

# The Catalytic Valorization of Lignin for the Production of Renewable Chemicals

Joseph Zakzeski, Pieter C. A. Bruijninx, Anna L. Jongerius, and Bert M. Weckhuysen\*

Utrecht University, Faculty of Science, Debye Institute for NanoMaterials Science, Inorganic Chemistry and Catalysis Group, Sorbonnelaan 16, 3584 CA Utrecht, The Netherlands

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## 1. Introduction

Biomass is an important feedstock for the renewable production of fuels, chemicals, and energy. As of 2005, over

3% of the total energy consumption in the United States was supplied by biomass, and it recently surpassed hydroelectric energy as the largest domestic source of renewable energy.<sup>1</sup> Similarly, the European Union received 66.1% of its renewable energy from biomass, which thus surpassed the total combined contribution from hydropower, wind power, geothermal energy, and solar power.<sup>2</sup> In addition to energy, the production of chemicals from biomass is also essential; indeed, the only renewable source of liquid transportation fuels is currently obtained from biomass.<sup>1</sup>

With the depletion of fossil fuels as a source for fuels, chemicals, and energy, the fraction of energy and chemicals supplied by renewable resources such as biomass can be expected to increase in the foreseeable future. Indeed, several governments have recently passed legislation mandating increases in the gross domestic energy and chemical production from renewable resources, especially biomass. The U.S. Department of Agriculture and U.S. Department of Energy set ambitious goals to derive 20% of transportation fuels and 25% of U.S. chemical commodities from biomass by 2030.<sup>1</sup> Similarly, in Europe, the Dutch Ministry of Economic Affairs set goals to derive 30% of transportation fuels from biomass and to have 20–45% of fossil-based raw materials substituted by biomass by 2040.<sup>3</sup> The European Union as a whole has set a mandatory target of 20% for renewable energy's share of energy consumption by 2020 and a mandatory minimum target of 10% for biofuels for all member states.<sup>4</sup> These goals have contributed to the intensified interest in the development of technology and processes for biomass valorization. Fortunately, the worldwide production capabilities for renewable and sustainable biomass production are enormous. In the United States alone, for example, over 370 million dry tons and 1 billion dry tons of annual biomass are obtainable from forest and agricultural lands, respectively, which can be produced sustainably with relatively modest changes in agricultural and forestry practices and land use.<sup>1</sup> Similarly large biomass production capacity is available in Europe, which could produce 190 million tons of oil equivalent (Mtoe) of biomass by 2010 with possible increases up to 300 Mtoe by 2030.<sup>5</sup> The size of this production is sufficient to supply virtually all of the raw materials now required for the chemical industry.<sup>6</sup>

One particular opportunity to help reach the ambitious goals established by the United States and European Union arises from the development of lignin valorization processes. Lignin is a natural amorphous polymer that acts as the essential glue that gives plants their structural integrity. It is a main constituent of lignocellulosic biomass (15–30% by weight, 40% by energy),<sup>1</sup> together with cellulose and

\* To whom correspondence should be addressed. E-mail: b.m.weckhuysen@uu.nl.



Pictured from left: Bert M. Weckhuysen, Joseph Zakzeski, Pieter C. A. Bruijninx, and Anna L. Jongerius.

Joseph Zakzeski was born in Carson City, Nevada, in 1982. He obtained his bachelor's degree (cum laude, highest distinction) in Chemical Engineering from the University of Illinois, Urbana–Champaign, in 2005. He completed his Ph.D. work in 2009 under the supervision of Prof. Alexis T. Bell at the University of California, Berkeley, on the production of synthons by catalytic oxidative carbonylation. He is currently a postdoctoral research fellow of the National Science Foundation International Research Fellowship Program under the guidance of Prof. Bert Weckhuysen at Utrecht University. His research focus is on the development of in situ spectroscopic characterization techniques to understand and optimize catalytic conversion routes for biomass valorization.

Pieter C. A. Bruijninx, born in 1979 in Roosendaal, The Netherlands, obtained both his master's degree (2002) and Ph.D. degree in Chemistry (2007) from Utrecht University (both cum laude, highest distinction). His doctoral studies were performed under the direction of Prof. Bert Klein Gebbink, Prof. Gerard van Koten, and Prof. Bert Weckhuysen and focused on the development of bioinspired oxidation catalysts and models for non-heme iron enzymes. After receiving his degree, he moved to the University of Warwick, U.K., to work as a postdoctoral research fellow in the group of Prof. Peter Sadler on an NWO Rubicon grant. In 2009, he joined the Weckhuysen group as an assistant professor to work on the catalytic conversion of biomass and renewables for the production of bulk and fine chemicals.

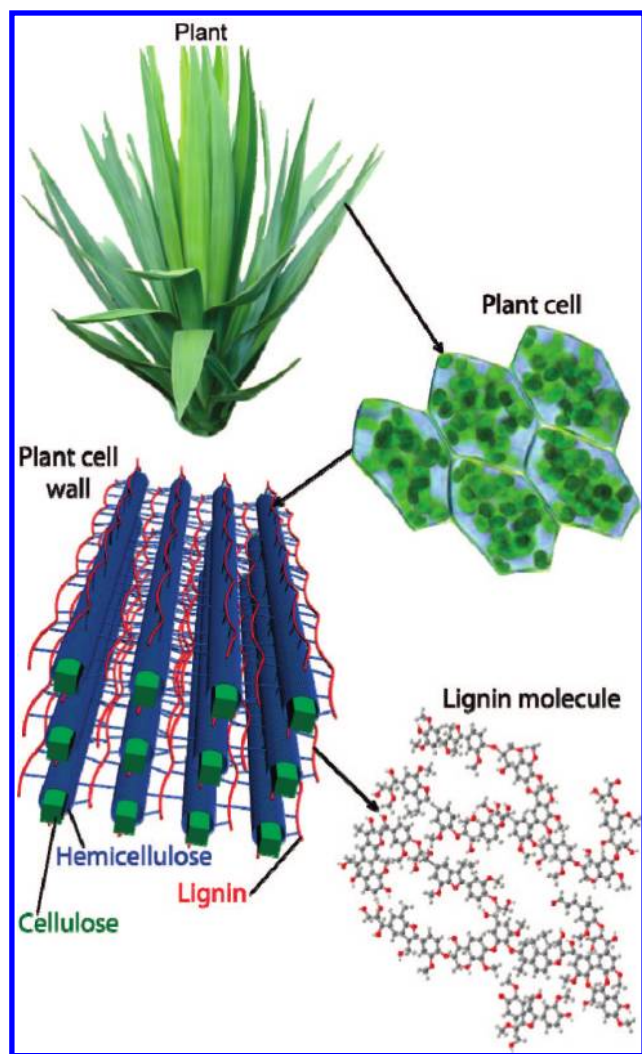
Anna L. Jongerius was born in Zaandam, The Netherlands, in 1985. She obtained her master's degree in Chemistry (cum laude, highest distinction) from the University of Amsterdam in 2008. As an undergraduate student, she worked on homogeneous transition metal catalyzed polymerization reactions in the laboratory of Dr. Bas de Bruin and Prof. Joost Reek at the same university. Currently she is working on her Ph.D. degree at Utrecht University under the guidance of Prof. Bert Weckhuysen. Her research focuses on the catalytic conversion of lignin and related model compounds into aromatic compounds.

Bert M. Weckhuysen, born in 1968 in Aarschot, Belgium, received his master's degree from Leuven University (Belgium) in 1991. After finishing his Ph.D. studies under the supervision of Prof. Schoonheydt in 1995 (cum laude, highest distinction), he worked as a postdoctoral fellow with Prof. Wachs at Lehigh University and with Prof. Lunsford at Texas A&M University. From 1995 until 2000, he was a research fellow of the Belgian National Science Foundation. Since 2000, Weckhuysen has been full professor of inorganic chemistry and catalysis at Utrecht University. He received several research awards, including the 2002 VICI award from The Netherlands Organization for Scientific Research (NWO), the 2006 Gold Medal from the Royal Netherlands Society of Chemistry (KNCV), the 2007 DECHEMA Award from The Max Buchner Research Foundation (Germany), and the 2009 Netherlands Catalysis and Chemistry Award from the KNCV Catalysis Section and The Netherlands Organization of Catalysis Industries. He is scientific director of the Dutch Research School for Catalysis (NIOK) and an elected member of the Young Academy of the Royal Dutch Academy of Sciences (KNAW), The Netherlands Academy of Technology and Innovation (NATI), and the Royal Holland Society of Sciences (KHMW).

hemicelluloses; however, lignin has received little attention relative to cellulose with regards to its valorization. For example, as of 2004, the pulp and paper industry alone produced 50 million tons of extracted lignin, yet the existing markets for lignin products remain limited and focus on low value products such as dispersing or binding agents. As a result, only approximately 2% of the lignins available from the pulp and paper industry are used commercially with the remainder burned as a low value fuel.<sup>7</sup> Nevertheless, lignin conversion has significant potential as a source for the sustainable production of fuels and bulk chemicals.<sup>1,6</sup> With its unique structure and chemical properties, a wide variety of bulk and fine chemicals, particularly aromatic compounds, as well as fuels are potentially obtainable from lignin. Indeed, lignin can be regarded as the major aromatic resource of the bio-based economy.

Catalysis is regarded as a key enabling technology for biomass conversion in general and for fulfilling the promise of lignin valorization in particular. The chemical literature on this topic is scattered, however, and focuses primarily on engineering and biology aspects of lignin rather than specifically on catalytic conversion or catalyst development, which is essential for efficient and selective lignin valorization processes.<sup>8</sup> As a result, the literature involving catalytic lignin valorization is scarce. In addition, given the different aims and focus, reports on catalytic lignin conversion involve a wide range of conditions, solvents, catalysts, and model compounds. To the best of our knowledge, a review unifying the literature on catalytic lignin valorization is lacking; indeed, previous reviews on biomass valorization have focused almost exclusively on cellulose with often only a paragraph devoted to lignin (see below).<sup>9–11</sup> A general review of chemical transformations of biomass by Corma and co-workers focuses on chemical intermediate platforms derived from saccharides, vegetable oils and animal fats, and terpenes.<sup>10</sup> Mäki-Arvela and co-workers, on the other hand, recently published a review on the synthesis of fine and specialty chemicals from wood and other biomass with a focus primarily on products obtainable from cellulose.<sup>11</sup> Most relevant to lignin valorization, Amen-Chen and co-workers published a review on the production of monomeric phenols obtained by the mostly noncatalytic thermochemical conversion of biomass.<sup>12</sup>

The purpose of this paper is to provide a comprehensive review of the catalytic lignin valorization literature. We believe that such a review will provide a perspective that would prompt the development of new catalysts and processes to valorize lignin. The aim is therefore to present the different approaches and strategies that have been reported for catalytic lignin conversion with a focus on the manufacture of valuable and useful bulk and platform chemicals. First, the reported lignin model compounds are introduced and their use discussed in terms of the ability to understand the lignin polymer as a whole and also to highlight possible reactions of chemicals obtained during degradation of processed lignin streams. Next, strategies for lignin dissolution are discussed. Finally, this review focuses on the different strategies for catalytic lignin conversion. These include, among others, (hydro)cracking, lignin reduction reactions, used to make fuels or bulk aromatic and phenolic compounds, and lignin oxidation reactions, used to make functionalized aromatics for the production of fine chemicals. We have concentrated our attention on those chemical routes that employ a heterogeneous or homogeneous catalyst.

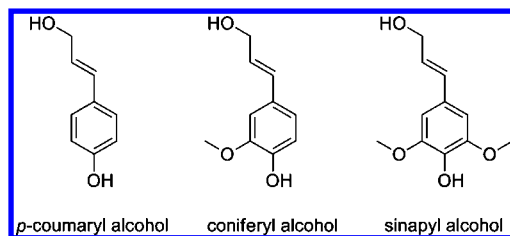


**Figure 1.** Schematic representation of the location and structure of lignin in lignocellulosic material. Adapted from Ritter.<sup>16</sup>

Although high value applications of macromolecular (high molecular weight) lignin are envisioned and include carbon fibers, polymer modifiers (high-value additives in lignin copolymers), adhesives, and resins (for formaldehyde-free applications), we focus exclusively on the production of value-added low molecular weight chemicals from lignin. Lignin valorization by biotechnological means, that is, through the enzymatic conversion/degradation of lignin or related model compounds, falls beyond the scope of this review.<sup>13</sup> In addition, the production or upgrading of bio-oils and biofuels are excluded unless they specifically include information on the conversion of lignin or relevant model compounds.

