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Review: Oxidation of Lignin Using Ionic Liquids—An Innovative Strategy To Produce Renewable Chemicals

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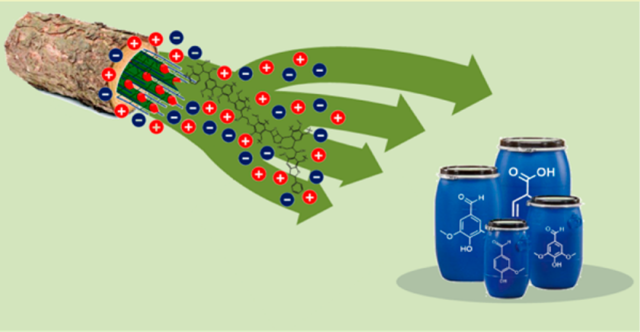

ABSTRACT: Lignin, one of the three subcomponents of lignocellulosic biomass (along with cellulose and hemicellulose), represents more than 20% of the total mass of the Earth's biosphere. However, essentially due to its complex structure, this renewable polymer derived from biomass is mainly burned as a source of energy in the pulp and paper industry. Today, the valorization of lignin into the production of chemical feedstocks represents a real challenge in terms of both sustainability and environmental protection. This review first briefly outlines the main points of this challenge and compares the different methods investigated by chemists over the past several decades, pointing out the major difficulties met. Next, the review highlights the recent use of ionic liquids (ILs) as solvents that have provided some new opportunities to efficiently convert lignin and lignin model compounds into value-added aromatic chemicals. Particular focus is given to these new strategies in terms of selectivity, separation and the unique compounds obtained for the oxidation of lignin using ILs. Finally, an assessment of the challenges that must be resolved in order for ILs to become an eco-friendly way of producing chemicals from biomass, including lignin, is proposed.

KEYWORDS: *Biomass valorization, Green processes, Ionic liquids, Lignin, Oxidation*

INTRODUCTION

Lignin and Structures. Lignocellulosic biomass is the world's most abundant renewable source recognized as a potential feedstock for producing chemicals,[1−3] fuels,[4,5] and materials.[6,7] It is composed predominantly of three subcomponents: semi-crystalline polysaccharide cellulose (38−50%), amorphous multicomponent polysaccharide hemicellulose (23−32%), and amorphous phenylpropanoid polymer lignin (15−25%).[8,9] Figure 1 indicates the location of lignin as an integral part of the secondary cell walls of lignocellulosic biomass such as plants and some algae,[10] and Figure 2 shows the average proportions of lignin, cellulose, and hemicellulose according to the selected biomass.[11]

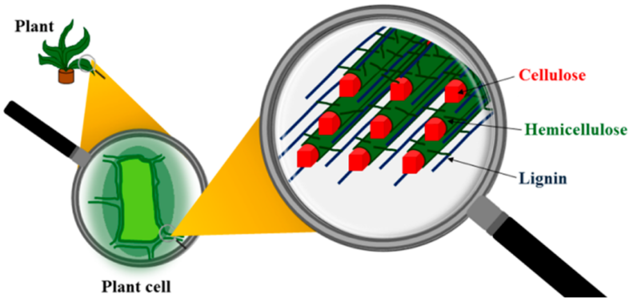

Figure 1. Schematic representation of the subcomponents in lignocellulosic material.

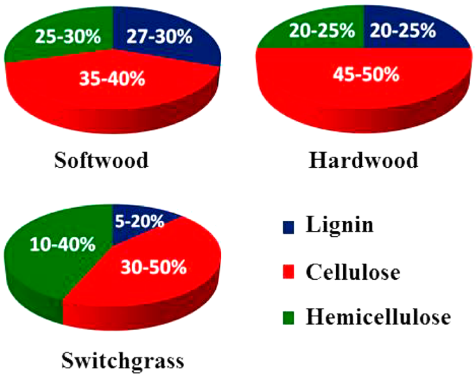

Figure 2. Average distribution of the three biopolymers in several representative biomass feedstocks (wt %).[11]

Lignin presents a complex, amorphous, polymeric structure, arising from enzymatic dehydrogenative polymerization of three phenylpropanoid monomers, namely, synapyl alcohol, coniferyl alcohol, and *p*-coumaryl alcohol (Figure 3).[12] Incorporated into the lignin polymeric structure, some subunits are identified by their aromatic ring structure such as guaiacyl type (4-alkyl-2-methoxyphenol), syringyl type (4-alkyl-2,5-dimethoxyphenol), *p*-hydroxyphenyl type, coniferyl alcohol

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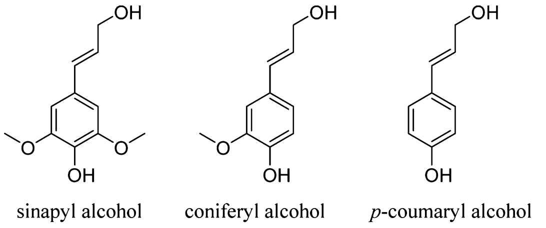
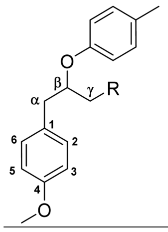


Figure 3. Three phenylpropanoid monomers at the base of lignin formation.

Table 1. Types and Frequencies of Inter-Subunit Linkages in Softwood and Hardwood Lignins (number of linkages per 100 C9 units)[10,15,16]

	linkage	softwood lignin	hardwood lignin
	β-O-4	49-51	65
	α-O-4	6-8	–
	β-5	9-15	6
	β-1	2	15
	5-5	9.5	2.3
	4-O-5	3.5	1.5
	β-β	2	5.5

fragment (4-(3-hydroxy-1-propenyl)-2-methoxyphenol), and phenylcoumaran (Figure 4). Several C−O and C−C interunit linkages including *β*-O-4, *α*-O-4, *β*-5, *β*−*β*, 4-O-5, 5−5, and *β*-1 are formed during the biosynthesis process of macromolecular lignin.[13,14] The most common linkage between the monomers is the *β*-O-4 ether bond, representing approximately 50% of all intersubunit bonds of this type (Table 1).[10,15,16]

The essential difference between lignin in hardwoods and softwoods is the number of methoxy groups on the aryl rings of the polymer. Softwoods form from the polymerization of coniferyl alcohol, which form from guaiacol and thus contain only one methoxy group per aromatic ring. Hardwood lignin, a polymerization product of both coniferyl and sinapyl alcohols, contains two and three methoxy groups per aromatic ring.[17] The additional methoxy groups on the aromatic rings prevent formation of some specific linkages, leading to more linear structures for the hardwood lignin compared to softwood.

What Is the Challenge for Lignin Valorization? Lignin represents about 20% of the total mass of the planet's biosphere, and despite being one of the three most abundant natural polymers on Earth with cellulose and chitin, almost 98% of lignin is burned as a source of energy, primarily in the pulp and paper industry, obtained as kraft lignin and lignosulfonates.[18,19] Nowadays, the existing markets for lignin products remain limited and focus mainly on low value products[20] such as dispersing, binding, or emulsifying agents,[21] low-grade fuel,[22,23] phenolic resins,[24] carbon fibers,[25,26] wood panel products,[27] automotive brakes, epoxy resins for printed circuit boards,[18] and polyurethane foams.[28] The absence of commercial high-value applications of lignin is mainly due to its heterogeneous molecular structure and the lack of effective modification and depolymerization methods.

In the current context of sustainable development and green chemistry,[29] lignin valorization represents an important challenge in the biorefinery area in order to diminish the reliance on oil.[30,31] Indeed, a biorefinery integrates biomass conversion processes and equipment to produce fuels, power, heat, and value-added chemicals from biomass. In this context, lignin is a widely available bioresource and presents a high potential for valorization. Lignin is the only renewable source of important and high-volume aromatic compounds.[32] The major reasons for combustion being the main application of this low value lignin include the following: (1) Lignin has a complex heterogenic structure and changes according to selected biomass sources, type of woods, season, and several growing parameters, such that it is difficult to know exactly the composition and the structure.[33] (2) The polyphenolic structure is chemically stable and difficult to transform or structurally modify; harsh reaction conditions are required to break down the polymer. (3) Petroleum-derived monomers are

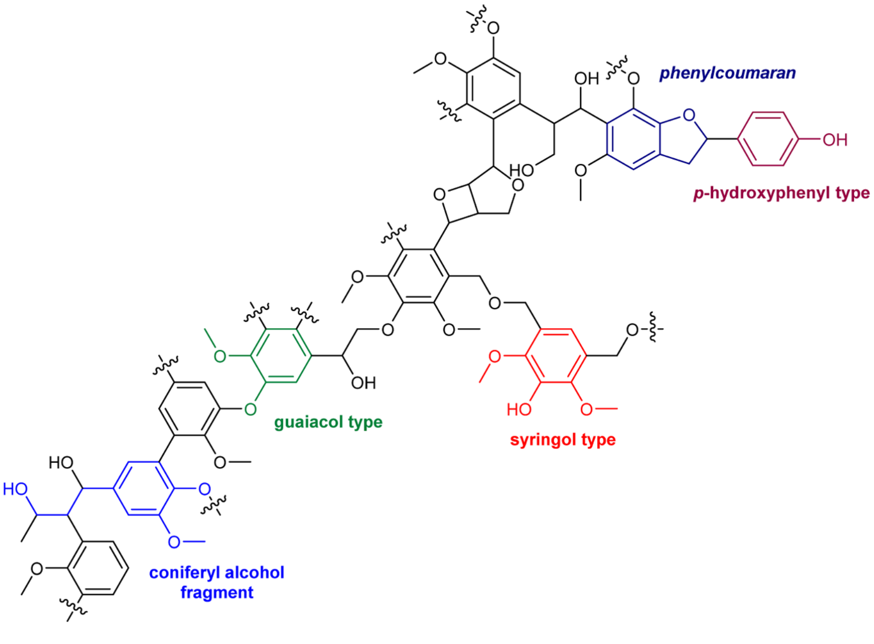


Figure 4. Representation of a structure of lignin showing main subunits.

