61
III	98	25.0	13.7	32.5	4.5	68
IV	97	21.2	5.1	29.4	6.8	58

[a] Homogeneous conditions.



Scheme 3.

Table 3. Oxidation of 1-(4-ethoxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol **14** with H_2O_2 and catalysts **I–IV**

Catalyst	Conversion (%)	Product yield (%)				Mass balance (%)
		15	**16**	**17**	**18**	
MTO[a]	95	3.4	24.4	5.8	7.3	48
I	48	3.1	28.0	15.1	1.0	87
II	78	25.0	22.1	4.6	5.2	73
III	74	14.0	17.8	8.3	12.6	72
IV	10	2.1	1.5	2.0	2.2	88

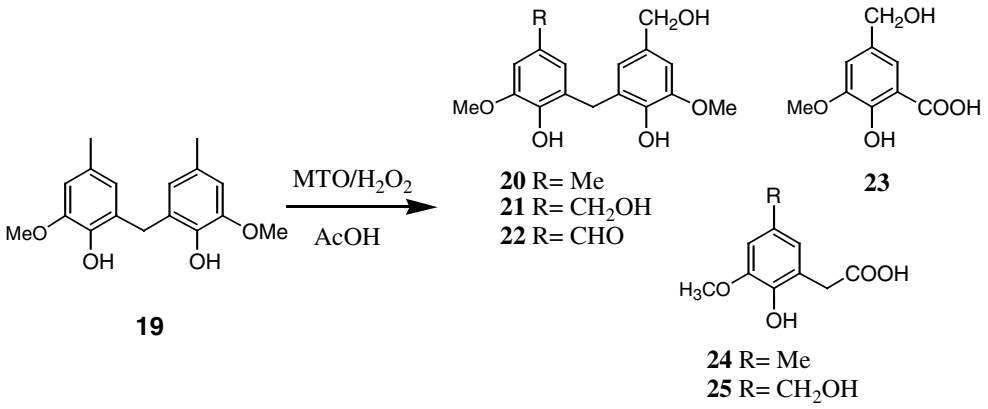
[a] Homogeneous conditions.

process with respect to MTO. This trend was especially evident in the oxidation of the less reactive compound **14**. More specifically, in this case supported MTO catalysts **I–IV** yielded % of mass balance ranging from 78.9% to 97.8% thus indicating the virtual absence of further oxidation products. In accordance with the lower reactivity displayed by the non-phenolic lignin model compounds toward oxidants,[12] low values of conversion of **14** were obtained with catalysts **I–IV** and H_2O_2 with respect to **10**.

Compound **16**, that is a typical acidolysis product from β-O-4 linkages, 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.[26]

In the case of compounds **17** and **18**, 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, probably a trimer or tetramer, that showed in GC–MS a molecular peak fragment corresponding to 4-ethoxy-3-methoxy benzyl alcohol substructure, could not be unambiguously identified.

Diphenylmethane subunits that are formed during lignin pulping processes (their amounts vary upon the specific wood species and pulping procedure used[27]) show high recalcitrance to oxidation and their efficient degradation requires severe reaction conditions in bleaching processes.[26] In order to study the reactivity of such lignin subunits toward the H_2O_2/supported MTO systems, two diphenylmethane lignin model compounds **19** and **26** were oxidized in the presence of catalysts **I–IV**. The oxidation of **19** performed under previously described experimental conditions gave products displaying varying degrees of oxidation at the benzylic positions, that is, compounds **20**, **21**, and **22**, while compound **23** showed alkyl side-chain oxidation and cleavage of the diphenylmethane bridge. Similarly, compounds **24** and **25** were derived via the oxidative cleavage of the other aromatic ring as displayed by the presence of the two carbon atom alkyl side chain (Scheme 4 and Table 4).



Scheme 4.

Table 4. Oxidation of 2,2′-methylenebis(6-methoxy-4-methylphenol) **19** with H_2O_2 and catalysts **I–IV**

Catalyst	Conversion (%)	Product yield (%)						Mass balance (%)
		20	**21**	**22**	**23**	**24**	**25**	
MTO[b]	98	2.6	1.5	T[a]	2.4	0.8	3.8	13
I	98	3.5	0.1	0.15	T[a]	0.2	8.0	15
II	98	2.9	0.3	0.2	1.0	0.1	1.4	11
III	98	21.1	0.4	T[a]	0.2	T[a]	1.8	29
IV	98	9.7	0.9	T[a]	0.2	0.4	0.4	17

[a] Traces.
[b] Homogeneous conditions.