## 2. Lignin Structure, Pretreatment, and Use in the Biorefinery

Lignin constitutes one of the three major components of lignocellulosic biomass, of which the other two components consist of cellulose and hemicellulose.<sup>14</sup> Lignin is a three-dimensional amorphous polymer consisting of methoxylated phenylpropane structures.<sup>15</sup> In plant cell walls, lignin fills the spaces between cellulose and hemicellulose, and it acts like a resin that holds the lignocellulose matrix together.<sup>16</sup> Cross-linking with the carbohydrate polymers then confers strength and rigidity to the system. Figure 1 depicts a



**Figure 2.** The three monolignols, the building blocks of lignin.

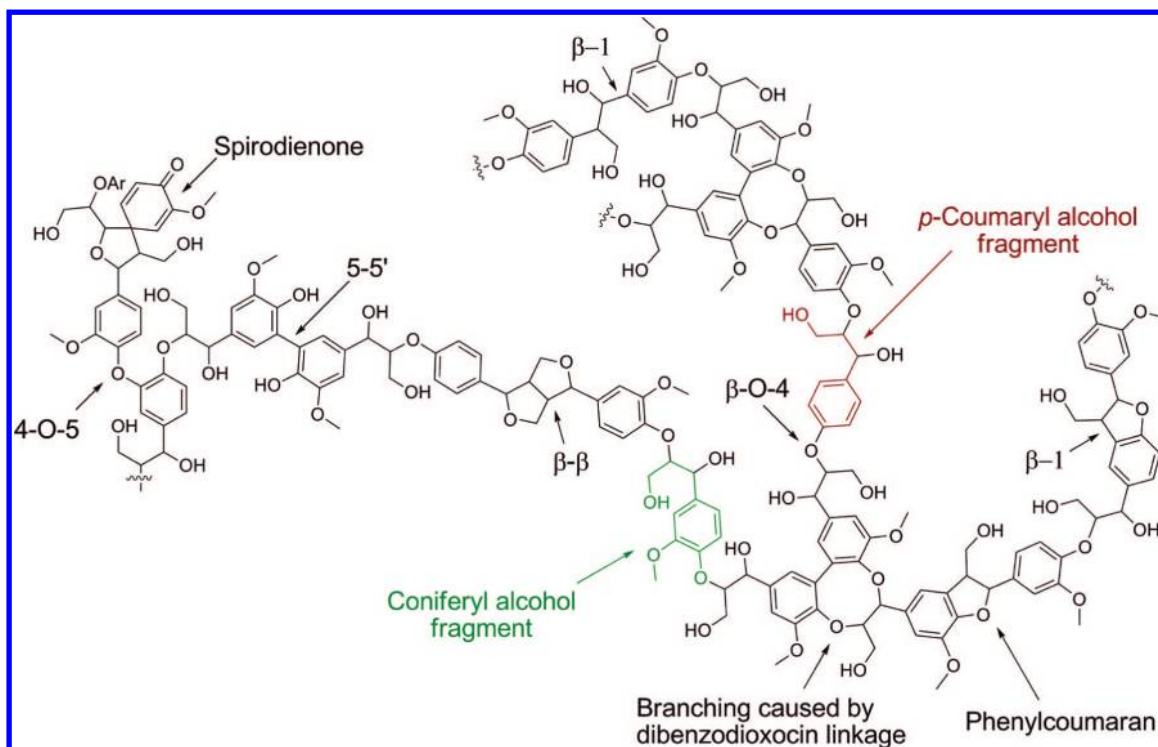
schematic representation of lignin in biomass, highlighting the location and structure of lignin.<sup>17</sup>

Considerable work has been done on the detailed structural characterization of these complex natural polymers and an understanding of both structure and function is evolving as a result. Advances in spectroscopy<sup>15</sup> coupled with oxidation/reduction,<sup>18,19</sup> ozonation,<sup>20,21</sup> photochemical degradation,<sup>22</sup> thermogravimetric analysis,<sup>23</sup> and computational studies<sup>24</sup> have elucidated many of the salient structural features, constituents, and linkages of lignin. The combination of wet chemical methods and, more recently, advanced NMR methods have led to further identification and quantification of the various moieties, end groups, and linkages. These studies have resulted in an improved structural characterization of lignins, yet uncertainty remains. Here, we give a short description of the general structural characteristics of lignin and refer to leading references for a more detailed account.<sup>25–29</sup> Although the exact structure of protolignin, the untreated lignin found in plants (also known as “native lignin”), is still unknown, the biosynthesis of lignin is thought to involve the polymerization of three primary monomers: *p*-coumaryl, coniferyl, and sinapyl alcohols, depicted in Figure 2.<sup>15</sup>

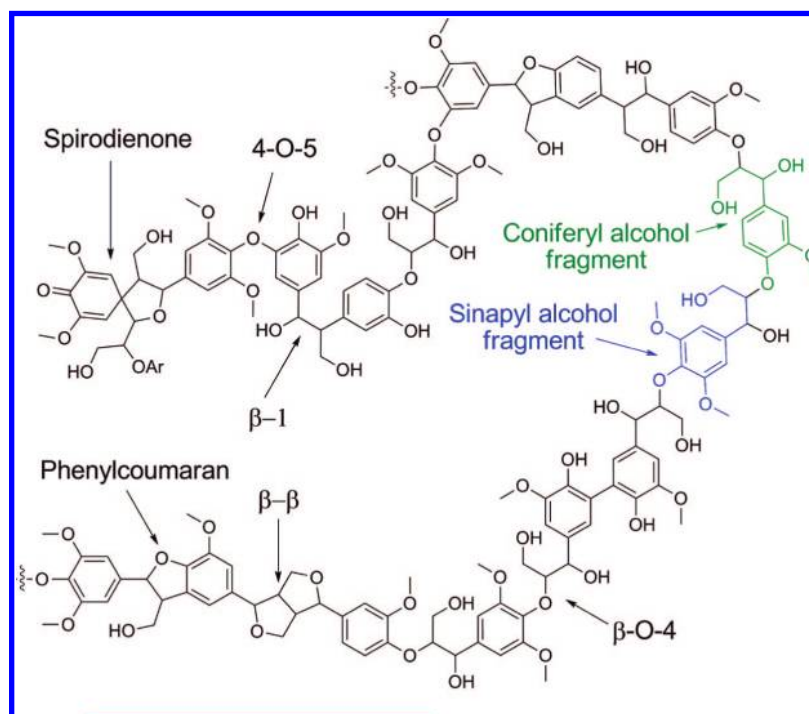
Polymerization by random phenol radical–radical coupling reactions under chemical control then leads to the formation of lignin vascular plants.<sup>25</sup> This current theory of lignification is under debate, however, because the involvement of enzymatic pathways, “dirigent” proteins, has been suggested.<sup>30</sup> The composition, molecular weight, and amount of lignin differ from plant to plant, with lignin abundance generally decreasing in the order of softwoods > hardwoods > grasses. Schematic representations of the softwood and hardwood lignin structures showing common linkages are depicted in Figures 3 and 4, respectively.<sup>31</sup> The structure is merely pictorial and does not imply a particular sequence.

The components derived from coniferyl, sinapyl, and *p*-coumaryl alcohol are indicated by color along with several examples of linkages between the components. The linkages, individually depicted in Table 1, include  $\beta$ -O-4, 5–5,  $\beta$ -5, 4-O-5,  $\beta$ -1, dibenzodioxocin, and  $\beta$ – $\beta$  linkages, of which the  $\beta$ -O-4 linkage is dominant, consisting of more than half of the linkage structures of lignin.<sup>15</sup> The relative abundance of the various linkages in softwoods, including spruce, and hardwoods, such as birch and eucalyptus, are also given in Table 1. As indicated, the dominant linkage in both softwood and hardwood is the  $\beta$ -O-4 linkage, consisting of approximately 50% of spruce linkages and 60% of birch and eucalyptus linkages. The identification and quantification of the various structures and linkages in lignin is a considerable challenge even with advanced NMR techniques because the lignin molecule is very complex.<sup>29</sup> In particular, distinguishing between completely etherified, semietherified, and completely nonetherified 5–5 moieties is very difficult, which results in uncertainty regarding the presence and relative abundance of these structures in





**Figure 3.** Schematic representation of a softwood lignin structure.



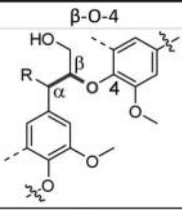
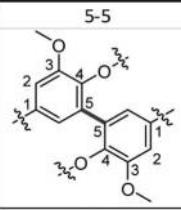
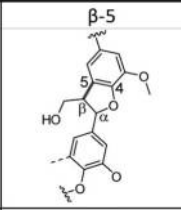

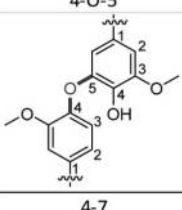
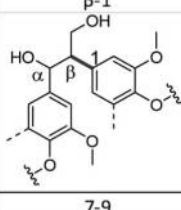
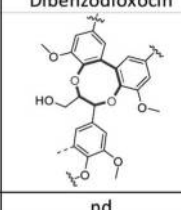
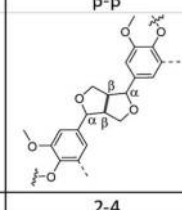
**Figure 4.** Schematic representation of a hardwood lignin structure.

lignin.<sup>27</sup> The composition of softwood and hardwood lignin varies in the relative abundance of the *p*-coumaryl, coniferyl, and sinapyl alcohols. Coniferyl alcohols constitute approximately 90% of softwood lignin, whereas roughly equal proportions of coniferyl alcohol and sinapyl alcohol appear in hardwood lignin, although many exceptions are known.<sup>32</sup> The additional methoxy groups on the aromatic rings prevent formation of 5–5 or dibenzodioxocin linkages, and thus cause the hardwood lignin polymer to form more linear structures relative to softwood.