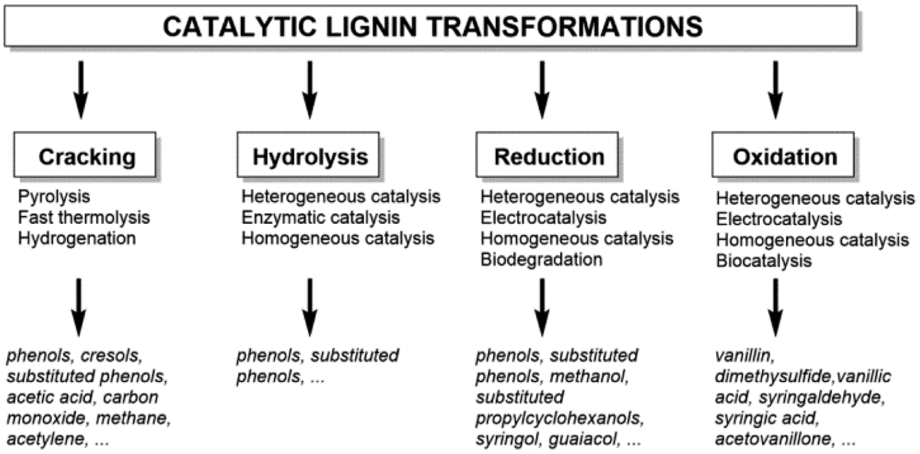


Figure 5. Main catalytic lignin transformations studied with some examples of the products obtained.

available for the production of synthetic plastic and polymers with cheap processes.

The need to develop new high-volume aromatics from lignin is nonetheless becoming both urgent, challenging, and a viable long-term opportunity if we consider the decline in petroleum resources and the projected increase in their price.[34] With most of 70 million tons of lignin accruing annually as a byproduct in pulping and used for energy generation, direct and efficient conversion of lignin to discrete molecules or classes of high-volume, low-molecular weight, aromatic molecules is an attractive goal. Moreover, the utilization of lignin does not compete with food, an ethical problem often encountered with renewable resources.[35]

Our group[36,37] and others[38−41] have recently been exploring the feasibility of using ionic liquids (ILs, commonly defined as a class of salts with low melting points, typically less than 100 °C)[42] to dissolve, separate, and recover cellulose, hemicellulose, and lignin from lignocellulosic biomass. ILs have already proven their ability to dissolve cellulose with no derivatization under mild conditions to provide a platform for a wide variety of new advances compounds.[43] The interactions between the anion and cellulose play a key role in the solvation of cellulose, and the nature of the IL ions was shown to be critical to the dissolution and also to the ultimate greenness of the processes.[43,44] Recently, ILs have also attracted a particular interest to dissolve lignin and extract it from lignocellulosic biomass.[45−47]

Despite the attention that has been paid to the use of ILs in several biorefinery concepts and the proven solubility of many types of lignins in ILs, the literature describing the oxidation of lignin in ILs is still modest. Herein, we will briefly review the oxidation of lignin leading to value-added chemicals from classical methods and then turn to the new methods using ILs. We will then discuss the advantages proposed for IL methods in terms of eco-compatibility, efficiency, and access to new chemicals. The focus of this review will be to evaluate these proposed opportunities for ILs as candidates for the challenging production of chemicals from renewable and available lignin.

CLASSIC METHODS OF LIGNIN OXIDATION

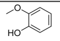
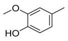
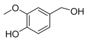
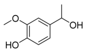
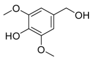
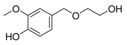
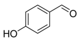
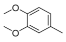
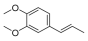
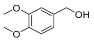
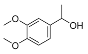
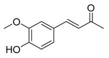
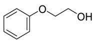
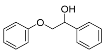
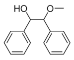
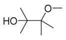
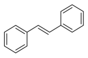
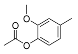
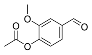
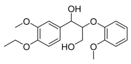
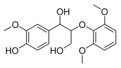
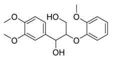
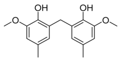
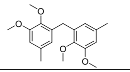
Oxidation Reactions of Lignin. Decomposition of lignin and its fragmentation to chemicals can be principally divided into lignin cracking or hydrolysis reactions, catalytic reduction reactions, and catalytic oxidation reactions (Figure 5). Contrary to hydrolysis and reduction reactions that disrupt the structure and remove chemical functionalities from lignin to produce simpler phenols,[48] oxidation reactions tend to form more complicated platform aromatic compounds with additional functionalities or to convert lignin directly to targeted fine chemicals. Moreover, oxidized biomass can be easily isolated via a simple filtration step in many cases.[49]

This part of our review is not meant to cover every published reference on lignin oxidation; rather, a discussion of the classical methods used to oxidize lignin is provided in order to understand the issues and identify the possible solutions that ILs might address. In 2010, the catalytic valorization of lignin for the production of renewable chemicals, including catalytic lignin transformations, was reviewed by Zakzeski et al.[50] Additionally, Crestini et al. reported the main oxidative strategies in lignin chemistry.[51] More recently, Zakzeski et al. focused their research on two routes: (1) the liquid-phase reforming of lignin using ethanol/water mixtures and (2) the reduction of solubilized lignin in the presence of noble metal catalysts and hydrogen for the production of aromatic chemicals.[52−54] A 2011 review by Chundawat et al. on the deconstruction of lignocellulosic biomass to fuels and chemicals did not discuss the oxidation route.[55] However, the catalytic oxidative processes of lignin are important ways to form more complex aromatic compounds with additional functionality.

Because of the complexity of lignin, most of the lignin oxidation studies were performed from model compounds. The list given in Table 2 is not exhaustive but indicates the main lignin model compounds used in the literature. The experimental conditions used and major observed products are also indicated. Increasingly, studies are being conducted on real samples of lignin such as sulfonated kraft lignin or lignin extracted from raw biomass.[51,56] However, this approach to producing chemicals from lignin is challenging, given the higher order complexity of real lignin to the simple model compounds previously studied. It also requires a new mindset because it has long been the goal of industry and researchers to destroy the lignin by oxidation (delignification processes),[57,58] whereas now the lignin has to be preserved when separated from the biomass so that it can be converted into useful chemical compounds.

Primary Strategies for Oxidation of Lignin. Historically, oxidative catalytic cleavage of lignin and lignin model compounds were performed via metal oxides,[59] nitrobenzenes,[60,61] or $CoCrO_4$.[60,61] Since the 2000s, new catalytic methods particularly investigated include biocatalysis, organo-