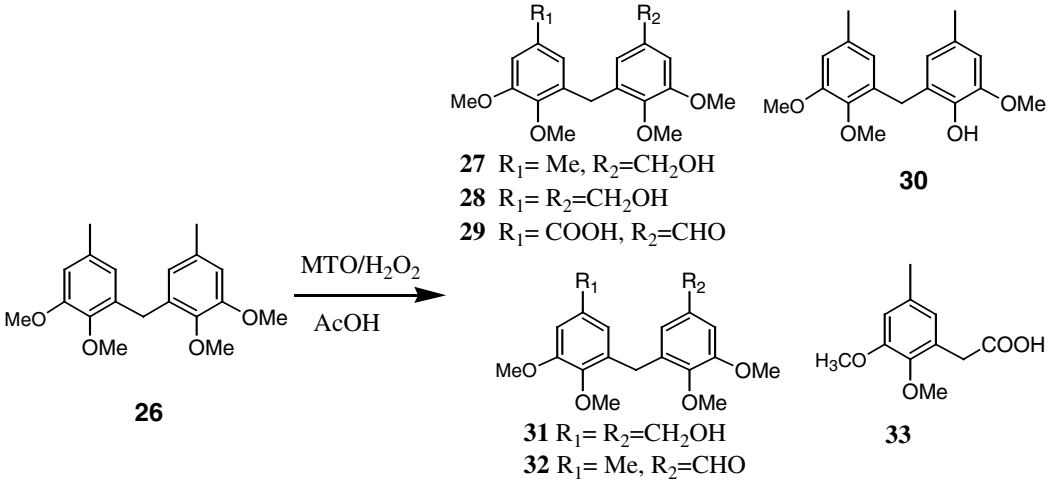
The recovery of compounds **23**–**25** is significant from an industrial point of view since it suggests that MTO based immobilized catalysts can effectively afford the oxidative degradation of otherwise recalcitrant technical lignins containing high amounts of oxidatively inert diphenylmethane subunits. When the non-phenolic diphenylmethane lignin model compound **26** was submitted to oxidation under the same experimental conditions, several products of side-chain oxidation to benzyl alcohol **27** and **28**, aldehyde and carboxylic acid, compound **29**, were detected. Moreover, products of demethylation at the alkyl-arylether moieties, **30**, **31**, and **32**, and deriving from the oxidative cleavage of one of the aromatic rings, compound **33**, were also found (Scheme 5 and Table 5).

It is interesting to note that the methyl ester of **33** (not shown) was previously recovered in low amounts after the ozonation of **26**.[28] In accordance with the displayed reactivity of MTO, it is likely that compound **33** was formed by the initial oxidative ring opening of one of the aromatic rings of compound **26** yielding the corresponding muconic acid derivative followed by a stepwise oxidative degradation.[28,29]

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[30] and by hydrogen peroxide biomimetic oxidation with manganese and iron porphyrins.[31] In the 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.

In the case of diphenylmethane model compounds **19** and **26** all catalysts **I**–**IV** showed enhanced reactivity as evidenced by the quantitative conversion of **19** (Table 4) and the 74–98% conversion range of **26** (Table 5). Thus, unlike other oxidants it appears that MTO based immobilized catalytic systems efficiently degrade diphenyl methane units. Furthermore, the mass balances at the end of the reactions were found to be significantly lower than the analogous mass balances observed for the reactions of β-O-4 arylether model compounds **10** and **14**, thus pointing out to the occurrence of additional and at the moment salient oxidative processes (Tables 4 and 5).

Some considerations can be drawn about the catalytic behavior of compounds **I**–**IV** depending on their structural properties. The reactivity and selectivity of immobilized MTO compounds can be finely tuned by the chemical and physical properties of the resin used as support. In this context, two main parameters appear of great relevance for the lignin model compound oxidations with poly(4-vinylpyridine) based catalysts: the reticulation grade of the resin and the oxidation state of the pyridinyl moieties (i.e., pyridine vs pyridine



Scheme 5.