## 2.1. The Use of Lignin in Current and Future Biorefinery Schemes

In direct analogy to a petroleum refinery, which produces fuels and chemicals from crude oil, a biorefinery is a facility that produces multiple products, including fuel, power, and bulk or fine chemicals, from biomass. It is important to note that the economic necessity for a lignocellulosic biorefinery to produce chemicals in addition to biofuels has been advocated.<sup>33</sup> Indeed, the produc-

**Table 1. Common Linkages and Approximate Abundance Connecting the Phenyl-propane Units in Softwood and Hardwood Lignin<sup>b</sup>**

Linkage						
Abundance per 100 C <sub>9</sub> -units	Softwood	Spruce [291,292]	45-50	19-22	9-12	nd
		Spruce [293]	nd	22	12	nd
		Spruce [294]	45	24-27	9	nd
		Spruce [27]	45	24-27 <sup>a</sup>	9	2
	Hardwood	Birch [291,292]	60	9	6	nd
		<i>Eucalyptus grandis</i> [295]	61	6	3	nd
		<i>Eucalyptus grandis</i> [28]	61	3	3	5
		<i>Paulownia fortunei</i> [26]	62	nd	11	3
Linkage						
Abundance per 100 C <sub>9</sub> -units	Softwood	Spruce [291,292]	4-7	7-9	nd	2-4
		Spruce [293]	nd	2	5	2.5
		Spruce [294]	nd	1	7	2
		Spruce [27]	nd	1	7	6
	Hardwood	Birch [291,292]	6.5	7	nd	3
		<i>Eucalyptus grandis</i> [295]	9	1	<1	3
		<i>Eucalyptus grandis</i> [28]	9	2	nd	3
		<i>Paulownia fortunei</i> [26]	nd	1	2	12

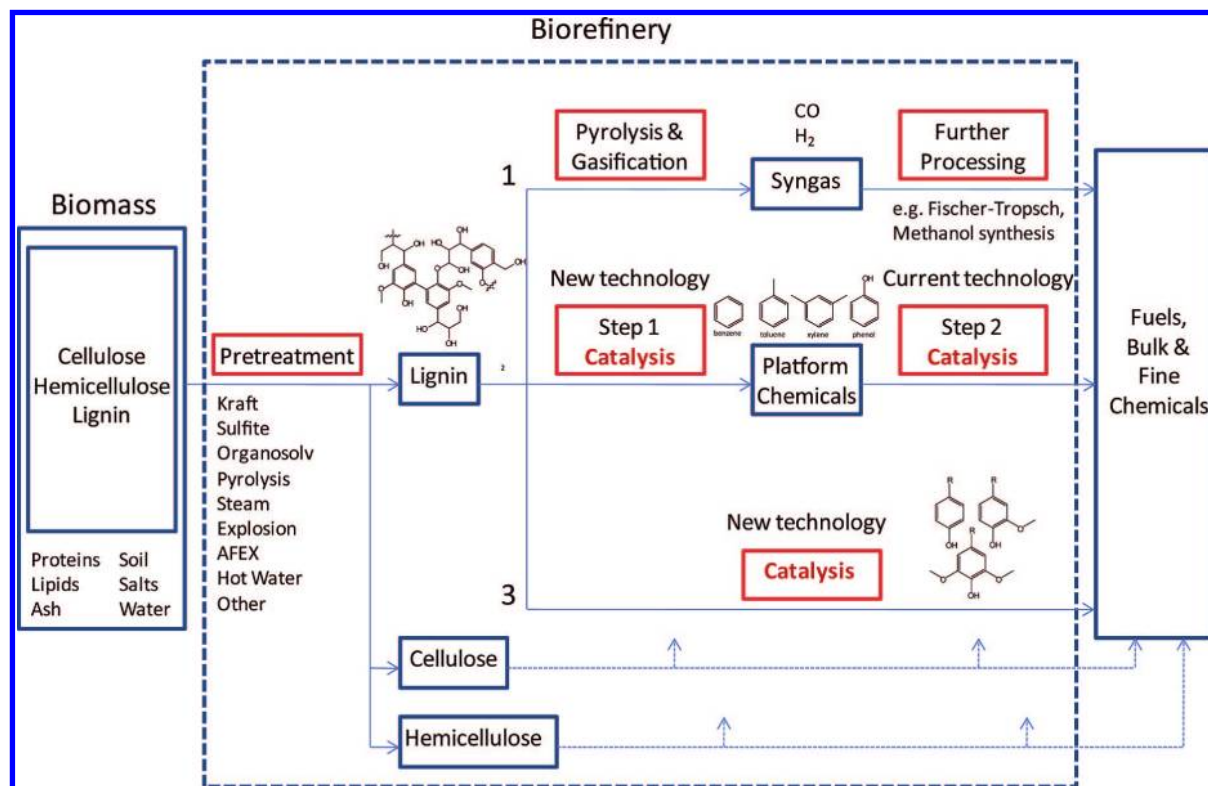
<sup>a</sup> Etherified 19; phenolic 5–8. <sup>b</sup> nd = not determined.

tion of *both* fuels and products is necessary to justify construction of the biorefinery in order to achieve a high energy impact and proper return on investment. In addition, valorization of *all* components of lignocellulosic biomass is essential for an economically viable biorefinery. Since lignin is a principle component of biomass, the biorefinery receives and processes enormous quantities of lignin,<sup>6</sup> and conversion of this component also to fuels and chemicals is imperative for economic profitability. (The International Lignin Institute (ILI) is an association that unites stakeholders from academia and industry with an interest in lignin valorization. ILI is guided by the vision of a future technology for multiproduct conversion of alternative lignocellulosic plants in environmentally proper cyclic processes where lignin is a major product, used at highest possible value. See also [www.ili-lignin.com](http://www.ili-lignin.com).) For example, with the concept of the biorefinery and valorization of all components in mind, PureVision Technology, Inc., has developed a biomass fractionation technology that produces value-added low molecular weight lignin, not just to be used as fuel but as a coproduct to the cellulose stream.<sup>34</sup> Nonetheless, methods for the conversion and application of lignin other than simply burning it for the production of process heat are generally lacking. A major effort is therefore needed to develop new technology for lignin valorization by converting it, at least partly, to value-added chemicals. For reviews on the production of transportation fuels from biomass and lignin streams, which falls beyond the scope of this work, the reader is referred to the reviews of Huber and co-workers,<sup>35,36</sup> Stöcker,<sup>37</sup> and Furimsky.<sup>38</sup>

Figure 5 depicts a biorefinery scheme in which the focus is on the lignin components; valorization of the other biomass components, such as cellulose and hemicelluloses, equally important for the biorefinery, will not be discussed here.

In the first step, plant material, containing lignocellulosic material consisting predominantly of cellulose, hemicelluloses, and lignin but also containing water, soil, salts, extractives, and other materials from nature, is harvested and transported to the biorefinery. The biomass is degraded and separated into its components by a pretreatment method, described in further detail below, to produce feed streams. The type of pretreatment method that can be economically and efficiently employed depends greatly on existing infrastructure, resources, and type of lignin sources available. Since the compositions of the feed streams depend on the pretreatment type (see below) and a wide variety of pretreatment streams and feedstocks are available, for highest efficiency, each biorefinery will be specifically suited to process the feeds indicated by the local environment.

As indicated by Gallezot,<sup>39</sup> three potential strategies for biomass valorization can be used, which are contained in Figure 5. In the first strategy, the biomass is gasified to synthesis gas or degraded by pyrolysis to a mixture of small molecules, which can be used to produce chemicals using technology developed for petroleum feedstocks.<sup>39</sup> In the second strategy, extensive removal of the functional groups present on the lignin monomers yields simple aromatic compounds such as phenol, benzene, toluene, and xylene. These platform chemicals are then reacted in a second step using existing catalytic technology developed for petroleum



**Figure 5.** Lignocellulosic biorefinery scheme with particular emphasis on the lignin stream. Components from the cellulose and hemicelluloses streams are integrated within the lignin framework, but the process arrows are not fully depicted for clarity.

refineries to produce bulk and fine chemicals. In the third strategy, biomass is converted directly to valuable chemicals in a one-pot fashion, which requires highly selective catalysts that disrupt specified functionalities and linkages.<sup>39</sup> This strategy is best suited for the production of fine chemicals with a high degree of functionality, such a vanillin, that already resemble the lignin structure, but more complicated target molecules may also be produced with additional improvements in catalytic technology. Indeed, this approach could yield a plethora of complex aromatics, otherwise not readily available via conventional petrochemical routes. Since each of these strategies is unlikely to yield a single product in high yield in the near or medium term, product separation is an important component of each process. The challenges in separation technology are manifold and its development should go hand in hand with improvements in conversion technology. In each case, after the catalytic processing of the lignin stream, the chemicals or fuels produced can then be purified and sold. In each of the strategies involved in the biorefinery operation, especially the latter two involving the selective formation of target molecules, the development of highly active and selective catalysts would significantly improve the feasibility, economics, and performance of each process. In fact, catalytic technology is considered the most important technological barrier to full realization of the biomass scheme.<sup>6</sup>

## 2.2. Lignin Pretreatment

As indicated above, the pretreatment of lignin is an important initial step in biorefinery operation. The pretreatment separates the principal components of biomass and related materials, degrades the extended polymer to smaller compounds, and occasionally causes other chemical transformations, such as the incorporation of sulfur, depending on the pretreatment method. Efficient biomass fractionation

is actually one of the major challenges posed to the biorefinery, because the complex structure of the plant cell wall and the high crystallinity of cellulose make the feedstock recalcitrant to separation into its components. It is important to stress that the structure of the isolated lignin stream is dependent on the isolation method employed. Consequently, isolation/pretreatment methods that result in consistent types of lignin of high quality and purity are highly desirable. A recent critical analysis of pretreatment technologies was published by Dale and co-workers, in which they divided the various pretreatment technologies into four categories: physical pretreatment (i.e., ball milling), solvent fractionation (including the organosolv process, which is described in more detail below, along with phosphoric acid fractionation and the use of ionic liquids), chemical pretreatment (acidic, alkaline, and oxidative), and biological treatment (using predominately fungi).<sup>40</sup> Gaspar and co-workers published a review focusing on polyoxometalates for the treatment of wood pulps. The feasibility of using these catalysts as an environmentally friendly replacement of chlorine-based chemical treatments in the pulp and paper industry for delignification is discussed.<sup>41</sup>

Several different lignin sources, derived from a specific form of biomass pretreatment, could be potentially used as feedstocks for lignin valorization in a biorefinery. These sources could originate either from pretreatments in the pulp and paper industries (i.e., kraft or lignosulfonate) or new feedstocks specific to the biorefinery scheme (i.e., organosolv). Each pretreatment method has both advantages and disadvantages, which will be discussed below. In addition, the various lignin pretreatments use different conditions and degradation techniques, including temperatures, pressures, solvents, and pH ranges, that uniquely alter the chemical structure and linkages of the protolignin to different extents. The lignin pretreatment thus influences the types of high-



**Table 2. Monomer Molecular Formulas and Weights of Lignin from Various Sources<sup>a</sup>** 6,296–298

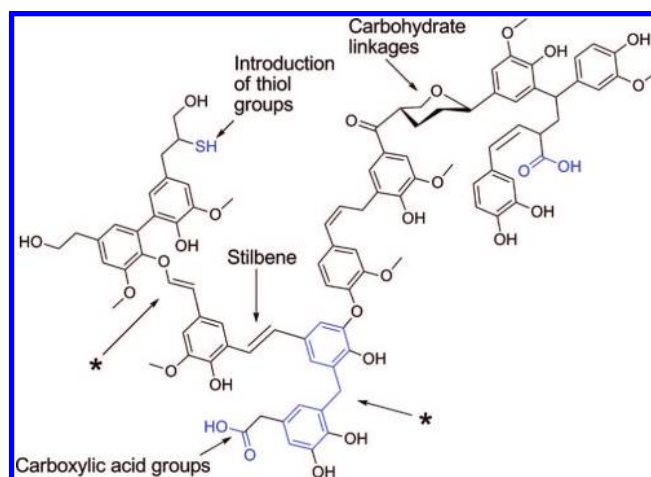
type	monomer molecular formula	monomer molecular weight	ref
kraft lignin	$C_9H_{8.5}O_{2.1}S_{0.1}(OCH_3)_{0.8}(CO_2H)_{0.2}$	180	6
technical kraft lignin	$C_9H_{7.98}O_{2.28}S_{0.08}(OCH_3)_{0.77}$	176.52	296
unreacted kraft lignin	$C_9H_{8.97}O_{2.65}S_{0.08}(OCH_3)_{0.89}$	189.73	297
lignosulfonate lignin (softwood)	$C_9H_{8.5}O_{2.5}(OCH_3)_{0.85}(SO_3H)_{0.4}$	215–254	6
lignosulfonate lignin (hardwood)	$C_9H_{7.5}O_{2.5}(OCH_3)_{0.39}(SO_3H)_{0.6}$	188	6
organosolv lignin	$C_9H_{8.53}O_{2.45}(OCH_3)_{1.04}$	nd	6
pyrolysis lignin	$C_8H_{6.3-7.3}O_{0.6-1.4}(OCH_3)_{0.3-0.8}(OH)_{1-1.2}$	nd	6
steam explosion lignin	$C_9H_{8.53}O_{2.45}(OCH_3)_{1.04}$	~188	6
dilute acid lignin	$C_9H_{8.53}O_{2.45}(OCH_3)_{1.04}$	~188	6
alkaline oxidation lignin	$C_9H_{8.53}O_{2.45}(OCH_3)_{1.04}$	~188	6
beech lignin	$C_9H_{8.83}O_{2.37}(OCH_3)_{0.96}$	nd	298

<sup>a</sup> nd = not determined

value products obtainable from biomass valorization and is an important consideration for biorefinery operation. A summary of the different lignin separation techniques is included in Table 2, which includes the monomeric molecular formula and weight.