Table 2. Main Lignin Model Compounds Studied in the Literature for Oxidation Reactions

name	structure	catalyst/oxidant/solvent	major products	ref.
guaiacol (2-methoxyphenol)		manganese acetate/air/water-acetonitrile mixture	polyguaiacols	74
3-methoxy-4-hydroxytoluene		manganese acetate/fungal manganese peroxidases/water	aldehydes, carboxylic acids	75
vanillyl alcohol (4-(hydroxymethyl)-2-methoxyphenol)		methyltrioxorhenium/H_2O_2/acetic acid	4-hydroxy-3-methoxybenzaldehyde, 4-hydroxy-3-methoxybenzoic acid	76
apocynol (1,2-(4-hydroxy-3-methoxy-phenoxy) ethanol)		mesoporous silica materials /H_2O_2/CH_3CN (microwave)	acetovanillone, vanillin, 2-methoxybenzoquinone	77
syringyl alcohol (4-(hydroxymethyl)-2,6-dimethoxyphenol)		manganese acetate/O_2/acidic water	methanol	78
vanillyl glycol (4-((2-hydroxyethoxy)methyl)-2-methoxyphenol)		fungal laccase/water	methanol, and polymeric quinoid products	79
4-hydroxybenzaldehyde		Co/Mn/Zr/Br catalyst/O_2/acetic acid	4-hydroxybenzoic acid	80
3,4-dimethoxytoluene		Co/Mn/Br catalyst/O_2/acetic acid	corresponding carboxylic acids, methy-3,4-dimethoxybenzoate	81
1-(3,4-dimethoxyphenyl)-1-propene		binucleus manganese complexes/H_2O_2/water	corresponding ketone, epoxides, and aldehyde.	82
veratryl alcohol ((3,4-dimethoxyphenyl)methanol)		laccase/water and Electrolysis/water	ketone, veratraldehyde	83
1-(3,4-dimethoxyphenyl)ethanol		binucleus manganese complexes/H_2O_2/water	ketone, veratraldehyde	82
vanillideneacetone ((*E*)-4-(4-hydroxy-3-methoxyphenyl)but-3-en-2-one)		copper hydroxide/O_2/water	vanillin	84
2-phenoxyethanol		dipicolinate vanadium complexes/air/DMSO	phenol, formic acid	85
1-phenyl-2-phenoxyethanol		dipicolinate vanadium complexes/air/DMSO	phenol, benzoic acid, formic acid,	85
1,2-diphenyl-2-methoxyethanol		dipicolinate vanadium complexes/air/DMSO	benzaldehyde, methanol, 2-methoxy-1,2-diphenylethan-1-one	85
pinacol monomethyl ether		dipicolinate vanadium complexes/air/DMSO	formic acid	85
(E)-1,2-diphenylethene		binucleus manganese complexes/H_2O_2/water	corresponding epoxide	82
3-methoxy-4-acetoxytoluene		manganese acetate/fungal manganese peroxidases/water	aldehydes, carboxylic acids	75
3-methoxy-4-acetoxybenzaldehyde		manganese acetate/fungal manganese peroxidases/water	aldehydes, carboxylic acids	75
1-(4-ethoxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol		methyltrioxorhenium/H_2O_2/acetic acid	4-hydroxy-3-methoxybenzoic acid, 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)ethan-1-one, 2,6-dimethoxyphenol	76
1-(4-hydroxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)propane-1,3-diol		methyltrioxorhenium/H_2O_2/acetic acid	4-hydroxy-3-methoxybenzoic acid, 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)ethan-1-one, 2,6-dimethoxyphenol	76
(1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol)		cobalt acetate or manganese acetate/O_2/acetic acid	4-methoxybenzaldehyde and derivatives	86
2,20-dihydroxy-3,30-dimethoxy-5,50-dimethyl-diphenyl methane		methyltrioxorhenium/H_2O_2/acetic acid	2-hydroxy-5-(hydroxymethyl)-3-methoxybenzoic acid, 2-(2-hydroxy-5-(hydroxymethyl)-3-methoxyphenyl)acetic acid	76
2,20,3,30-tetramethoxy-5,50-dimethyl-diphenylmethane		methyltrioxorhenium/H_2O_2/acetic acid	2-(2,3-dimethoxy-5-methylphenyl)acetic acid	76

metallic catalysis, and biomimetic catalysis. These strategies were widely reviewed and discussed by Crestini et al.,[51] and thus, we report here only some important references and highlight the recurring problems identified for each of these catalytic methods.

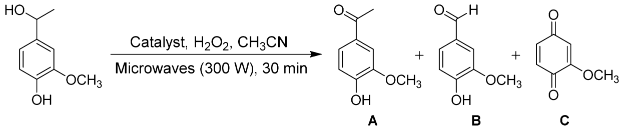
Overall, oxidation of lignin by the biocatalysis processes is efficient but requires some specific conditions due to the presence of enzymes.[62] Organometallic routes include catalysis by methyltrioxorhenium (MTO),[63] cobalt salen complexes/O_2,[64] manganese salen complexes/H_2O_2,[65] Cu^{2+}/O_2,[66] and Mn^{3+}/H_2O_2.[67] Despite the good results obtained, these systems suffer from several problems including catalyst decomposition (Co(sulfosalen),[64,68] Mn salen[65,69]) or lack of selectivity for lignin (e.g., the Cu-based catalyst formed from diimine type ligands depolymerizes the model carbohydrate dextran showing inadequate selectivity for application in pulp bleaching).[70,71] Biomimetic catalysis has also been applied to lignin oxidation and is essentially based on the use of metalloporphyrins in the presence of H_2O_2.[72] The stability of the catalyst also represents a key parameter in these experiments. For example, the use of a montmorillonite clay makes the supported catalyst stable, recyclable, and efficient for the oxidation of lignin.[73]

Novel and Recent Strategies for Oxidation of Lignin. In the past few years, some novel strategies for oxidation of lignin and lignin compounds have been investigated, such as electrochemistry,[87−91] use of mesoporous materials,[77] photocatalysis,[92] and use of vanadium-based catalysis.[85,93] Here, we review these new strategies to understand what new problems these techniques have encountered in the oxidation of lignin.

First, contrary to heterogeneous and homogeneous catalysis, electrochemical catalysis does not require specific additives or evolved catalysts.[87] In this sense, it could be considered as an efficient, low-cost, and eco-friendly method. Electrochemical degradation of kraft lignin using a $Ti/TiO_2NT/PbO_2$ electrode at 60 °C produced a 13% reduction in the C−O−C group content and a 44% increase in C═O groups, with the identification of vanillin and vanillic acid by high-performance liquid chromatography.[88] The electro-oxidation of syringaldehyde produced the corresponding acid and dimers, in small amounts, providing evidence for the polymerization of lignin fragments through radical reactions.[89] The main problem with electrochemical processes remains the low concentration of lignin required by this technology, and thus, the treatment of large volumes of lignin important to any commercial process has not yet been possible.[90,91]

More recently, Badamali et al. proposed the oxidation of apocynol under microwave irradiation in the presence of mesoporous MCM-41, HMS, SBA-15, and amorphous silica as catalysts with H_2O_2 as oxidant and acetonitrile as solvent.[77] These systems allowed the production of acetovanillone, vanillin, and 2-methoxybenzoquinone after only 30 min of irradiation (Table 3). The amorphous silica material was found to be very active, but the lack of selectivity in this case is inconvenient.

Table 3. Oxidation of Apocynol over Mesoporous Silica Catalysts[77]



		product yield (%)			product selectivity (%)		
catalyst[a]	conversion (%)	A	B	C	A	B	C
blank	–	–	–	–	–	–	–
MCM-41	72	18	5	23	39	11	49
HMS	16	6	–	–	>99	–	–
SBA-15	36	18	–	–	>99	–	–
silica-5	94	10	–	11	47	–	53

[a] Ordered mesoporous silica: MCM-41 (Mobil Composition of Matter No. 41). HMS (hexagonal mesoporous silica). SBA-15 (Santa Barbara amorphous type material).

Tonucci et al. studied the photo-oxidation of two commercial Ca^{2+} and NH_4^+ lignin derivatives in the presence of H_2O_2 (Fenton system) in water at ambient temperature and pressure leading to fractions with reduced degrees of polymerization of the material.[92] The most abundant compounds obtained were vanillin and coniferyl aldehyde, but hydroxymethoxy-acetophenone and coniferyl alcohol were also observed. Traces of phenol, 2-hydroxybenzyl alcohol, and salicylaldehyde were also identified. The authors discussed different photocatalytic systems in order to obtain selective cleavage of aliphatic C−C bonds without loss of organic material and preservation of the aromatic rings. The Fenton system was not appropriate because of the almost complete degradation of the organic matter, mainly to CO_2, but the TiO_2 photo-oxidation represented a good compromise in terms of efficiency and selectivity.[92]

Vanadium catalysis was recently investigated to cleave the C−C bond of 1,2-hydroxyether compounds and form acetic acid, benzoic acid, phenol, 2-phenoxyacetophenone, benzaldehyde, methanol, and benzoin methyl ether.[85] Dipocolinate vanadium(V) complexes oxidized the pinacol monomethyl ether lignin model compound. The main problem here was the long reaction time required (e.g., one week). Interestingly, the same research group observed remarkably different selectivities for the aerobic oxidation of a phenolic lignin model compound at 80 °C for 48 h in the presence of two vanadium-based catalysts. However, the yields into different chemicals need to be increased to make this process useable and efficient.[93]

It is clear that lignin oxidation has interested chemists for a long time. The main studies have concerned catalytic transformations based on enzymes and organometallic catalysts, but very recently some new techniques have appeared in the literature. However, some problems need to be resolved, such as the lack of selectivity, decomposition of the catalyst, low amounts of lignin required (e.g., in electrochemical studies), and difficult separation of products after the reactions are complete. It is in this context that we will explore the possibilities proposed for ILs to improve the oxidative processing of lignin and lignin model compounds.