Table 5. Oxidation of 1,1′-methylenebis(2,3-dimethoxy-5-methylbenzene) **26** with H_2O_2 and catalysts **I**–**IV**

Catalyst	Conversion (%)	Product yield (%)							Mass balance (%)
		27	**28**	**29**	**30**	**31**	**32**	**33**	
MTO[b]	93	T[a]	9.6	24.3	T[a]	T[a]	T[a]	T[a]	44
I	74	9.9	0.5	0.7	T[a]	0.4	2.1	T[a]	43
II	75	0.8	0.7	5.3	2.1	0.7	5.2	4.9	47
III	83	T[a]	T[a]	2	0.9	T[a]	7.3	3.1	34
IV	98	1.6	2.0	1.9	1.8	1.9	2.1	2.3	18

[a] Traces.
[b] Homogeneous conditions.

N-oxide as anchorage site for the rhenium atom). In the first case, the catalyst obtained with the most reticulated resin, PVP-25%/MTO (catalyst **II**), was more reactive than that characterized by a low value of this parameter (PVP-2%/MTO, catalyst **I**) in the oxidation of monomeric and dimeric β-O-4 lignin model compounds (Tables 1–3). Moreover, irrespective of the reticulation grade, with the increase of the oxidation state of the resin, that is poly(4-vinylpyridine) vs poly(4-vinylpyridine-*N*-oxide), the reactivity of the catalyst appears to increase, as shown, for example, by the reactivity of catalysts **I** (PVP-2%/MTO) and **III** (PVPN-2%/MTO) toward the oxidation of all model compounds studied. The effect of the resins on the reactivity of MTO in the activation of hydrogen peroxide is in accordance with several data previously reported on the oxidation of natural substances.[12,19]

Overall, the data presented and discussed so far point toward the conclusion that the immobilized heterogeneous catalytic systems based on H_2O_2/and MTO catalysts **I–IV** are able to extensively oxidize both phenolic and non-phenolic, monomeric, and dimeric, lignin model compounds. In all examined cases the cleavage of the alkyl side chain, or both alkyl side-chain oxidation and aromatic ring cleavage were the operative processes. Recalcitrant diphenylmethane units were also efficiently degraded.

2.2. Oxidative degradation of lignins

Once the reactivity of immobilized MTO catalytic systems toward lignin model compounds was clarified, our attention was focused on the oxidation of the lignin biopolymer. Technical lignins are samples of lignin recovered after commercial delignification processes. As such they are chemically modified and contain significative amounts of carbon–carbon and carbon–oxygen condensed subunits heavily recalcitrant to further oxidation treatments. The renowned inert nature of such lignins necessitates the existence of multiple oxidative bleaching stages in a modern pulp mill. In an effort to thoroughly examine and verify the ability of immobilized MTO catalystic systems **I–IV** to degrade the complex network of such phenolic and non-phenolic lignin structures, present during bleaching processes, we selected a hydrolytic sugar cane lignin (SCL) and a red spruce kraft lignin (RSL) as representative examples of *para*-hydroxyphenyl-guaiacyl, and guaiacyl lignins.

These lignins were then submitted to oxidation with H_2O_2 and the catalytic systems **I–IV** in acetic acid at 25 °C. Homogeneous oxidations were also carried out with the H_2O_2/MTO system as reference runs. After the reactions, the lignins were recovered by filtration. The oxidized samples were then phosphitylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane in the presence of a known amount of cholesterol as internal standard followed by quantitative ^{31}P NMR acquisition.[13,14] Table 6 shows the amounts of the different labile protons present in these lignins, expressed as mmol/g of lignin, as measured by the enumerated procedure. Since the oxidations were carried out in glacial acetic acid, the occurrence of acidolytic side processes should also be taken into account when interpreting the following data.[11,32] For this reason data regarding the control homogeneous experiments carried out by treating the samples with acetic acid alone are also reported in Table 6.