### 2.2.1. Kraft Lignin Process

The most dominant chemical pulping technique employed is the kraft lignin process, which employs high pHs and considerable amounts of aqueous sodium hydroxide and sodium sulfide at temperatures between 423–453 K for about 2 h to degrade lignin in a stepwise process.<sup>6</sup> Kraft lignin streams are currently produced commercially, for instance, by MeadWestvaco, the world's largest producer of kraft lignin, and by the LignoBoost technology, a process owned by Metso Corporation, in which lignin is extracted from pulp mill black liquor.<sup>42,43</sup> As the most dominant process, considerable infrastructure of the kraft lignin process is already established, which is advantageous industrially. The kraft lignin process, however, is highly energetically integrated, and the plant as a whole depends on lignin from wood as fuel for process heating, so it is not likely to serve as a source of lignin for biorefinery operation.<sup>6</sup> Ragauskas and co-workers have detailed the process chemistry surrounding kraft pulping including a description of the primary linkages in lignin and the ways in which these linkages are disrupted during the kraft process.<sup>15</sup> The review includes an overview of lignin degradation and condensation reactions, and it provides a discussion of the nature of residual lignin in kraft pulps.<sup>15</sup> The structural changes that occur to lignin as a result of chemical bleaching during the kraft pulping process are described by Gierer et al.<sup>44,45</sup> It is important to note that 5–5 linkages are highly refractory because they typically survive and are even formed during the kraft pulping process. Pulping is caused by nucleophilic attack on electron-deficient conjugated and carbonyl structures, while bleaching is caused by electrophilic attack of electron-rich centers in aromatic nuclei and unsaturated, ring-conjugated side chains.<sup>44,45</sup> A model structure for kraft pine lignin is presented in Figure 6.<sup>6,46</sup> A recent NMR study of technical lignin found most of the structures present in milled wood lignin. In addition, some new types of functional groups and linkages are introduced during the pulping process, such as stilbenes, which are formed from the cleavage of  $\alpha$ -aryl ether linkages of phenylcoumaran structures.<sup>47</sup> Contrary to earlier reports, neither diphenylmethane structures nor vinyl aryl ether structures could be detected by NMR spectroscopy.<sup>47</sup> Despite the high quantity of sulfides employed, relatively little sulfur is contained in the product stream following degradation relative to the lignosulfonate process.



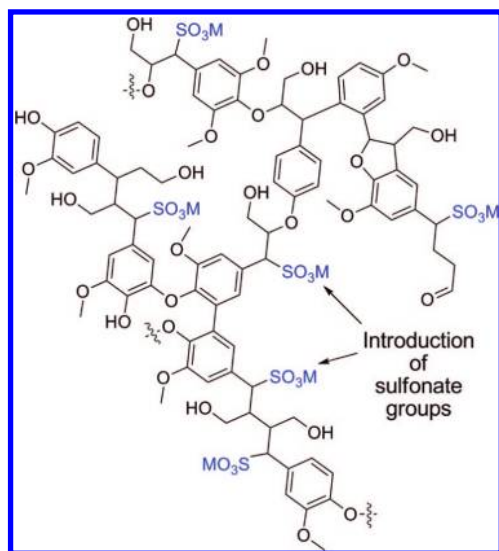
**Figure 6.** Model depicting structural features characteristic of kraft pine lignin.<sup>6,46</sup> Contrary to earlier reports, a recent study showed no evidence for the presence of either diphenylmethane or vinyl aryl ether linkages in kraft lignin (see \* in the figure).<sup>47</sup>

### 2.2.2. Lignosulfonate Process

The sulfite pulping treatment yielding lignosulfonates is also relatively common in the pulp and paper industry, and a summary on lignosulfonate lignin processes was published by Lin and co-workers.<sup>48</sup> The lignosulfonate process is conducted between pH 2 and 12 using sulfite with usually either calcium or magnesium as the counterion.<sup>6</sup> The product is typically soluble in water and in some highly polar organics and amines.<sup>6</sup> Lignosulfonate feedstreams derived from sulfite lignin treatment exhibit a higher average molecular weight and higher monomer molecular weights than kraft lignin as a result of incorporation of sulfonate groups on the arenes. A model structure for lignosulfonate lignin is depicted in Figure 7.

### 2.2.3. Organosolv Process

Organosolv lignin is obtained by treatment of wood or bagasse, the fibrous residue that remains after plant material (i.e., sugar cane) is crushed to extract juice or sap, with various organic solvents.<sup>6</sup> The Alcell process, no longer operational but previously demonstrated at a Repap Alcell pilot plant, is the most well-known process in the organosolv lignin category, and it involved dissolution of lignin in either ethanol or ethanol/water mixtures.<sup>49–51</sup> Lignol Energy Corporation in Canada recently modified the pretreatment developed at the Repap Alcell pilot plant and began operation of a pilot plant to again produce organosolv lignin of high purity and potentially high value.<sup>52</sup> The principle advantages of the organosolv process is that it forms separate streams



**Figure 7.** Model depicting structural features characteristic of lignosulfonate lignin.<sup>6,46</sup>

of cellulose, hemicelluloses, and lignin, allowing valorization of all components of lignocellulosic biomass, and the process is generally considered environmentally friendly because it does not use the sulfides and harsh conditions used in the kraft or lignosulfonate processes. The organosolv lignin is therefore typically very low in sulfur content (see Table 2, entry 6), and it is typically of higher purity than lignin obtained from other methods, which has important ramifications for its valorization to high-value chemicals. The principle disadvantage of the process is the high cost of solvent recovery.

#### 2.2.4. Other Processes

Pyrolysis lignin could also be considered a possible feedstock; its monomeric molecular formula is given in Table 2, entry 7. The pyrolysis process typically involves relatively high temperatures (723 K) for short gas residence times, typically 2 s.<sup>6</sup> No waste except flue gas and ash is produced during the process. However, the principle disadvantage is the high level of carbohydrate consumption required to fuel the process.<sup>6</sup> It has been suggested that pyrolysis lignin has structural characteristics significantly different from the other processes in that it involves C<sub>8</sub>- rather than C<sub>9</sub>-derived oligomers,<sup>49,50</sup> with possible unique opportunities to make specific aromatic hydrocarbons not available via other processes.

The steam explosion process involves steam impregnation under pressure followed by rapid pressure release, which separates the lignocellulosic components and also ruptures the linkages in the lignin structure.<sup>53</sup> In a typical treatment, wood or bagasse is exposed to steam at 1.38–3.45 MPa and 453–503 K for 1–20 min before rapid pressure release.<sup>6</sup> Molecular weight distribution in this process could be similar to the organosolv process. In addition, this process similarly uses no sulfur, and obtaining a separate cellulose stream is also possible.<sup>6</sup> Li and co-workers recently applied a steam explosion pretreatment process to both softwoods and hardwoods.<sup>54</sup> They noted that the process with SO<sub>2</sub> preimpregnation allowed efficient extraction of lignin from hardwood, but only low fractionation efficiencies were observed with softwoods.<sup>54</sup>

Several other methods for pretreating and isolating lignin are available, including the ammonia fiber explosion (AFEX) process<sup>55</sup> and the hot water process. More detailed informa-

tion about these processes can be found in references by Bozell et al.<sup>6</sup> and Kamm et al.<sup>56</sup> The dilute acid process provides effective separation of the lignin from the other biomass streams but suffers from low yields and also corrosion of equipment from the acidic environment.<sup>6</sup> The alkaline oxidation process uses O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> to degrade lignin, which is then easy to recover.<sup>6</sup> The process suffers from slow delignification rates, which is the principle reason that the process is not used extensively. Both methods provide lignin monomers with similar weight distributions as the organosolv lignin.<sup>6</sup>

### 3. Lignin Model Compounds and Product Streams

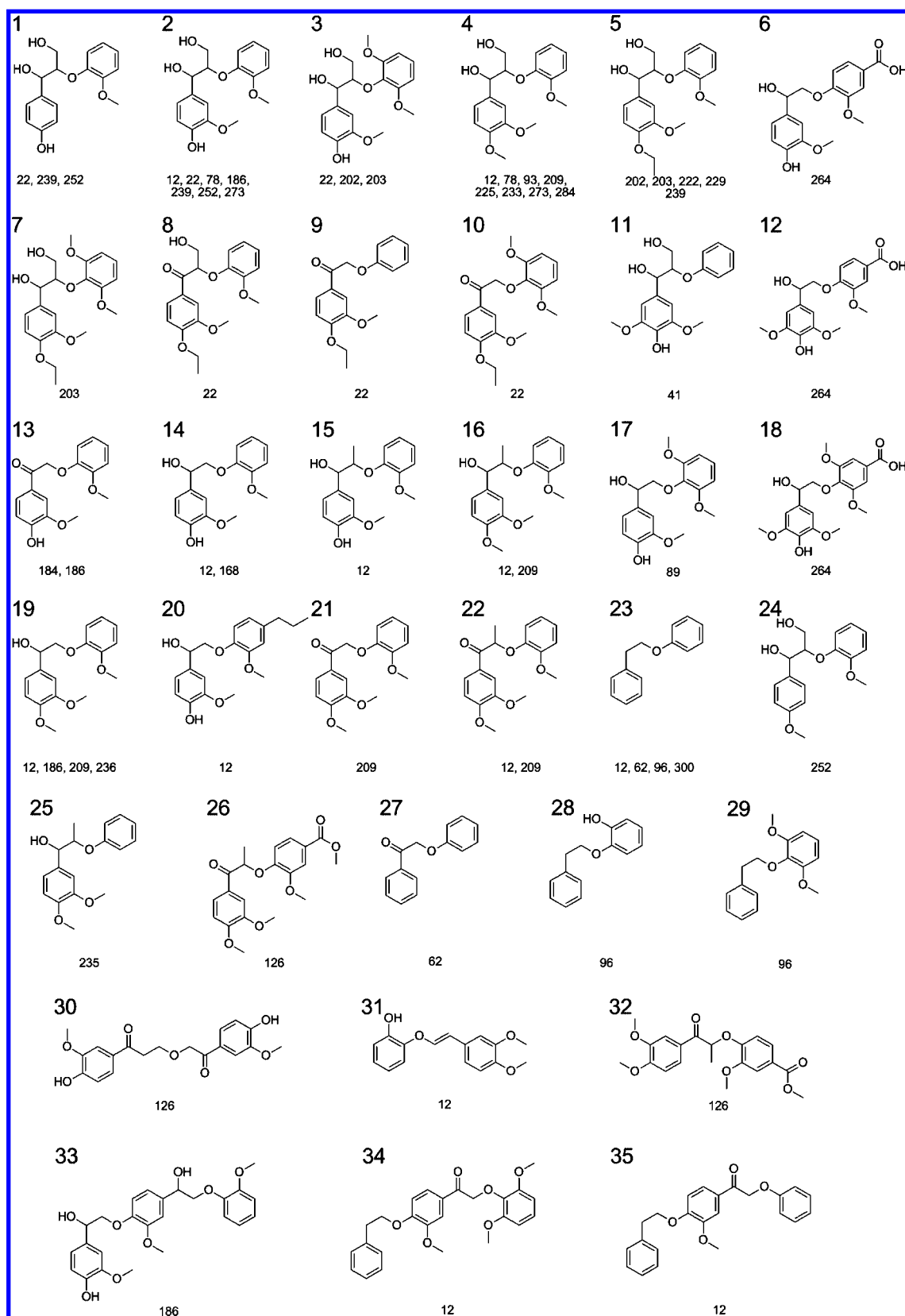
The complexity and variability of lignin has prompted the use of several simpler, low molecular weight lignin model compounds in the study of lignin valorization. The use of lignin model compounds serves several primary purposes. The first purpose is that they contain linkages that resemble those found in the lignin polymer and thus their reactivity provides insight into the degradation and reaction of the polymer structure as a whole. The second purpose arises because the molecules used as model compounds are often found in lignin degradation streams after depolymerization of the lignin polymer; development of methods for their valorization to high-value chemicals is therefore important. Third, the model compounds present fewer analytical challenges relative to the complicated lignin polymer and the plethora of products obtained therefrom. Because they often contain only one type of linkage in the model compound, analysis of the reaction paths, and thus catalytic performance, is similarly simplified. Below we give the structures of the lignin model compounds reported in the literature and the products obtained from their reactions. Because many of the model compounds differ only by the number and type of functional groups (i.e., an additional methoxy group on an aromatic ring or one replacing a hydroxyl group), only representative lignin model compounds are depicted rather than the structure and reactivity of every reported model compound. Model compounds are grouped by type, and only general reaction paths are given. The particular catalysts used are discussed later. The references in which the reaction types are reported are indicated by the numbers given under the compounds or near the arrows.