■ OXIDATION OF LIGNIN USING IONIC LIQUIDS

Use of Ionic Liquids for Lignocellulosic Processes. The pioneering applications of room-temperature ILs on lignin model chemistry to produced chemicals were reported in 2002 by Moens, presenting acetylation reactions.[94] Since then, multifunctional uses of ILs with respect to lignin model compounds and lignin samples processing have been reported. Very recently, Welton et al. provided a critical review on the deconstruction and fractionation of lignocellulosic biomass in a process step that is commonly called pretreatment using ILs.[95] The advantages brought by ILs included the dissolution of lignin and the simultaneous disruption of the lignin and

Table 4. Experimental Conditions of Lignin Model Compounds Oxidation Using Ionic Liquids

entry	substrates	catalysts	oxidant	experimental conditions	IL[a]	role of IL	recycling	ref
1	2,6-dimethoxyphenol, coniferyl alcohol	*M. albomyces* laccase		IL (0–40 mol %), water, pH 6.0, 20 h, rt	[Amim]Cl	enhancement of the solubility of substrates and products	not investigated	97
2	veratryl alcohol	TSIL[b] (Co salen complexes) (10 mol %), pyridine (10 mol %)	air (bubbling)	distilled water, base, pH 12.5, 80 °C, time not indicated	TSIL-salen-Co hexafluorophosphate, TSIL-salen-Co tetrafluoroborate[b]	catalyst of the reaction	not investigated	98
3	(3,4-dimethoxyphenyl)methanol	Fe porphyrin (Fe(TPPS$_4$) and Fe(Cl$_8$TPPS$_4$)[c]	$H_2O_{2\,(aq)}$	6 h, rt	[C$_4$mim][PF$_6$]	good immobilization of the porphyrin catalysts	catalysts recycled and reused five times	99
4	activated primary alcohols, (3,4-dimethoxyphenyl)methanol, 5-(hydroxymethyl)-2-methoxyphenol	VO(acac)$_2$ (5 mol %), DABCO (10 mol %)[d]	O_2 (0.1 MPa)	80–95 °C 6–24 h	[C$_4$mim][PF$_6$], [C$_4$mpy][PF$_6$], [C$_4$mpyr][NTf$_2$], [C$_6$mim][CF$_3$SO$_3$]	solvent of reaction (solubilization of catalysts and substrates)	catalytic system recycled and reused three times	100
5	cinnamyl alcohol, veratryl alcohol, guaiacol, syringol, vanillyl alcohol, 3,3′-dimethoxy-5,5′-dimethyl-1,1′-biphenyl 2,2′-diol, 1-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)ethane	Co(salen) or CoCl$_2$·6H$_2$O (0.24 mol %), NaOH (48 mol %)	O_2 (0.5 MPa)	3 h, 80 °C	[C$_2$mim][Et$_2$PO$_4$]	easy dissolution of the catalyst and lignin model compounds, stabilization of intermediates	not investigated	101
6	syringaldehyde	Mn(NO$_3$)$_2$ (20 wt %)	air (6.5 MPa)	24 h, 100 °C	[C$_2$mim][CF$_3$SO$_3$]	solvent of the reaction	not investigated	102
7	benzyl alcohol, substituted benzyl alcohols	nanopalladium(0) (1 mol %), pyridinium salt of iron bis(dicarbollide) (10 mol %)	O_2 (0.4 MPa)	18 h, 120 °C	[C$_4$mim][PF$_6$]/[C$_4$mim][MeSO$_4$] (2:1, V/V)	stabilization of nanoparticles, solubilization of lignin model compounds	catalyst reused five times	103

[a] [Amim]Cl: 1-allyl-3-methylimidazolium chloride. [C$_4$mpyr][NTf$_2$]: 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide. [C$_6$mim][CF$_3$SO$_3$]: 1-hexyl-3-methylimidazolium trifluoromethanesulfonate. [C$_2$mim][Et$_2$PO$_4$]: 1-ethyl-3-methylimidazolium diethyl phosphate. [C$_2$mim][CF$_3$SO$_3$]: 1-ethyl-3-methylimidazolium trifluoromethanesulfonate. [C$_4$mim][MeSO$_4$]: 1-butyl-3-methylimidazolium methylsulfate. [b] TSIL: task-specific ionic liquid, see Figure 6. [c] Fe(TPPS$_4$): iron(III) 5,10,15,20-tetrakis(4′-sulfonatophenyl)porphyrin. Fe(Cl$_8$TTPPS$_4$): iron(III) 5,10,15,20-tetrakis(2′,6′-dichloro-3′-sulfonatophenyl)porphyrin. [d] DABCO: 1,4-diazabicyclo[2.2.2]octane.

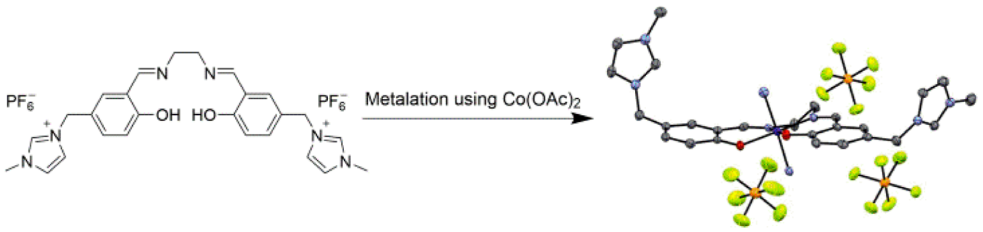


Figure 6. Structure of hexafluorophosphate-based TSIL-salen catalyst.[98]

hemicellulose network. The review described the main work on acid hydrolysis processes and discussed especially two biomass processes: (1) the ionosolv process, for the delignification of biomass by dissolving the lignin in an IL while the cellulose remains undissolved and (2) the dissolution process with an IL capable of dissolving cellulose. However, this review did not cover the opportunities to isolate new chemicals from lignin.

Mora-Pale et al. also discussed the advantages of IL-based processes compared to classic methods of lignocellulose pretreatment.[96] In their conclusion, the authors pointed to the potential high value of lignin in the large-scale diversified manufacture of high-value chemicals, traditionally obtained from petroleum. Indeed, the use of ILs is now essentially focused on the dissolution of cellulose and the separation of lignin (i.e., pretreatment), but perhaps the real challenge is the production of chemicals from lignin.

Very recently, Yinghuai et al. reported on applications of ILs in lignin chemistry.[104] The main work again concerned the extraction of lignin in ILs. Although few studies have been reported concerning the conversion of lignin to value-added chemicals in ILs until now, it is clear that current strategies to produce these value-added chemicals from lignin are typically based on a two-step process. First, lignin is depolymerized into simpler aromatic compounds using ILs as solvents, and then, the resultant aromatic compounds are transformed leading to some value-added chemicals. The challenges for lignin processing in ILs from dissolution to isolation to conversion are also discussed by Hossain and Aldous.[105] Once again, the review was focused on the extraction of lignin from lignocellulosic biomass, considered as a vital step by the authors. However, we believe that the possibilities afforded by using ILs are larger than simple separation of biopolymers and represent an important route to a "one-pot" dissolution−transformation−separation process for access to value-added chemicals.

Binder et al. studied the conversion of lignin model compounds such as eugenol (4-allyl-2-methoxyphenol) by dealkylation reaction in ILs using supported metal and Lewis and Brönsted acid catalysts, mainly obtaining 4-propylguaiacol with good yields depending on the conditions.[106] This method was shown to be efficient on some model compounds to produce different alcohols, but acidic catalysis failed in the conversion into monomeric products from organosolv lignin.

In this context, the oxidation of lignin model compounds, lignin samples, or lignin extracted directly from raw biomass coupled to the use of ILs represents an innovative opportunity for the production of high value-added aromatic chemicals. Using the limited examples reported in the literature using model lignin or available lignin samples, we will now discuss how ILs can offer new strategies and new results in the oxidation of lignin. Critical analysis of these studies should help to offer an overall understanding of the very different approaches to lignin oxidation and allow recommendations to facilitate exploration of this area.

Oxidation of Lignin Model Compounds Using Ionic Liquids. As we explained previously, mainly because of the complexity of its structure, oxidation of lignin is often performed on model compounds. Table 4 summarizes the different studies performed on these simpler substrates, indicating the catalysts, the oxidant, experimental conditions carried, and ILs used. The main role of the ILs in the experiment and the details of the attempted IL recycling after the oxidative reaction have been also specified. Catalysts studied include an enzyme (Table 4, entry 1) and a metal-functionalized IL (Table 4, entry 2), but most are metal catalysts based on iron, cobalt, and manganese (Table 4, entries 3−6). One paper also reported the use of nanoparticles in an IL mixture for the oxidation of benzyl alcohols (Table 4, entry 7). Except for one oxidative system based on the use of hydrogen peroxide (Table 4, entry 3), air or pure oxygen were chosen as oxidants in all the studies. Interestingly, these three oxidants are particularly interesting from the green chemistry point of view, avoiding the production of toxic waste.[29,107,108]

In the first entry of Table 4, Lahtinen et al. investigated the efficiency of a laccase enzyme (*M. albomyces*) to catalyze the oxidation of coniferyl alcohols in the presence of allyl-3-methylimidazolium chloride ([Amim]Cl) in an aqueous medium (from 0 to 40 mol %).[97] The authors compensated the decrease in enzyme activity with increasing concentrations of [Amim]Cl by increasing the enzyme dosage. The IL was used in this reaction to enhance solubility of the substrate and the products, which led to the formation of β-5, β−β, β-O-4, and α-C=O/β-O-4 dimers, α-O-4/β-O-4 trimers, and a coniferyl alcohol dehydropolymer. Interestingly, the dehydropolymer formed in the presence of 1-allyl-3-methylimidazolium chloride ([Amim]Cl) was structurally different and showed clearly a higher average molar mass, compared to the polymer formed in water. Indeed, the 2D NMR analysis revealed that the dehydropolymer formed in the presence of [Amim]Cl contained less β-O-4, slightly less β-5 structures, and more β−β structures.