Overall Table 6 displays the oxidation of both SCL and RSL with H_2O_2 and immobilized catalytic MTO systems **I–IV**. These oxidations caused an appreciable decrease in the content of aliphatic OH groups. This is indicative of the occurrence of side-chain oxidation reactions. Moreover, all lignin samples showed an increased content of COOH units after the treatments in accordance with the displayed reactivity of MTO with the model compounds depicted in Schemes 2, 4, and 5. For SCL the decrease in the amount of the condensed units, apparent under all experimental conditions, suggests a structure more prone to further oxidation and solubilization compared to RSL. Furthermore, the actual decrease in the amounts of condensed units points toward the lack of radical coupling processes which are common events in many oxidative pathways involving peroxide. These data are in accord with a concerted oxygen atom transfer from the activated rhenium peroxy

Table 6. Oxidation of hydrolytic sugar cane lignin (SCL) and red spruce kraft lignin (RSL) with H_2O_2 and catalysts **I–IV**

Lignin[a] treatment	Aliphatic OH (mmol/g)	Condensed OH (mmol/g)	Guaiacyl OH (mmol/g)	*para*-Hydroxy phenyl OH (mmol/g)	COOH (mmol/g)
SCL/CH3COOH	1.70	0.82	0.50	0.56	0.81
SCL/MTO/H_2O_2[c]	0.92	0.29	0.35	0.55	1.26
SCL/**I**/H_2O_2	1.55	0.63	0.60	0.67	0.87
SCL/**II**/H_2O_2	1.26	0.49	0.58	0.52	1.01
SCL/**III**/H_2O_2	1.32	0.48	0.47	0.56	1.07
SCL/**IV**/H_2O_2	1.63	0.75	0.38	0.50	1.76
RSL/CH_3COOH	1.59	0.71	0.28	[b]	0.88
RSL/MTO	0.53	0.29	0.17	[b]	1.50
RSL/**I**/H_2O_2	1.05	0.88	0.44	[b]	1.18
RSL/**II**/H_2O_2	1.08	0.62	0.31	[b]	1.51
RSL/**III**/H_2O_2	1.13	0.81	0.41	[b]	1.22
RSL/**IV**/H_2O_2	0.91	0.48	0.25	[b]	0.88

[a] RSL, Red spruce kraft lignin MW 28000; SCL, Sugar Cane hydrolysis lignin.
[b] Not present.
[c] Homogeneous conditions.

complexes to the lignin substrate. Unlike SCL, the amounts of condensed units in red spruce lignin (RSL) did not display as clear a trend. These moieties were found to somewhat increase after oxidation with catalytic systems **I** and **II**, while they were found to decrease with catalytic systems **II** and **IV**. Overall, however, the variations in condensed moieties detected were always modest (Table 6).

Even if the efficiency of homogeneous MTO toward the oxidation of SCL and RSL was found to be appreciably higher than that of immobilized catalysts **I**–**IV**, overall all the supported catalysts were found to be rather reactive toward lignins. This implies that there is not any prohibitive kinetic barrier to the approach of the heterogeneous catalyst to the polymeric substrate. Alternatively, the possibility that small oxidized fragments may work as oxidation carriers cannot be ruled out.

The content of guaiacyl units in lignins treated with MTO and catalytic systems **I**–**IV** allowed to further evolve into the different selectivities operating between homogeneous and immobilized MTO catalysts. In fact, the guaiacyl (G) units were found decreased upon H_2O_2/MTO treatments; on the contrary in the presence of catalysts **I**–**IV** an increase of the G units was evidenced both on the RSL and the SCL (Table 6). The increase of G units in treated lignins may be explained by the occurrence of aliphatic lignin side-chain oxidation processes with C–H insertion reactions and Dakin-like reactions on α-carbonyl units, rather than aromatic ring oxidations. These reactions occurring preferentially on the aliphatic lignin interunit linkages would lead to residual lignins with a higher phenolic content. Our findings are in accord with the reported reactivity of immobilized MTO catalysts. In fact, the nitrogen ligands present on the polymeric support are able to tune the Lewis acidity and the reactivity of MTO. Moreover, it has been reported that supported MTO shows a higher stability of the corresponding peroxo complex intermediates yielding to a tendency to perform C–H insertion and Dakin-like reactions on α-carbonyl units rather than aromatic ring oxidation.

Our experimental data with the lignin oxidation reactions clearly indicate the occurrence of different reaction pathways between soluble and immobilized catalysts. These data are extremely significant and relevant since they address the issue of selectivity during the oxidative modification of lignins. The selective degradation of interunit linkages with the eventual production of more soluble, easily oxidizable products represents a formidable task toward the development of novel green lignin bleaching and modification processes.