#### 3.1. $\beta$ -O-4 Linkage Model Compounds

The most abundant linkage in lignin is the  $\beta$ -O-4 linkage.<sup>15,29</sup> The ether bond is readily cleaved; indeed, the cleavage of these bonds during alkaline pulping constitutes the principle pathways in which the lignin is depolymerized.<sup>15</sup> The fragmentation of these linkages tends to lead to the generation of water-soluble compounds containing phenolic hydroxyl groups.<sup>15</sup> Figure 8 depicts model compounds containing the  $\beta$ -O-4 linkage, and chemical transformations of these model compounds are depicted in Scheme 1.

The most important reactions of model compounds containing a  $\beta$ -O-4 linkage involve disruption of that linkage to form simpler model compounds resembling the *p*-coumaryl, coniferyl, and sinapyl alcohol building blocks. Secondary products obtained during the fragmentation include 3-hydroxypropaldehyde and arenes with various aldehyde or alkane side chains. Once fragmented, the resulting compounds are subject to transformations specific





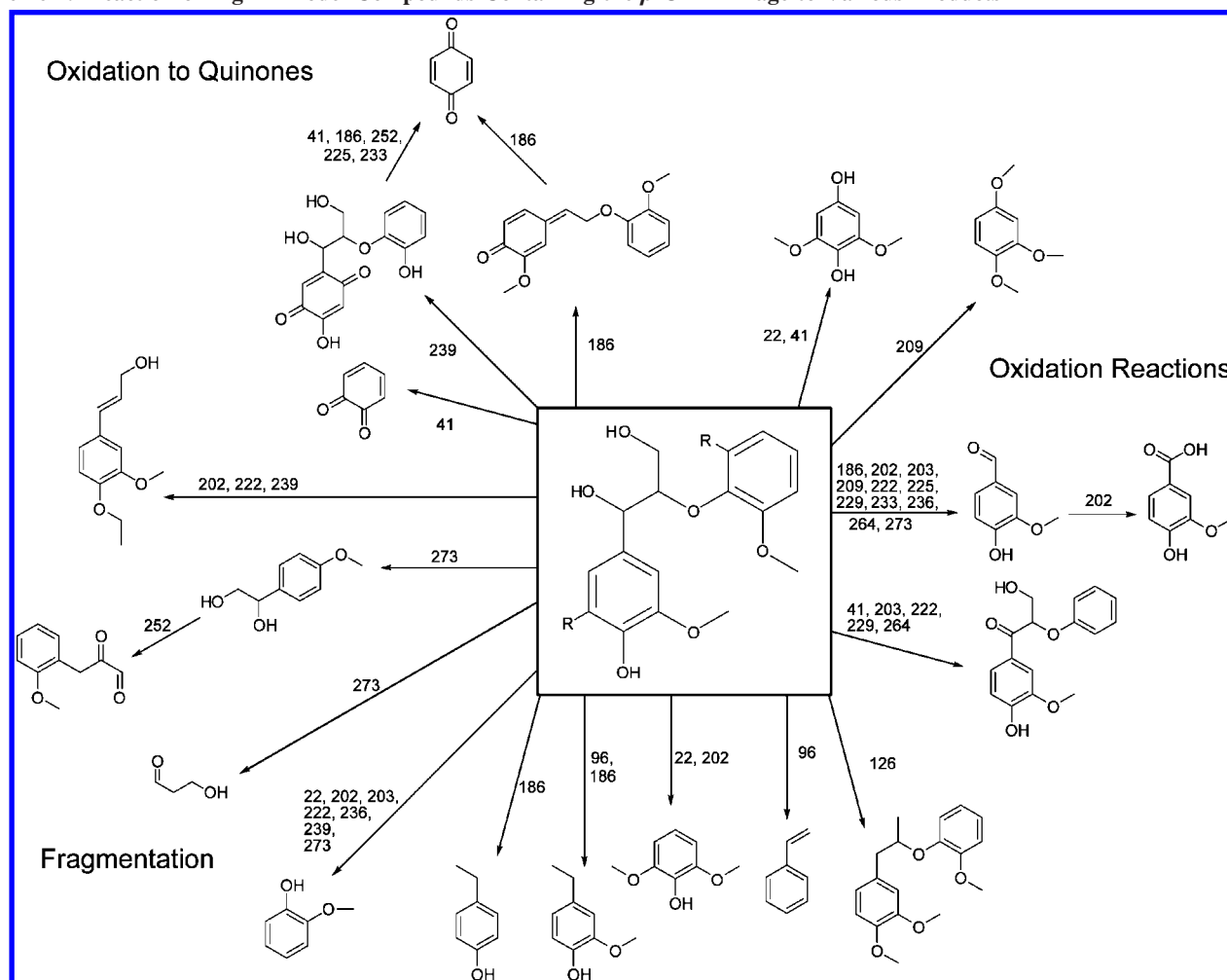
**Figure 8.** Lignin model compounds mimicking the  $\beta$ -O-4 linkage.

to *p*-coumaryl, coniferyl, and sinapyl alcohols, discussed below (see Schemes 6–9). Common subsequent reactions involve oxidation of coniferyl alcohol to form vanillin or oxidation of the aromatic ring to form quinones. Several transformations in which the  $\beta$ -O-4 bond remains intact have been reported, including the oxidation of the alcohol group positioned on the  $\alpha$ -carbon to the corresponding aldehyde.

Several quinone species were also reported in which only one of the arene rings in the model compound is oxidized.

### 3.2. Carbon–Carbon Linkage Model Compounds

The carbon–carbon bonds in lignin constitute some of the most difficult bonds to break, and many of these linkages

Scheme 1. Reaction of Lignin Model Compounds Containing the  $\beta$ -O-4 Linkage to Various Products<sup>a</sup>

<sup>a</sup> The number on the arrow refers the reader to the article in which the reaction was reported. We refer to Figure 8 for the model compounds used in these reactions.

tend to survive the pulping process.<sup>15</sup> The development of catalysts capable of performing these disruptions (particularly the aryl–aryl linkages) is therefore a considerable challenge that has not yet been adequately addressed. Although carbon–carbon linkages are present in the native lignin polymer, additional carbon–carbon bonds can be formed during lignin pretreatment, such as in alkali-promoted condensation reactions during kraft pulping.<sup>15</sup> Figure 9 depicts model compounds containing the 5–5,  $\beta$ -1, and other related C–C bonded compounds. Model compounds with these linkages usually involve dimeric arenes with varying methoxy and hydroxyl substituents on the arene, resembling dimers of *p*-coumaryl or coniferyl alcohols. Typical reaction products are depicted in Scheme 2 and include examples in which the carbon–carbon bonds are broken to yield monomeric compounds. Oxidation of compounds containing a 5–5 bond can also give rise to products with additional ether linkages in addition to the 5–5 bond, as well as oxidative cleavage of the arene ring to form polycarboxylic acids. Compounds containing 5–5 bonds are also subject to reduction and hydrogenation, resulting in linked cyclohexane or cyclohexylbenzene products, or to repolymerization to yield compounds more resembling the lignin parent structure. Transformations involving compounds with  $\alpha$ -1 or  $\beta$ -1 linkages principally involve reaction of the R-group on the arene or oxidation of the hydroxyl group on one of the arenes

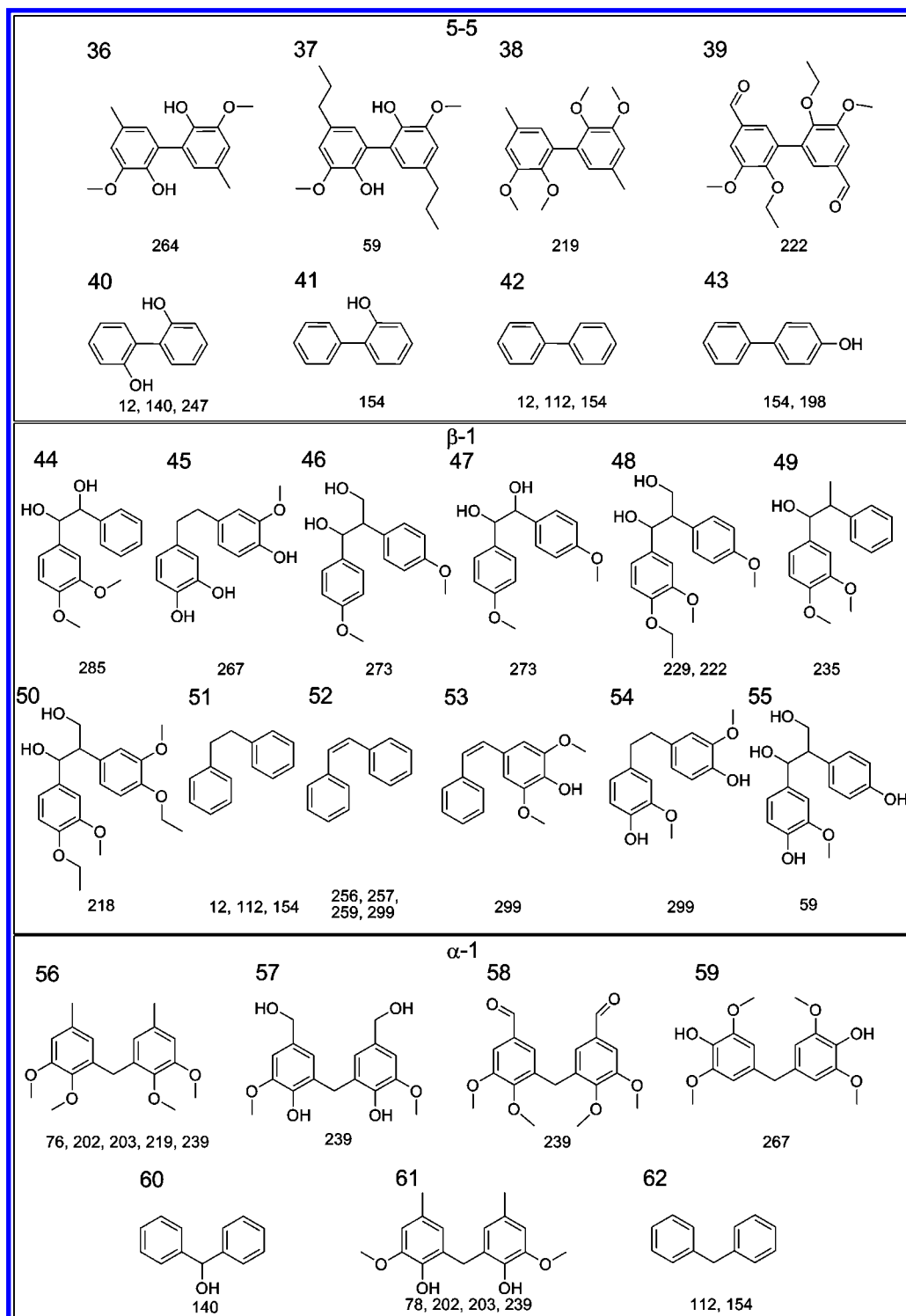
to form quinones, although instances involving the fragmentation of the dimer to monomers through disruption of the  $\alpha$ -1 or  $\beta$ -1 bond have also been reported.