Some supplementary investigations to understand the interactions between the enzyme structures and the IL ions and to determine the mechanisms of the enzyme inactivation are needed to explain the differences in the reactivities reported. For example, it is probable that the structure and/or activity of the laccase were affected by the presence of IL having an impact on the substrate preference or specificity. Indeed, biocatalysis in ILs have shown different types of improvements in many reactions,[109−111] and it was reported recently that laccase performance depends strongly on the nature of the anion.[112,113] The increasing number of enzymatic oxidations in the presence of ILs reported in the literature[114,115] may shortly lead to the

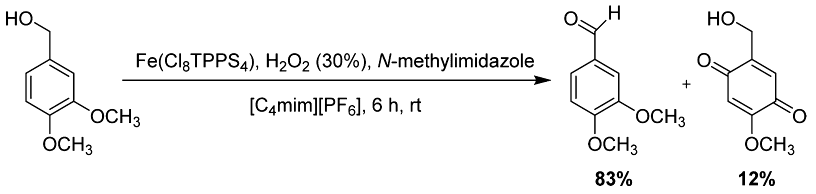


Figure 7. Oxidation of veratryl alcohol catalyzed by Fe(Cl_8TPPS$_4$) in [C_4mim][PF_6].[99]

understanding of mechanisms allowing the oxidation of lignin compounds.

On the basis of their previous work on veratryl alcohol oxidation with salen-Co catalysts under alkaline conditions,[116,117] Sonar et al. chose to associate the catalyst and an IL by synthesizing two task-specific ionic liquids (TSILs)[118,119] capable of chelating cobalt(III) to easily prepare IL-salen complexes that are water stable (Figure 6 and Table 4, entry 2).[98] Interestingly, the crystal structures of these two TSILs Co complexes showed a cobalt(III) metal center and the presence of three tetrafluoroborate or hexafluorophosphate anions in the asymmetric unit required to account for the overall neutral charge of the complex (Figure 6). The use of these Co complexes as catalyst (10 mol %) and pyridine as axial ligand (10 mol %) at a pH of 12.5 allowed the selective oxidation of veratryl alcohol, using air as the source of oxygen (80 °C, constant air bubbling), to afford moderate yields of veratraldehyde (24−56%, according to the experimental conditions). No evidence of further oxidation to the carboxylic acid was detected.

This study, based on the use of TSILs as catalysts, is the only reported example using TSILs for lignin oxidation. Despite the low yields obtained and further studies needed, the use of TSILs may bring new opportunities to this research field. For example, some TSILs have already been used for working with cellulose, but these were chosen primarily for their physicochemical properties such as polarity and hydrogen-bonding allowing direct dissolution, depolymerization, and conversion of cellulose to sugars.[120]

Metal-based TSILs have been reported for catalysis in organic chemistry with good efficiencies.[121,122] Thus, an interesting strategy for oxidation of lignin might include immobilization of a TSIL catalyst in an IL solvent to perform the oxidation reaction, facilitate the isolation of the products, and improve the recyclability of the catalyst.

The most studied model lignin oxidations are based on metal catalysts associated to an oxidant (Table 4). Kumar et al. also studied the oxidation of veratryl alcohol, while testing two water-soluble iron(III) porphyrins as catalysts; iron(III) 5,10,15,20-tetrakis(4′-sulfonatophenyl)porphyrin, (Fe(TPPS$_4$)); and iron(III) 5,10,15,20-tetrakis(2′,6′-dichloro-3′-sulfonatophenyl)porphyrin, (Fe(Cl_8TTPPS$_4$)) in the presence of hydrogen peroxide (30% aqueous) as oxidant; and 1-butyl-3-methylimidazolium ([C_4mim][PF_6]) as solvent (Figure 7 and Table 4, entry 3).[99] Veratraldehyde was obtained as a major product for both catalysts with 69% and 83% yields in the presence of Fe(TPPS$_4$) and Fe(Cl_8TTPPS$_4$), respectively, after optimization of experimental conditions (6 h, room temperature, 10 mol % catalyst, 1 equiv of H_2O_2 (30%),[C_4mim][PF_6], and *N*-methylimidazole). A minor product, 2-hydroxymethyl-5-methoxy-2,5-cyclohexadiene-1,4-dione, was also detected with yields of 8% and 12% for the two metalloporphyrins.

The non-coordinating nature and weak nucleophilicity of [C_4mim][PF_6] enhanced the reactivity by stabilizing the highly charged iron-peroxo or iron-oxo intermediate generated during the reaction.[123] Thus, the activity of the water-soluble iron(III) porphyrins was clearly higher in the IL than in aqueous solutions, allowing the recycling of the catalysts as well as their reuse five times without significant change of activity. The stabilizing effect of ILs on catalysts such as these metalloporphyrins has been widely reported in different oxidative systems[124,125] and represents a real strength for the future uses of metal-based catalysts involved in lignin oxidation processes.

The vanadium-based catalyst previously discussed in this review was also investigated in ILs (Table 4, entry 4).[100] Indeed, various activated primary alcohols were selectively oxidized into their corresponding acids or aldehydes with excellent yields using different ILs such as 1-butyl-3-methylimidazolium hexafluorophosphaste ([C_4mim][PF_6]), 1-butyl-1-methylpyrrolidinium hexafluorophosphaste ([C_4mpyr][PF_6]), or 1-hexyl-3-methylimidazolium trifluoromethanesulfonate ([C_6mim][CF_3SO_3]). For example, the oxidation of 4-methoxybenzyl alcohol, initially chosen as substrate, led to 90% yield and an excellent selectivity for the corresponding aldehyde (99%) under optimized conditions (2 mol % VO(acac)$_2$, 6 mol % DABCO, O_2, 15 h, and 95 °C; Figure 8). The catalytic system was recycled and reused three times without a decrease in catalytic activity.

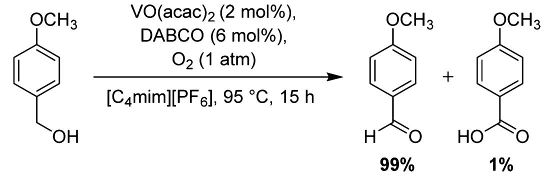


Figure 8. Oxidation of (4-methoxyphenyl)methanol catalyzed by vanadium in [C_4mim][PF_6].[100]

The authors showed the oxidation of two lignin model compounds, veratryl alcohol and vanillyl alcohol, using [C_4mim][PF_6] as solvent with, respectively, 96% (94%) and 94% (82%) conversion (yield) to the corresponding aldehydes (optimized experimental conditions: 12 h, 80 °C, 5 mol % VO(acac)$_2$, and 10 mol %).[126] In this case, the role of the pyrrolidinium- and imidazolium-based ILs is essentially to facilitate the dissolution of both catalyst and substrate and to allow easy recycling of the catalytic system by full extraction of benzaldehyde and benzoic acid using ethyl ether at the end of the reaction. However, no differences were obtained in terms of conversions and isolated yields based on the IL used, most likely because the chosen ILs were too similar.