3. Conclusions

Immobilized MTO catalytic systems **I**–**IV** were found to be efficient catalysts for the oxidation of phenolic and non-phenolic lignin model compounds with environmental benign H_2O_2 as the oxygen atom donor. Exceptional reactivity toward monomeric and dimeric, phenolic and non-phenolic lignin model compounds was apparent as displayed with alkyl side chains being subjected to oxidation and fragmentation reactions as well as aromatic moieties being hydroxylated, demethylated and oxidative ring-opening reactions. The efficiency of catalysts **I**–**IV** was also found to be high toward recalcitrant condensed lignin model compounds such as phenolic and non-phenolic diphenylmethanes. Such compounds were found to be subjected to both alkyl side-chain oxidation and cleavage of the diphenylmethane bridge and of the aromatic rings.

Technical lignins, such as hydrolytic sugar cane lignin (SCL) and red spruce kraft lignin (RSL), displayed oxidative activity with immobilized catalytic systems **I**–**IV**. Our data suggest that the lower Lewis acidity of immobilized MTO catalysts **I**–**IV** with respect to homogeneous MTO would direct their reactivity toward aliphatic C–H insertion and Dakin-like reactions rather than aromatic ring oxidation, thus resulting in a final product with a higher amount of free phenolic guaiacyl groups.

Our data indicate that immobilized MTO catalytic systems are significant potential candidates for the development of alternative totally chlorine free delignification processes and environmentally sustainable lignin selective modification reactions.

4. Experimental

^{1}H 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 of 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 and co-workers.[20,21] The chemical shifts were referenced to phosphoric acid.

4.1. Preparation of lignin model compounds

Lignin model compounds 1-(4-hydroxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)-3-hydroxypropanol **10**, 1-(4-ethoxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol **14**, 2,2′-methylenebis(6-methoxy-4-methylphenol) **19**, and 1,1′-methylenebis(2,3-dimethoxy-5-methylbenzene) **26** were synthesized according to literature procedures.[33,34]

4.2. Preparation of supported MTO catalysts

Poly(4-vinylpyridine)/MTO (PVP-2%/MTO **I**, PVP-25%/MTO **II**, and PVPN-2%/MTO **III**) and polystyrene/MTO (PS-2%/MTO **IV**) catalysts were prepared

as previously reported.[12] In summary, MTO (77 mg, 0.3 mmol) was added to a suspension of the appropriate resin (600 mg) in ethanol (4 mL) or tetrahydrofuran in the case of polystyrene. The mixture was stirred for 1 h using a magnetic stirrer. Coacervates were found to envelop the solid core dispersed in the medium and hexane (5 mL) was added to harden the capsule walls. The solvent was removed by filtration, and the solid residue was washed with ethyl acetate and finally dried under high vacuum. In every case, MTO was completely included into the polymer. This result was confirmed by spectroscopic analysis of the residue obtained after evaporation of the organic layers. The catalysts were used without any further purification.

4.3. Quantitative ^{31}P NMR

Derivatization of the lignin samples with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane was performed as previously described.[20,21] 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.

4.4. 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 of the active species) 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 was than derivatized with bis(trimethylsilyltrifluoroacetamide) (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 min, 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 mass balance reported in Tables 1–5 is the sum of the % of unreacted substrate and the oxidation products.

The identification of vanillin **2**, 2,6-dimethoxyphenol **12**, 4-ethoxy-3-methoxybenzaldehyde **15**, and (2*E*)-3-(4-ethoxy-3-methoxyphenyl)acetaldehyde **16** 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**, (2*E*)-3-(4-ethoxy-3-methoxyphenyl)prop-2-en-1-ol **18**, [3-(2,3-dimethoxy-5-methylbenzyl)-4,5-dimethoxyphenyl]methanol **27**, 4-(hydroxymethyl)-2-[5-(hydroxymethyl)-2,3-dimethoxybenzyl]-6-methoxyphenol **28**, 3-(5-formyl-2,3-dimethoxybenzyl)-4,5-dimethoxybenzoic acid **29**, and 2-(2,3-dimethoxy-5-methylbenzyl)-6-methoxy-4-methylphenol **30** were assigned by comparison with the GC–MS fragmentation spectra of original compounds.[16,29,35–37]

4-Hydroxy-3-methoxybenzoic acid **3**, (2*Z*)-3-(5-oxo-2,5-dihydrofuran-3-yl)acrylic acid **4**, 3,4-dimethoxybenzal-