Recent studies have suggested that dibenzodioxocin structures play an important role in lignin and actually are involved in a significant amount of the 5–5' linked structural units present in lignin. These new structural insights have not been yet reflected in model compound studies. Further investigation of this particular structural unit is therefore warranted.

### 3.3. $\beta$ -5 Linkage Model Compounds

The  $\beta$ -5 linkage is often found in a five-membered ring linking two aromatic structures via both a carbon–carbon and a carbon–oxygen bond. Figure 10 depicts model compounds containing  $\beta$ -5 or similar linkages, and reactions of model compounds containing these linkages are depicted in Scheme 3.

The formation of monomeric compounds, such as vanillin or vanillic acid, from model compounds with these linkages requires rupture of both of these bonds. Because of the inherent complexity in selectively disrupting both bonds, products resulting from the disruption of only one bond (i.e., the  $\alpha$ -O-4 ether linkage) to form  $\beta$ -1 linkage compounds are also observed as products of compounds containing the



**Figure 9.** Lignin model compounds mimicking the 5–5,  $\beta$ -1, or  $\alpha$ -1 bond linkages. Contrary to earlier reports, a recent study showed no evidence for the presence of diphenylmethane ( $\alpha$ -1) linkages in kraft lignin.<sup>47</sup>

$\beta$ -5 linkage. In some instances, the  $\beta$ -5 bond remains intact and products resulting from the oxidation of one of the arene rings are observed.

Several researchers have used benzofuran and dihydrobenzofuran as a model for the  $\beta$ -5 linkage in lignin. The benefits of using this compound in such a capacity include the limited and relatively simple products obtained after its transformation, as indicated in Scheme 4. The products include those that result from the hydrogenation of the arene ring leaving the ether linkage intact, disruption of the ether linkage leaving the arene ring intact, or combinations thereof. Simple

hydrocarbons, including ethylbenzene or phenol, were obtained along with functionalized alkanes following cleavage of the  $\beta$ -5 bond and alkanes with the  $\beta$ -5 bond intact.<sup>57</sup> Study of this compound as a  $\beta$ -5 linkage model allows relatively simple determination of catalytic selectivity toward either arene hydrogenation or ether linkage disruption.

### 3.4. $\alpha$ -O-4 and 4-O-5 Linkage Model Compounds

Model compounds of the presumed  $\alpha$ -O-4 linkages in lignin have also been reported; however, modern NMR



**Oxidation to Quinones**

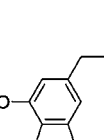
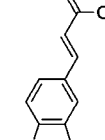
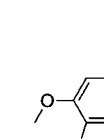
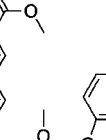
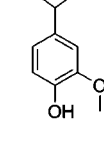
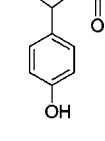
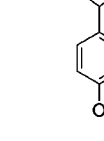
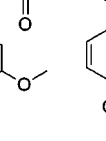
**Oxidation**

**Reduction**

**Repolymerization**

**Oxidation**

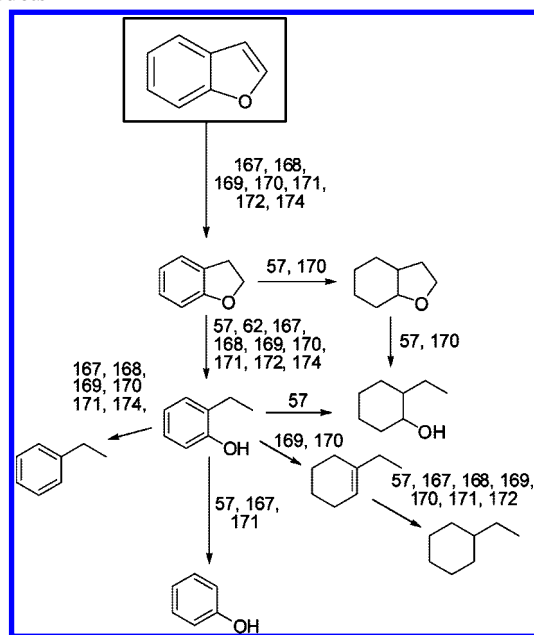
**Fragmentation**

<p><b>63</b></p>  <p><b>12</b></p>	<p><b>64</b></p>  <p><b>252</b></p>	<p><b>65</b></p>  <p><b>252</b></p>	<p><b>66</b></p>  <p><b>222</b></p>
<p><b>67</b></p>  <p><b>57,62,112,167, 168, 169, 170, 171, 172, 174</b></p>	<p><b>68</b></p>  <p><b>167, 168, 169, 170, 171, 173</b></p>	<p><b>69</b></p>  <p><b>226</b></p>	<p><b>70</b></p>  <p><b>173</b></p>

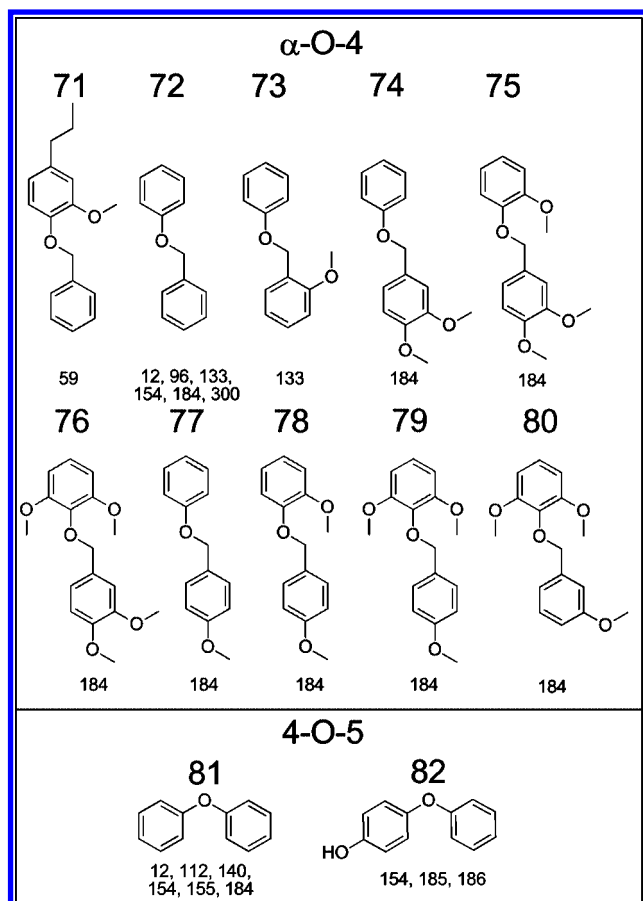
experiments do not confirm the presence of noncyclic  $\alpha$ -O-4 moieties. Instead, it was suggested that these  $\alpha$ -O-4 linkages are present only as part of the dibenzodioxocin or phenylcoumaran structural units. The chemistry of the reported model compounds is therefore of interest to the degradation of these 8- and 5-membered ring structures. The 4-O-5 aryl-aryl ether linkage is, however, present in lignin mainly as the result of oligomer-oligomer couplings and leads to branching of the polymer. Some model compounds have

The most prominent reaction of the  $\alpha$ -O-4 and 4-O-5 compounds, which are depicted in Figure 11, involves rupture of the ether linkage to form (substituted) phenol (see Scheme 5). Additional products formed through rupture of this linkage are benzene for 4-O-5 containing compounds, or toluene for  $\alpha$ -O-4 containing compounds. These molecules can be subsequently reduced to cyclohexane or methylcyclohexane, respectively. The hydrogenation of a single

**Scheme 4. Reaction of the Simple Lignin Model Compound Benzofuran Containing the  $\beta$ -5 Linkage to Various Products<sup>a</sup>**



<sup>a</sup> The number on the arrow refers the reader to the article in which the reaction was reported.



**Figure 11.** Lignin model compounds mimicking the  $\alpha$ -O-4 or 4-O-5 linkage.

aromatic ring, in which  $\alpha$ -O-4 linkage remains intact, has been reported. With regards to oxidation reactions, several benzaldehydes were observed following rupture of the  $\alpha$ -O-4 bond followed by oxidation of the resulting alcohol. Other

products include 4-hydroxybenzaldehyde, which is further reacted to form polymers,<sup>58</sup> and cyclic alkanes.<sup>59</sup>

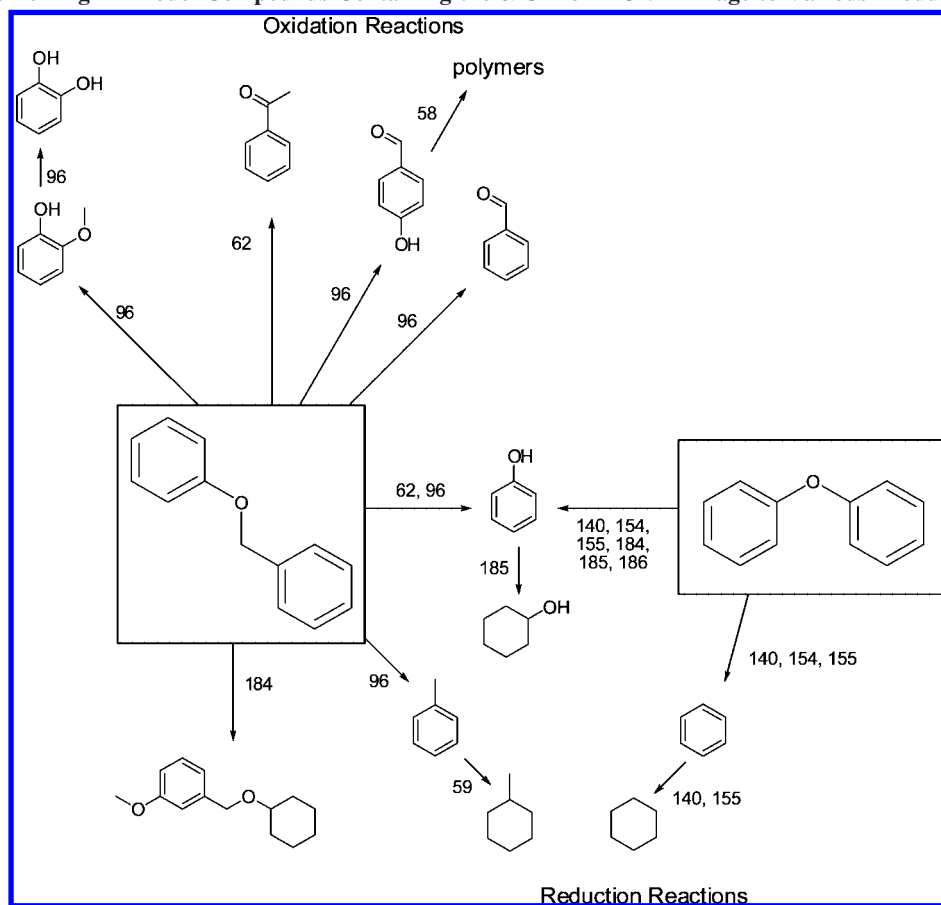
### 3.5. *p*-Coumaryl, Coniferyl, And Sinapyl Alcohol Model Compounds

Inspection of the schemes presented above indicates that several of the products obtained from disruption of the various linkages in the lignin polymer resemble the *p*-coumaryl, coniferyl, and sinapyl alcohol constituents from which the lignin polymer is composed. Considerable effort has therefore been placed on the conversion of the model compounds representing these alcohols to other target molecules. The monolignol *p*-coumaryl alcohol is the least functionalized monomer that is used to construct the lignin macromolecule. Figure 12 depicts the lignin model compounds that are similar to or can be thought to be derived from the *p*-coumaryl alcohol monomer, which may be found in lignin process streams following degradation of the lignin polymer. Scheme 6 depicts representative reactions of *p*-coumaryl type compounds reported in the literature.