Before testing their oxidative system using Co(salens) and Co salt catalysts on lignin samples, Zakzeski et al. studied the oxidation of lignin model compounds (5,5′ model compounds and β-O-4 model compounds) in the presence of O_2 as oxidant

Table 5. Properties and Composition of the Technical Lignins[139]

technical lignins	ash (%)	moisture content (%)	carbohydrates (%)	nitrogen (%)	sulfur (%)	molecular weight (Da)	characteristic composition	processing methods
kraft lignin	0.5−3.0	3.0−6.0	1.0−2.3	0.05	1.0−3.0	1500−25,000	increasing of phenolic hydroxyl and carboxyl groups, biphenyl, quinine and catechol structures	sulfate kraft cooking
soda lignin	0.7−2.3	2.5−5.0	1.5−3.0	0.2−1.0	0.0	1000−15,000	increasing of *p*-hydroxyl units and carboxyl groups (for nonwood lignins); high silicate and nitrogen contents	soda or soda-anthraquinone processes
organosolv lignin	1.7	7.5	1.0−3.0	0.0−0.3	0.0	500−5000	lignin of high quality; high chemical purity	organosolv pulping
hydrolysis lignin	1.0−3.0	4.0−9.0	10.0−22.4	0.5−1.4	0.0−1.0	5000−10,000	many condensed structures	enzymatic hydrolysis
lignosulfonates	4.0−8.0	5.8	−	0.02	3.5−8.0	1000−150,000	phenolic hydroxyl, carboxylic, and sulfur containing groups	byproduct of sulfite cooking
IL lignin	0.6−2.0	−	0.1	−	1.5	~ 2000	−	IL processing

and 1-ethyl-3-methylimidazolium diethyl phosphate ([C_2mim][Et_2PO_4]) as solvent (Table 4, entry 5).[101] Here, the strategy was to use an IL known to be an excellent solvent for the dissolution of lignocellulosic biomass and in particular cellulose.[127] Thus, the catalytic oxidation of the cinnamyl alcohol, a model compound containing a propyl chain with a carbon−carbon double bond, occasionally observed in lignin streams in pretreatment methods, mainly led to cinnamaldehyde (leaving the carbon−carbon double bond intact). Under these conditions (0.24 mol % $CoCl_2 \cdot 6H_2O$, 0.5 equiv of NaOH, O_2, [C_2mim][Et_2PO_4], 3 h, and 80 °C) cinnamic acid formation was also observed, as well as the disruption of the double bond forming benzoic acid or epoxide.[101]

The benzyl functionality in veratryl alcohol was also selectively oxidized to form veratraldehyde, presenting excellent turnover frequency (1440 and 1300 h^{-1} using $CoCl_2 \cdot 6H_2O$ and Co(salen), respectively).[101] However, phenolic functional groups contained in guaiacol, syringol, and vanillyl alcohol remained intact, although the benzyl alcohol group in the latter was oxidized to form vanillin. In addition to the easy solubilization of substrates and catalysts in the chosen IL, the extraction of products with ethyl acetate or diethyl ether was especially easy. However, the recycling of the IL was not investigated in this study.

The authors also investigated the influence of reaction conditions, such as temperature, oxygen pressure, and base loading, and studied the mechanisms through an in situ spectroscopic investigation (ATR-IR, Raman, and UV−vis spectroscopy) on the model compounds to determine the role of NaOH.[128] Theses analyses suggested that several reactive intermediates were stabilized by the IL, particularly a superoxide radical anion that is not readily formed in traditional solvents. Among the tested ILs, [C_2mim][Et_2PO_4] led to the maximum activity, suggesting that this IL favored coordination of the substrate to the cobalt.[101]

It is important to note that the solvation powers of ILs are not their only advantage. These solvents can also stabilize the catalysts or even the reactive intermediates, playing an important role in the mechanisms and leading sometimes to different results not obtained in classical media. For example, Stärk et al. tested the oxidation of syringaldehyde as a model compound before they applied their oxidative system to real lignin samples (20 wt % $Mn(NO_3)_2$ as catalyst, 6.5 MPa O_2 as oxidant, [C_2mim][CF_3SO_3] as solvent, 24 h, 100 °C) and showed the formation of 2,6-dimethoxybenzoquinone, which was not obtained with non-IL solvents (Table 4, entry 6).[102]

It is interesting to note that the ILs used for the studies performed on lignin model compounds are not the same as those selected for real lignin sample experiments. Indeed, publications reporting the oxidation of both model compounds and real samples involve ILs known to efficiently dissolve lignocellulosic biomass, such as alkyl phosphate- or alkylsulfonate-based ILs,[43,95,129,130] rather than classic ILs, such as chloride-, hexafluorophosphate-, triflate- or bis(trifluoromethylsulfyl)imide-based ILs.

The acetate-based ILs, recently investigated for their great results in dissolution or pretreatment of raw biomass,[37,131−133] have not been reported for oxidation reactions, probably because of the lack of stability against the oxidative conditions. However, our group showed that polyoxometalate (POM) catalysts in [C_2mim][OAc] can oxidize and degrade the lignin contained in woody biomass (pine sawdust).[134] This system was used for delignification, but no degradation of the IL was observed under these conditions.

Another efficient method studied for the oxidation of lignin compounds was based on the use of nanoparticles (Table 4, entry 7). IL-stabilized nanopalladium(0) associated to a pyridinium salt of iron bis(dicarbollide) co-catalyst were efficient for the oxidation of benzyl alcohol and substituted derivatives to produce aromatic aldehydes with yields between 77% and 93% (O_2 as oxidant, 18 h, 120 °C, and [C_4mim][PF_6]/[C_4mim][$MeSO_4$] mixture as solvent).[103] As it was widely showed, ILs represent a flexible and opportune platform to prepare, solubilize, and stabilize Pd nanoparticles, acting as a solvent, stabilizer, ligand, and/or support for transition metal nanoparticles.[135−138] In this particular study,[103] in addition to the stabilizing effect on Pd nanoparticles, the high solubility of the co-catalyst in the IL mixture improved the transport of oxygen to the active metal centers and increased the yields.[103] The main advantage of this system remains its robustness and its recyclability with high product selectivity.

In conclusion, the choice of ILs in the described oxidative systems applied to lignin model compounds is based on several parameters. These include (1) the ability to solubilize the substrates and the catalysts, (2) the stabilizing effect of the ILs on catalysts or reactive intermediates, (3) the easy separation and opportunity for recycling, and (4) the unique reactivity, not obtained with non-IL chemistry.

Oxidation of Lignin Samples Using Ionic Liquids. Because of the structural complexity of natural lignins, most of the studies reported to date have used pure lignin model compounds as discussed above (Table 4). The challenge,

Table 6. Experimental Conditions of Lignin Oxidation Using ILs

entry	substrate	catalyst	oxidant	experimental conditions	IL[a]	role of IL	recycling	ref
1	AlcellTM organosolv lignin, soda lignin	Co(salen) or $CoCl_2 \cdot 6H_2O$ (0.24 mol %), NaOH (48 mol %)	O_2 (0.5 MPa)	3 h, 80 °C	$[C_2mim][Et_2PO_4]$	easy dissolution of the catalyst and lignin samples	not investigated	101
2	organosolv lignin	Mn, Fe, Cu metal salts (2 wt %, 20 wt %)	air (8 MPa)	24 h, 100 °C	$[C_2mim][CF_3SO_3]$, $[C_2mim][MeSO_3]$, $[C_2mim][EtSO_4]$, $[C_1mim][MeSO_4]$	solvent of the reaction	attempted IL recycling	102
3	organosolv lignin	$CuSO_4$ (1 wt %)	O_2 (2.5 MPa)	1.5 h, 175 °C	$[C_1mim][Me_2PO_4]$ $[C_1py][Me_2PO_4]$, $[MeEt_3N][Me_2PO_4]$, $[C_1morph][Me_2PO_4]$	solvent of the reaction, easy separation	IL phase reused six times	140
4	organosolv lignin	nanopalladium(0) (1 mol %, pyridinium salt of iron bis(dicarbollide) (10 mol %)	O_2 (0.4 MPa)	120 °C, 18 h	$[C_4mim][PF_6]/[C_4mim][MeSO_4]$ (2:1, V/V)	stabilization of nanoparticles, solubilization of lignin sample	catalyst reused five times	103
5	kraft lignin	electrochemistry: use of an active ruthenium/vanadium/titanium mixed oxide as electrodes		1.0, 1.3, 1.5, and 1.7 V oxidation potentials investigated	$[Et_3NH][MeSO_3]$	easy dissolution of lignin sample, solvent of reaction	IL easily regenerated	144
6	rubber wood	no added catalyst	O_2 (9.4 L min^{-1})		$[C_1mim][MeSO_4]$	solvent of the reaction	not investigated	145

[a] $[C_2mim][Et_2PO_4]$: 1-ethyl-3-methylimidazolium diethyl phosphate. $[C_2mim][CF_3SO_3]$: 1-ethyl-3-methylimidazolium trifluoromethanesulfonate. $[C_2mim][MeSO_3]$: 1-ethyl-3-methylimidazolium methansulfonate. $[C_2mim][EtSO_4]$: 1-ethyl-3-methylimidazolium ethylsulfate. $[C_1mim][MeSO_4]$: 1,3-dimethylimidazolium methylsulfate. $[C_1mim][Me_2PO_4]$: 1,3-dimethylimidazolium dimethyl phosphate. $[C_1py][Me_2PO_4]$: 1-methylpyridinium dimethyl phosphate. $[MeEt_3N][Me_2PO_4]$: *N*-methyl-*N*-triethylammonium dimethyl phosphate. $[C_1morph][Me_2PO_4]$: dimethylmorpholinium dimethyl phosphate. $[Et_3NH][MeSO_3]$: triethylammonium methansulfonate.