Table 7. Mass spectrometric data of compounds **9**, **11**–**33**

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		180 (M+, 37), 151 (100), 109 (17), 95 (10), 81 (20), 65 (25)
16		124 (M+, 74), 109 (100), 81 (75), 77 (4), 65 (7)
17		336 (M+, 12), 316 (6), 207 (20), 117 (29), 75 (100), 73 (89)
18		280 (M+, 6), 206 (24), 103 (18), 73 (100)
20	–Si(CH$_3$)$_3$	448 (M+, 3), 313 (78), 299 (49), 207 (43), 132 (48), 117 (83), 75 (98), 73 (100)
21	–Si(CH$_3$)$_3$	464 (M+, 4), 282 (8), 207 (100), 85 (61), 73 (98)
22	–Si(CH$_3$)$_3$	534 (M+, 2), 516 (8), 309 (17), 287 (24), 197 (85), 147 (52), 73 (100)
23	–Si(CH$_3$)$_3$	356 (M+, 12), 341 (23), 309 (18), 207 (100), 132 (31), 117 (61), 75 (88), 73 (81)
24	–Si(CH$_3$)$_3$	340 (M+, 8), 339 (22), 309 (24), 147 (38), 117 (32), 75 (54), 73 (100)
25	–Si(CH$_3$)$_3$	414 (M+, 36), 413 (100), 309 (38), 251 (46), 207 (75), 73 (79)
27	–Si(CH$_3$)$_3$	404 (M+, 12), 351 (6), 347 (8), 207 (43), 73 (100)
28	–Si(CH$_3$)$_3$	492 (M+, 21), 462 (16), 207 (100), 73 (87)
29	–Si(CH$_3$)$_3$	432 (M+, 12), 431 (38), 401 (8),281 (6), 207 (100), 96 (16), 73 (43)
30	–Si(CH$_3$)$_3$	374 (M+, 92), 344 (100), 313 (20), 193 (36), 162 (28), 151 (32), 73 (81).
31	–Si(CH$_3$)$_3$	464 (M+, 12), 404 (9), 207 (100), 73 (68)
32	–Si(CH$_3$)$_3$	446 (M+, 2), 431 (46), 207 (100), 73 (49)
33	–Si(CH$_3$)$_3$	282 (M+, 38), 252 (12), 223 (18), 208 (43), 193 (21), 73 (100)

[a] Underivatized; –Si(CH$_3$)$_3$: trimethylsilylated with *N*,*O*-bis(trimethylsilyl)-acetamide.

dehyde **7**, 3,4-dimethoxybenzoic acid **8**, and methyl (2*Z*)-3-(5-oxo-2,5-dihydrofuran-3-yl)acrylate **9** were recovered in appreciable amount after flash chromatography of the respective crude and characterized by ^{1}H NMR and ^{13}C NMR analyses.

(2*E*)-3-(4-Ethoxy-3-methoxyphenyl)acrylaldehyde **17**, 2-[2-hydroxy-5-(hydroxymethyl)-3-methoxybenzyl]-6-methoxy-4-methylphenol **20**, 2,2′-methylenebis[4-(hydroxymethyl)-6-methoxyphenol] **21**, 4-hydroxy-3-[2-hydroxy-5-(hydroxymethyl)-3-methoxybenzyl]-5-methoxybenzaldehyde **22**, 2-hydroxy-5-(hydroxymethyl)-3-methoxybenzoic acid **23**, (2-hydroxy-3-methoxy-5-methylphenyl)acetic acid **24**, [2-hydroxy-5-(hydroxymethyl)-3-methoxyphenyl]acetic acid **25**, 4-(hydroxymethyl)-2-[5-(hydroxymethyl)-2,3-dimethoxybenzyl]-6-methoxyphenol **31**, 3-(2,3-dimethoxy-5-methylbenzyl)-4-hydroxy-5-methoxybenzaldehyde **32**, and (2,3-dimethoxy-5-methylphenyl)acetic acid **33** were identified on the basis of the fragmentation spectra and comparison with literature data. The fragmentation patterns are shown in Table 7. Selected data for compounds **3**, **4**, **7**, **8**, and **9**:

4.5. 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^+).

4.6. (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^+).

4.7. 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^+).

4.8. 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^+).

4.9. 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^+).

4.10. Oxidation of lignin. General procedure

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

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