The catalytic conversion of the *p*-coumaryl fragment or related model compounds, indicated in Scheme 6, has been demonstrated through several routes, including oxidations, reductions, alkylations, and repolymerizations. The reduction reactions often involve removal of the *para*-substituent R to form phenol, which can then be further reacted to form cyclohexane and other related products. Alkylation reactions involve migration of the CH<sub>3</sub> group of the methoxy functionality to the aromatic ring, which is potentially useful for the formation of xylene- or toluene-like products. Of the oxidation reactions, the most prominent involve the oxidation of the R group, often an alkyl group, into 4-hydroxybenzaldehyde.<sup>60</sup> Further oxidation of this aldehyde to the corresponding acid was also demonstrated.<sup>61</sup> Several metalloporphyrin catalysts effectively oxidized the hydroxyl functionality on the aromatic ring to form quinones or, in some instances, oxidatively cleaved the benzene ring itself to form noncyclic carboxylic acids. The repolymerization of the *p*-coumaryl model compounds to more complicated structures resembling those in the lignin polymer itself was reported.<sup>62,63</sup> These reactions can be used to synthesize other lignin model compounds for additional study (such as the formation of  $\beta$ -O-4 linkages), but otherwise the repolymerization should be suppressed during lignin valorization to avoid unwanted, often difficult to analyze products. The *p*-coumaryl structures have also been alkylated through the migration of a methoxy methyl group to the aromatic ring.

As indicated by the vast number of model compounds depicted in Figure 13 and the extensive reaction network depicted in Scheme 7, the coniferyl alcohol fragment has been studied in great detail, and a wide range of reaction pathways have been demonstrated in the literature.

As with *p*-coumaryl alcohol, oxidation of the *para*-substituent R forms several aromatic compounds including the highly valued vanillin, which can be further oxidized to form 3-methoxy-4-hydroxybenzoic acid and other related compounds. Several researchers have reported the formation of quinones, either directly from coniferyl alcohol or indirectly through the oxidation of intermediate products. With regards to the reduction reactions, formation of phenol is preceded by the production of catechol, which appears as a result of cleavage of the ether bond in the 3-methoxy functionality and the carbon-carbon bond between the R-group and the arene. Reduction of catechol itself was

Scheme 5. Reaction of Lignin Model Compounds Containing the  $\alpha$ -O-4 or 4-O-5 Linkage to Various Products<sup>a</sup>

<sup>a</sup> The number on the arrow refers the reader to the article in which the reaction was reported. We refer to Figure 11 for the model compounds used in these reactions.

demonstrated to form cyclohexanediol. A variety of products were reported from further conversion of phenol, including benzene, cyclohexene, cyclohexane, and cyclohexanone. Routes to form higher hydrocarbons from phenol, such as cyclohexylbenzene or 4-hydroxycyclohexylbenzene, were also reported. Repolymerization reactions occur also for *p*-coumaryl alcohol, including the formation of 5–5 bonds, a distinctive bond found most prevalently in softwoods, and also  $\beta$ -5 bonds.<sup>63</sup> These bonds are important linkages that occur in the lignin polymer itself. As with the linkages formed with *p*-coumaryl alcohol, these compounds can also serve as lignin model compounds to study the lignin polymer itself, although the formation of these linkages is similarly best avoided during lignin valorization.

Scheme 8 depicts reactions of compounds bearing a 3,4-dimethoxy fragment, which are derivatives of coniferyl alcohol. The oxidation of these compounds, particularly veratryl alcohol to veratryl aldehyde, has been extensively studied because veratryl alcohol itself is an important target compound for biomass valorization. Other products include quinones, acids, and products formed as a result of the oxidative ring cleavage to form nonaromatic carboxylic acids.

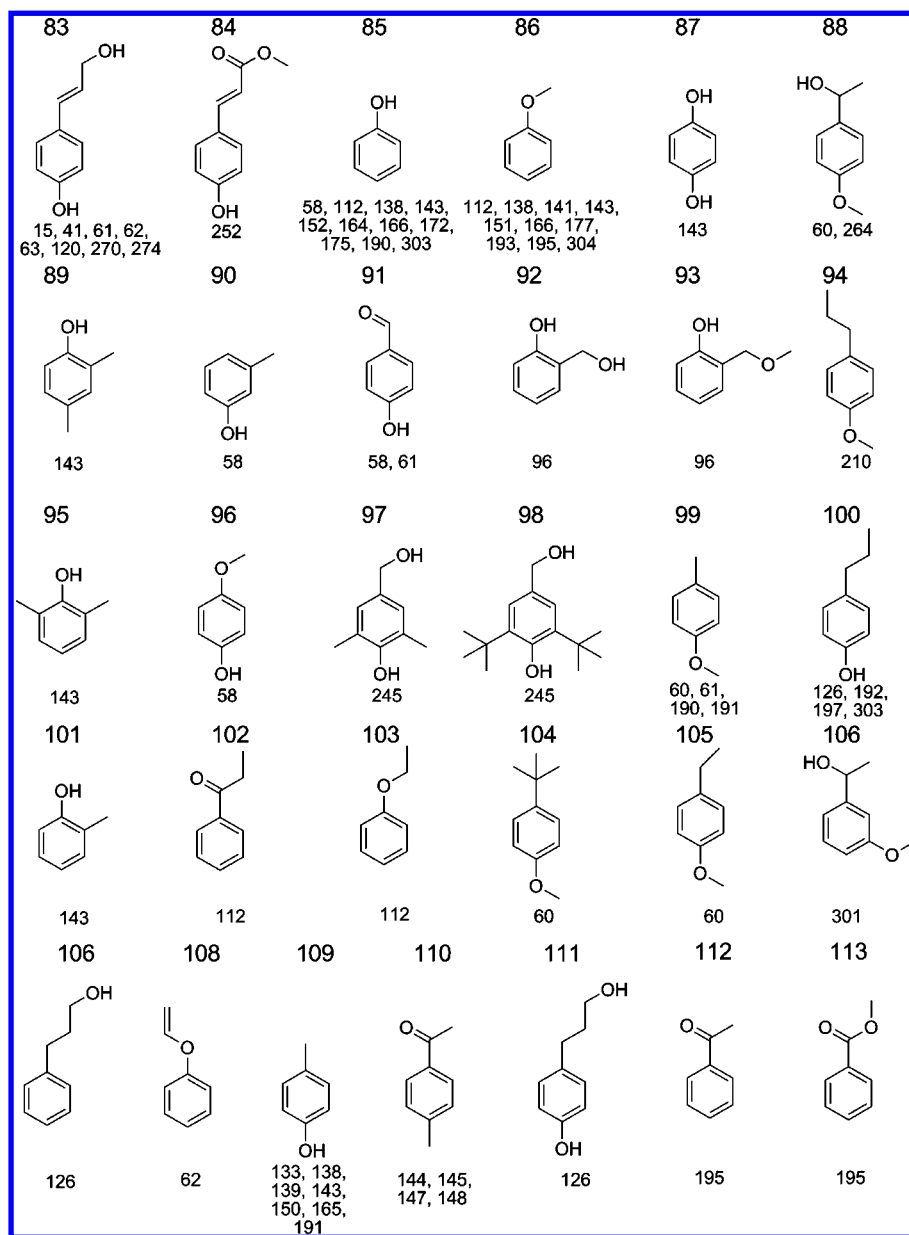
In contrast to the *p*-coumaryl and coniferyl alcohol moieties, the sinapyl alcohol fragment, of which model compounds are depicted in Figure 14, is not as susceptible to repolymerization because of the presence of the 3,5-dimethoxy groups. These groups occupy positions on the ring where otherwise 5–5 bonds can form, and thus their presence prevents this polymerization from occurring. Since the sinapyl alcohol fragments are much more prevalent in

hardwoods, the decreased occurrence of the 5–5 bonds also causes the hardwood to adopt a more linear conformation than softwood, which is more branched because of the 5–5 structure. Typical reactions involve the oxidation of the R-group to form aldehydes and acids, and the formation of quinones from sinapyl alcohol has also been reported. Reduction reactions principally involve removal of the R group from the ring, demethylation, or demethoxylation.

### 3.6. General Considerations

The preceding sections have shown that a multitude of compounds have been used to model the lignin macromolecule or its degradation products (Figures 8–14). The reported studies on all of these model compounds have given invaluable information regarding the chemistry of lignin and possible transformations to value-added products. Some of the model compounds employed are particularly attractive, however, because they more accurately capture the salient features of the monomers and linkages found in the lignin polymer. The most relevant compounds used to model the  $\beta$ -O-4 bonds, therefore, contain the  $C_\gamma$ -OH functionality and hydroxyl or methoxyl groups on the aromatic ring to more closely resemble the coniferyl or sinapyl alcohol components from which lignin is principally comprised. Some examples include compounds **1–5** in Figure 8. Similarly, model compounds used to represent the 5–5 carbon–carbon linkage in lignin are best represented by model compounds that resemble two linked coniferyl alcohol monomers, for example, compounds **36–38** (Figure 9). The rupture of the



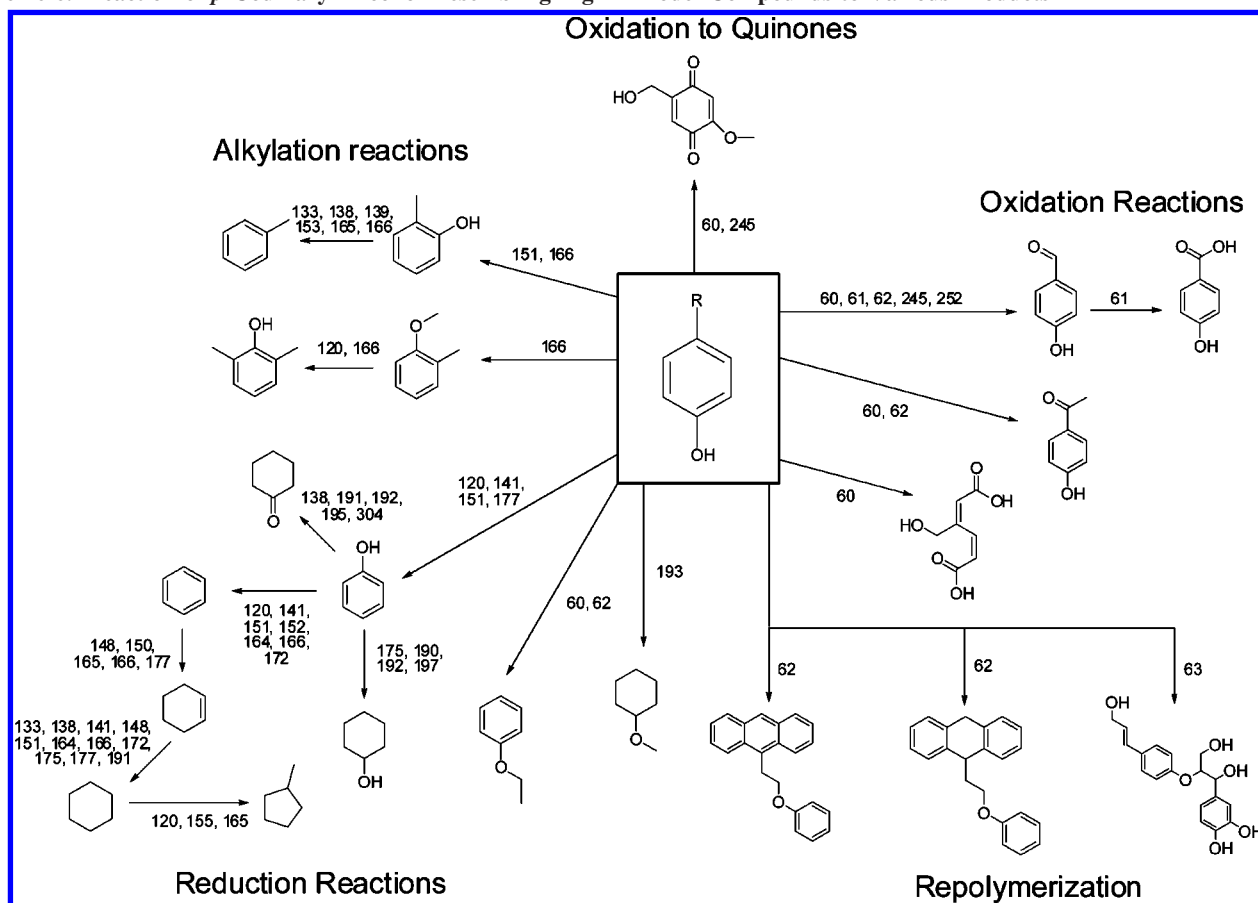


**Figure 12.** Lignin model compounds resembling *p*-coumaryl alcohol or its derivatives.

carbon–carbon bond in these compounds is most likely to resemble the rupture of similar bonds in lignin because of the proximity of the appropriate functional groups. As with the  $\beta$ -O-4 model compounds,  $\beta$ -1 linkages are best represented by models containing a  $C_\gamma$ -OH group (Figure 9, compounds **46**, **48**, or **50**) since the presence of this functional group is likely to influence the rupture of the  $\beta$ -1 linkage. With these suggestions in mind, improvements to the model compounds used to represent the  $\alpha$ -O-4 linkage could be realized with the addition of a  $C_\gamma$ -OH or  $(C_\beta$ -OH)- $C_\gamma$ -OH functional group to the model compounds depicted in Figure 11. Similar improvements would be realized with the addition of methoxy and hydroxyl functionality to the model compounds used to represent the 4-O-5 bonds. The reactivities of the model compounds with these functionalities in the correct positions are more likely to resemble those of lignin itself, and thus better conclusions can be drawn from reactions of these compounds. It is important to note that recent NMR experiments suggest that  $\alpha$ -O-4 linkages are only found as part of dibenzodioxocin

or phenylcoumaran units. More extensive studies and better models for these particular ring systems are therefore desired.