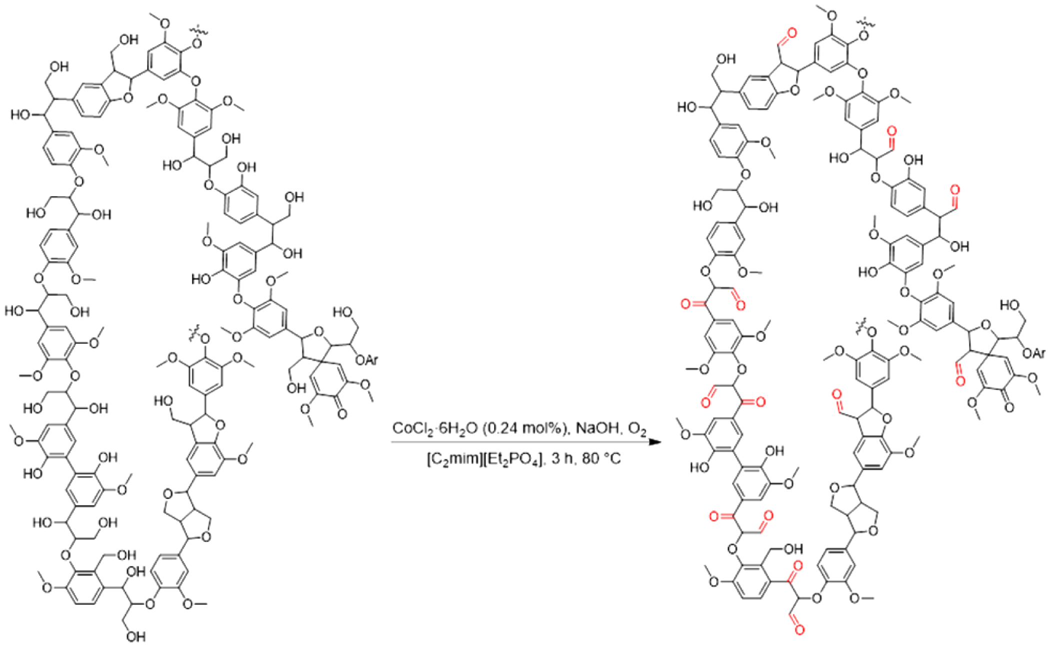


Figure 9. Proposed structural changes in lignin samples as a result of oxidation catalyzed by Co(salen) in $[C_2mim][Et_2PO_4]$.[128]

however, for application to the biorefinery area, is to valorize the widely available (and variable) lignins that are byproducts of cellulose isolation and to produce new biosourced aromatic compounds. Currently, an important amount of lignin is incinerated to produce process steam and energy, and only a very small part is used for the production of value-added products.[18] Technical lignins are isolated as byproduct-streams in lignocellulosic biorefineries such as kraft, soda, organosolv, hydrolysis lignins, and lignosulfonates.[139] Their structures and the impurities they contain are directly dependent on the associated processing method. The main properties of these different available technical lignins are summarized in Table 5.

As reported in Table 6, most of the oxidation experiments using ILs on lignin samples were performed with organosolv or soda lignins (Table 6, entries 1−4). In fact, these types of technical lignins have compositions and structures close to natural lignin and are sulfur free, with a high chemical purity.[139−143] One example from rubber wood was also reported (Table 6, entry 6).

The main processing methods investigated used metal catalysis (Table 6, entries 1−3), but the use of nanoparticles as catalysts (Table 6, entry 4) and electrocatalysis (Table 6, entry 5) were also studied. Thus far, the ILs used to study bulk lignin oxidation have been only those known to efficiently dissolve lignin, such as phosphate and sulfate-based ILs.

On the basis of their results obtained from lignin model compounds and previously described in this review (Table 4, entry 5), Zakzeski et al. were tested their oxidative conditions ($CoCl_2·6H_2O$ as catalyst, NaOH, O_2, $[C_2mim][Et_2PO_4]$ as solvent, 3 h, 80 °C) on an Alcell organosolv lignin, extracted from mixed hardwoods (maple, birch, and poplar) by an organosolv process using aqueous ethanol, and on a soda lignin, extracted from grass (Table 6, entry 1).[128] Even if several of the alcohol functional groups in the lignin were oxidized to the corresponding aldehydes, the absence of monomeric products suggested that O−C−O and C−C linkages remained intact, as shown in the proposed structure (Figure 9).

Additionally, these conclusions were supported by model compound experiments and spectroscopic analysis. No difference was observed between the organosolv lignin and soda lignin in this study because of their similar composition.[139] The diethyl phosphate-based IL properties, including high oxygen solubility and lignin dissolution ability, allowed the oxidations to proceed under mild conditions (O_2, 3 h, 80 °C).[128] However, the recycling of the ILs should be investigated to improve the greenness of the process.

Another relevant study in the area was recently published by the Wasserscheid group, using a multiparallel batch reactor system to screen several ILs and metal salt catalysts in the oxidative depolymerization of an organosolv lignin extracted from beech (Table 6, entry 2).[102] Among all the Mn, Fe, and Cu metal salts tested, the most effective was $Mn(NO_3)_2$ in 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ($[C_2mim][CF_3SO_3]$), which oxidatively cleaved lignin to give phenols, unsaturated propylaromatics, and aromatic aldehydes. A large scale batch reaction (11 g of lignin, 24 h, 100 °C, and 84×10^5 Pa air) was conducted in a 300 mL autoclave resulting in 66.3% conversion and separation of several compounds such as vanillin, vanillic acid, syringaldehyde, syringol, syringic acid, sinapinic acid, 2,6-dimethoxy-1,4-benzoquinone (DMBQ, Figure 10), coniferyl fragments, and some nonidentified lignin fragments (Table 7).

Interestingly, by adjusting the reaction conditions and the catalyst loading, the selectivity of the process could be shifted from syringaldehyde as the major product to DMBQ isolated as a pure substance in 11.5 wt % overall yield by an extraction/crystallization process.[102] This compound is particularly

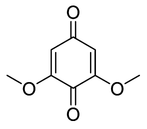


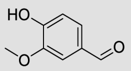
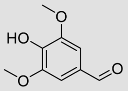
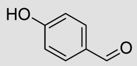
Figure 10. Structure of 2,6-dimethoxy-1,4-benzoquinone (DMBQ).

Table 7. Products Obtained by Extraction with Different Solvents After the Organosolv Lignin Oxidation Catalyzed by $Mn(NO_3)_2$ in ILs[102]

ionic liquid[a]	extracting agent	identified products
$[C_1mim][MeSO_4]$	toluene	n.i.,[b] vanillin, syringaldehyde
	dichloromethane	syringol, vanillin, syringaldehyde
	ethyl acetate	vanillic acid, syringol, vanillin, n.i.
$[C_2mim][MeSO_3]$	toluene	n.i., vanillin, DMBQ,[c] syringaldehyd,
	dichloromethane	vanillic acid, n.i., vanillin, DMQB, syringaldehyde
	ethyl acetate	vanillic acid, syringol
$[C_2mim][EtSO_4]$	toluene	syringol, vanillin, DMBQ, syringic acid, syringaldehyde, sinapinic acid
	dichloromethane	syringol, vanillin, DMBQ, syringaldehyde
	ethyl acetate	n.i., vanillin, DMBQ, syringaldehyde
$[C_2mim][CF_3SO_3]$	toluene	n.i., DMBQ
	dichloromethane	syringol, vanillin, DMBQ, n.i., syringaldehyde
	ethyl acetate	conyferyl-fragment, sinapinic acid

[a] $[C_1mim][MeSO_4]$: 1,3-dimethylimidazolium methylsulfate. $[C_2mim][MeSO_3]$: 1-ethyl-3-methylimidazolium methansulfonate. $[C_2mim][EtSO_4]$: 1-ethyl-3-methylimidazolium ethylsulfate. $[C_2mim][CF_3SO_3]$: 1-ethyl-3-methylimidazolium trifluoromethanesulfonate. [b] n.i.: nonidentified lignin fragment. [c] DMBQ: 2,6-dimethoxy-1,4-benzoquinone.

Table 8. Products of Lignin Oxidation Catalyzed by $CuSO_4$[140]

ionic liquid[a]	conversion (%)	yield (%)		
		vanillin 	syringaldehyde 	*p*-hydroxybenzaldehyde 
blank [b]	100	10.2	5.6	3.5
$[C_1mim][Me_2PO_4]$ [c]	100	14.7	8.8	6.2
$[C_1py][Me_2PO_4]$ [c]	100	14.5	8.7	5.9
$[MeEt_3N][Me_2PO_4]$ [c]	93	12.3	7.1	5.4
$[C_1morph][Me_2PO_4]$ [c]	86	11.2	6.5	4.4

[a] Experimental conditions: 2.5 g of lignin, 47.5 g IL, 0.025 g $CuSO_4$, 2.5 MPa O_2, 175 °C, and 1.5 h. [b] Experimental conditions: 2.5 g of lignin, 47.5 g NaOH (2M), 0.025 g $CuSO_4$, 2.5 MPa O_2, 175 °C, and 1.5 h. [c] $[C_1mim][Me_2PO_4]$: 1,3-dimethylimidazolium dimethyl phosphate. $[C_1py][Me_2PO_4]$: 1-methylpyridinium dimethyl phosphate. $[MeEt_3N][Me_2PO_4]$: *N*-methyl-*N*-triethylammonium dimethyl phosphate. $[C_1morph][Me_2PO_4]$: dimethylmorpholinium dimethyl phosphate.

interesting as a potential antitumor agent and as a synthon in organic chemistry.[146−148]

This study showed changes in the yields of formed products, according to the selected IL ($[C_1mim][MeSO_4]$, $[C_2mim][MeSO_3]$, $[C_2mim][EtSO_4]$, or $[C_2mim][CF_3SO_3]$) and chosen experimental conditions (catalyst loading, extracting solvent). However, the authors did not explain these selectivity changes, and such understanding of the chemistry involved in the explored conditions will be the key to future exploitation and development of lignin oxidative processes involving IL technology.

An attempt at IL recycling was performed, but the procedure required multiple filtration steps leading to important IL losses. This recycling procedure needs to be improved in order to recover the IL and improve the economic viability of the process.

Very recently, Shiwei et al. also studied the oxidation of an organosolv lignin extracted from mixed hardwoods (Table 6, entry 3). They proposed the production of high value-added aromatic aldehydes in four dimethyl phosphate-based ILs catalyzed by $CuSO_4$ in the presence of O_2.[140] The conversion of lignin reached a range of 86−100% with the optimized conditions (1.5 h, 175 °C), and the total yield into identified aromatic aldehydes (vanillin, syringaldehyde, and *p*-hydroxybenzaldehyde) ranged from 19.3% to 29.7% (Table 8).

In comparison to aqueous NaOH processes, the lignin conversion and the yield of aromatic aldehydes were higher in the IL process. Additionally, the products and IL phase were easily separated, allowing the recycling and reuse of the IL phase containing the $CuSO_4$ catalyst with good activity six times.

The ILs, chosen for their dissolution ability, present a weaker alkali environment than NaOH, increasing the oxidative activity of the active oxygen.[149] The authors attributed the difference of yields in aromatic compounds to the solubility of lignin in the studied ILs. However, this conclusion lacks full support, and more investigation of the chemistry is required to clearly understand the mechanisms of oxidation in these ILs.

Zhu et al., who developed an oxidative method using nanoparticles associated to a specific co-catalyst for benzyl alcohol model compounds (Table 4, entry 7), applied the same conditions to an organosolv lignin (M_w = 2113 g mol^{-1}) leading to a 72% conversion after 18 h at 120 °C (Table 6, entry 4).[103] The major products identified were syringaldehyde, vanillin, and *p*-hydroxybenzaldehyde, with 2,6-dimethoxy-1,4-benzoquinone as a minor product. In addition to easily dissolving the lignin sample, the $[C_4mim][PF_6]/[C_4mim][MeSO_4]$ mixture (2:1, V/V) facilitated the catalyst recycling at the end of the reaction. The nanopalladium and water-insoluble co-catalyst remained in the $[C_4mim][PF_6]$ phase while water-soluble $[C_4mim][MeSO_4]$ was extracted to the aqueous phase. After drying, the recovered catalysts were still active for three additional reactions with a lignin conversion of 70%, 65%, and 68%, respectively.

On the basis of the lignin electrochemistry in $[C_2mim][NTf_2]$ developed by Chen et al.,[150] an electro-catalytic oxidative process was recently envisaged from kraft lignin in the presence of the protic triethylammonium methanesulfonate ($[Et_3NH][MeSO_3]$) IL using an active ruthenium/vanadium/titanium mixed oxide electrode (Table 6, entry 5).[144] Vanillin and some other aromatic compounds such as benzaldehyde, 3-furaldehyde, *m*-tolualdehyde, acetovanillone, syringol, 2-methoxy-4-vinylphenol, diphenylether, and guaicol were identified by gas chromatography−mass spectrometry (GC-MS) and high-performance liquid chromatography (HPLC). In this work, the IL provided a suitable medium for dissolution of lignin but also ensured electrolysis at high potentials and promoted an oxidative lignin cleavage mechanism. This mechanism was widely studied previously by monitoring the electrolysis of several phenolic ethers selected as lignin model compounds.[86,151] However, in this case, the IL was easily regenerated from the aqueous solutions.[144] A clear advantage of this electrochemical method is the selective formation of smaller molecular weights products by choosing the applied potential. The low amount of substrate used in the electrochemical system remains, however, limiting for semi-industrial applications.

Finally, Shamsuri et al. reported the production of vanillin by oxidation of rubber wood using 1,3-dimethylimidazolium methysulfate ($[C_1mim][MeSO_4]$) in the presence of O_2 (Table 6, entry 6).[145] Reaction times (2, 4, 6, 8, and 10 h), reaction temperatures (25, 40, 60, 80, and 100 °C), and O_2 concentration (2.4, 4.7, 7.1, and 9.4 L min^{-1}) were specifically studied to determine the optimal conditions for vanillin production. In fact, the process was performed in two separated steps: (1) the isolation of lignin from rubber wood by using $[C_1mim][MeSO_4]$ as reported previously,[152] followed by (2) the oxidation of the extracted lignin using oxygen. This unique example performing the oxidation of raw biomass using ILs clearly demonstrates that the challenge to produce aromatic compounds from lignocellulosic biomass remains difficult and not complementally possible yet.

In conclusion, the research on lignin valorization using ILs may be in its infancy, but the first examples from the literature to oxidize real lignin samples are very encouraging, clearly showing new chemistry and thus new opportunities (e.g., obtaining new compounds, finding new selectivity, and often better yields compared to classical conditions). Analysis of these studies allows us to develop several different possible approaches to the oxidation of lignin using ILs and provide some recommendations (provided in the next section) to better explore the role of the ILs in these reactions.

■ SUMMARY AND OUTLOOK

The oxidation of lignin has attracted interest for a long time, but currently, only 2% of lignin, one of the most available bioresource on our planet, has been chemically valorized. Since the 2000s, catalytic methods based on enzymes and organometallic catalysts have allowed access to aromatic compounds from lignin despite the lack of selectivity and low catalyst stability.

In the context of green chemistry and the biorefinery concept, low energy and clean separations of products from lignin oxidation remain a real challenge. ILs may prove advantageous in this regard with their unique properties as solvents that can dissolve raw biomass at low temperatures and pressures. As we have reported in this review, the oxidation of lignin model compounds and lignin samples using ILs can lead to valuable platform aromatic compounds such as vanillin, vanillic acid, and many others that might replace petroleum-based feedstocks.

This review has also shown that the ILs used, mainly based on phosphate and sulfonate anions, are stable against oxidation and able to dissolve lignin. In many cases, the IL phase and the catalyst could be easily separated from the products and reused without loss of efficiency. However, the most important point demonstrated by the use of ILs in lignin oxidation processes may be selectivity. For example, some ILs were shown to selectively dissolved lignin rather than cellulose or hemicellulose.[153] Moreover, access to new compounds, unobtainable under more classic conditions was also demonstrated. The possible control of this selectivity to a specific reactivity by changing the experimental conditions (IL nature, reaction temperature, catalyst loading, extracting solvent, etc.) opens the door to new applications for lignin oxidation using ILs for the production of value-added chemicals.

Still a major point that now needs resolution is the development of low energy separations to isolate each compound after oxidation. There is also concern regarding the source for available lignin because the pulp and paper industry (kraft lignin and lignosulfonates) is either cutting back production or would have to replace the energy obtained from burning lignin in their processes. Nonetheless, the design of ILs and their unique property sets give us an opportunity to develop truly new methods to easily oxidize, extract, and separate chemicals from the oxidation of lignin, offering hope for a much greater valorization of lignin in the future.

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R.D.R. is co-owner of 525 Solutions.

Biographies

Dr. Gregory Chatel received his master's degree from the University of Savoie, France (2009) and his doctoral degree from the University of Grenoble, France (2012). In 2013, Dr. Chatel joined Prof. Robin D. Rogers'group at The University of Alabama as a postdoctoral research fellow. His research was focused on the application of ionic liquids in green chemistry, separation, and biomass processing. Dr. Chatel joined the Institut de Chimie des Milieux et Matériaux of the University of Poitiers, France, in September 2013, as an assistant professor in order to develop a biomass valorization program based on nonconventional media/techniques.

Prof. Robin D. Rogers obtained both his B.S. in chemistry (1978, summa cum laude) and his Ph.D. in chemistry (1982) at The University of Alabama and currently serves as Robert Ramsay Chair of Chemistry, Distinguished Research Professor, and Director of the Center for Green Manufacturing at UA. His research interests cover the use of ionic liquids and green chemistry for sustainable technology through innovation and include materials (advanced polymeric and composite materials from biorenewables), separations (novel strategies for separation and purification of value-added products from biomass), energy (new lubricant technologies and selective separations), and medicine (elimination of waste while delivering improved pharmaceutical performance).

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