Taken together, the schemes presented above indicate that cleavage of the primary linkages of the lignin forms monomeric aromatic compounds, which are often highly functionalized with alcohol, aldehyde, ether, or acid substituents. These monomeric compounds are then susceptible to an extensive array of transformations principally either reductive in nature, forming simple hydrocarbons, or oxidative in nature, forming aromatics with increased or specifically targeted functionality. The oxidative route requires the development of catalysts that selectively disrupt the linkages in lignin to form specific aromatic alcohols, aldehydes, acids, and other specially functionalized aromatics that are difficult to produce. These aromatic compounds may be highly functionalized, requiring several synthetic steps from petroleum feedstocks, or require expensive platform molecules. An exemplary high-value lignin-derived product is vanillin (3-methoxy-4-hydroxybenzaldehyde), which is already currently produced by the Borregaard Ingredients corporation

Scheme 6. Reaction of *p*-Coumaryl Alcohol Resembling Lignin Model Compounds to Various Products<sup>a</sup>

<sup>a</sup> The number on the arrow refers the reader to the article in which the reaction was reported. We refer to Figure 12 for the model compounds used in these reactions.

from softwood lignin.<sup>64</sup> Vanillin is used extensively in foods and perfumes because of its flavor but also finds use in medicinal applications or as a platform chemical for pharmaceuticals production.<sup>65,66</sup> The reductive route requires developing catalysts that partially or completely remove the alcohol, aldehyde, ether, and acid substituents from the monomers formed after lignin depolymerization to form simple aromatics, including benzene, toluene, xylene, and phenol. These simple aromatic compounds can then be reacted, using existing technology, to a plethora of useful chemicals. A graphical depiction of these transformations is given in Figure 15, adapted from Bozell<sup>6</sup> and Koutinas et al.<sup>67</sup> These chemicals and other high-value products, such as *p*-substituted benzyl alcohols or aldehydes, are useful for the production of plastics and other polymers, pigments, dyes, resins, and many other products.<sup>6,58</sup>

#### 4. Biorefineries Revisited

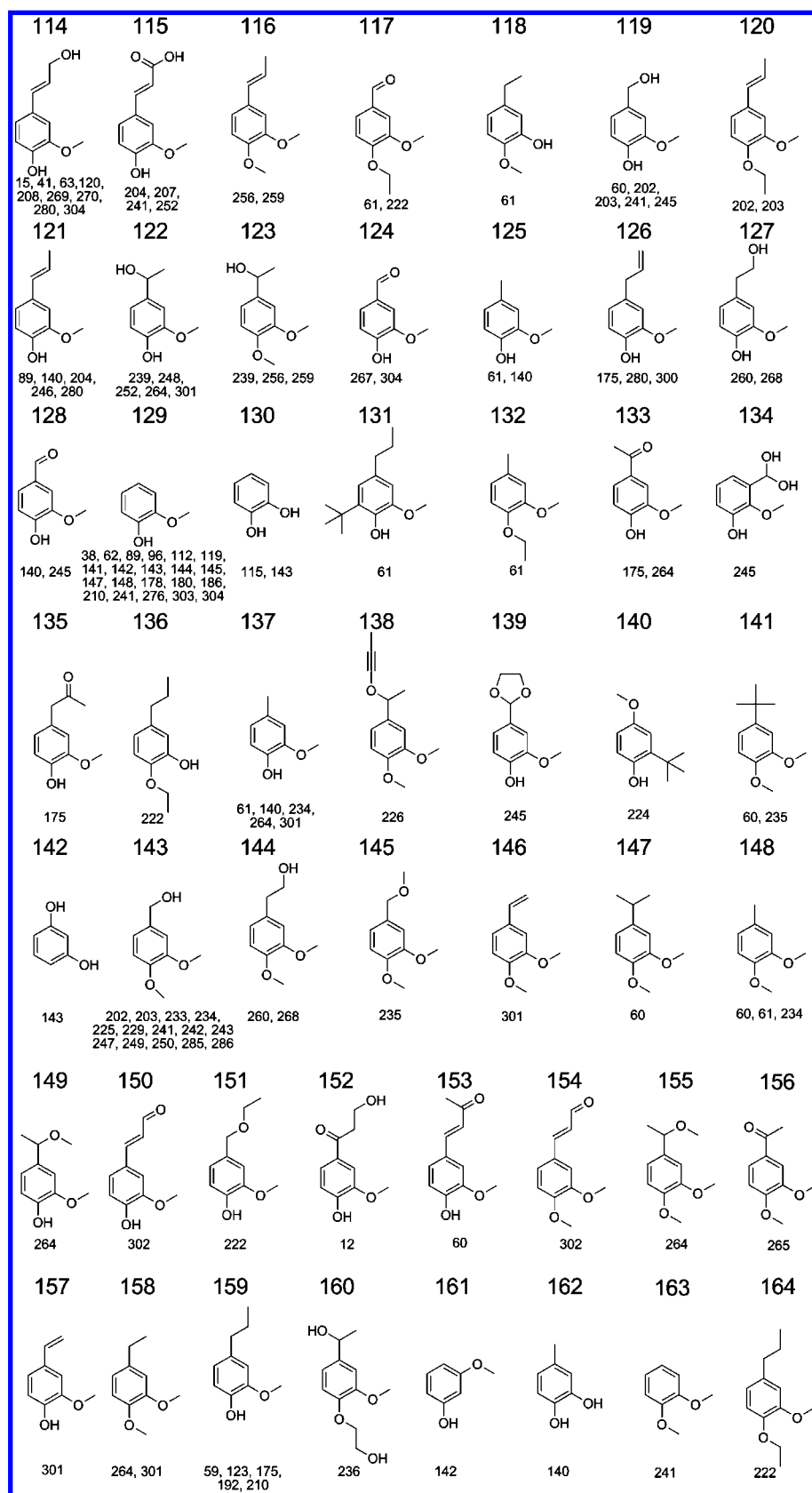
As indicated, a tremendous array of products is potentially obtainable by lignin valorization, and considerable effort has been placed to developing processes that specifically disrupt the linkages in lignin to produce valuable target chemicals. The realization of fully integrated biorefinery schemes for lignin valorization requires specific catalytic technology to perform the transformations. The biomass source and pre-treatment method dictates the performance required of the catalyst in terms of robustness, selectivity (in terms of disrupting specific lignin linkages), activity, and recyclability. For example, dirtier feedstreams require more robust cata-

lysts, which often has implications on the types of processes that can be realistically employed. Knowledge of the types of catalysts available, their characteristics, and the types of transformations that they perform are thus essential for the development of efficient biorefineries. In the following sections, we detail the reported catalytic lignin valorization technology that could aid in the development of such biorefinery schemes. We first discuss lignin dissolution and its importance to catalysis, which has specific implications especially for processes such as the organosolv method. We then discuss the various catalysts and processes developed for lignin transformations to specific target chemicals.

### 5. Lignin Dissolution

#### 5.1. General Characteristics

The dissolution of lignin and other lignocellulosic materials is critically important for efficient valorization of biomass but remains a challenge because of the particular properties of the structures of cellulose, hemicellulose, and lignin. In fact, it has been recognized that the insolubility of wood in common solvents has severely inhibited efforts to valorize wood and its components.<sup>68</sup> This difficulty arises because the complicated three-dimensional lignin network in wood is interlinked with the other lignocellulosic components and thus binds the entire wood architecture together (see above).<sup>68</sup> The complicated lignocellulosic structure serves to protect the plant species from microbial attack and provides resistance to the elements, yet it also makes the material



**Figure 13.** Coniferyl alcohol resembling lignin model compounds.

recalcitrant to chemical reaction or fermentation to useful products.<sup>69</sup> Crystalline cellulose itself has low accessibility to enzymatic hydrolysis, and the presence of lignin and hemicelluloses also protects the cellulosic material from reaction.<sup>69</sup> Complicating the issue, the lignocellulose structure and composition vary significantly and depend on factors

such as the plant species, plant parts, and growth conditions.<sup>69</sup> Noncovalent hydrophobic interactions between the aromatic rings in lignin, for example, may also hinder reactions between lignin macromolecules and reactants.<sup>70,71</sup> These interactions are species-dependent and are found most commonly in softwood lignins, less in hardwood, and not at



**Oxidation to Quinones**

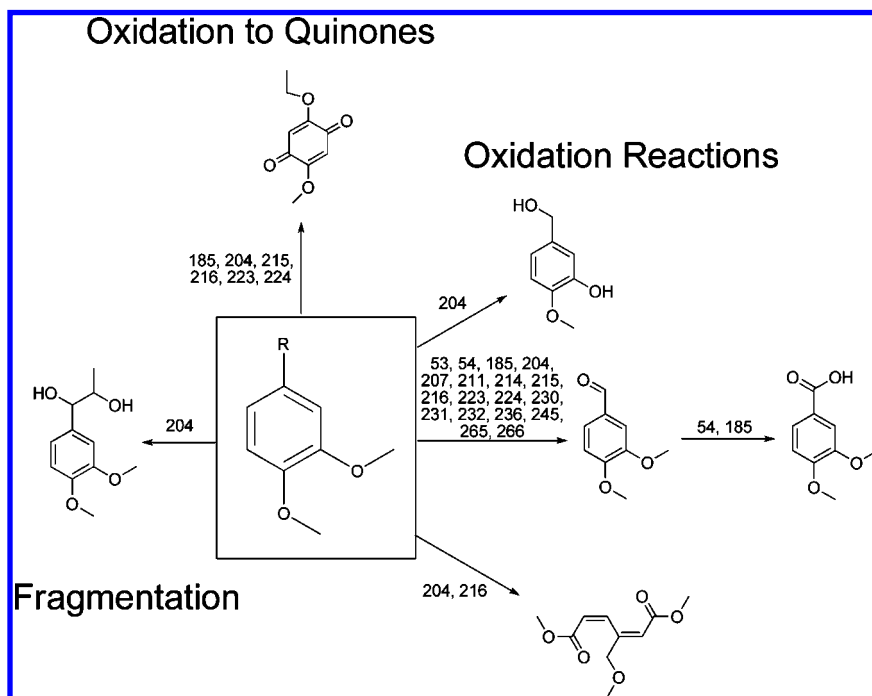
**Oxidation Reactions**

**Reduction Reactions**

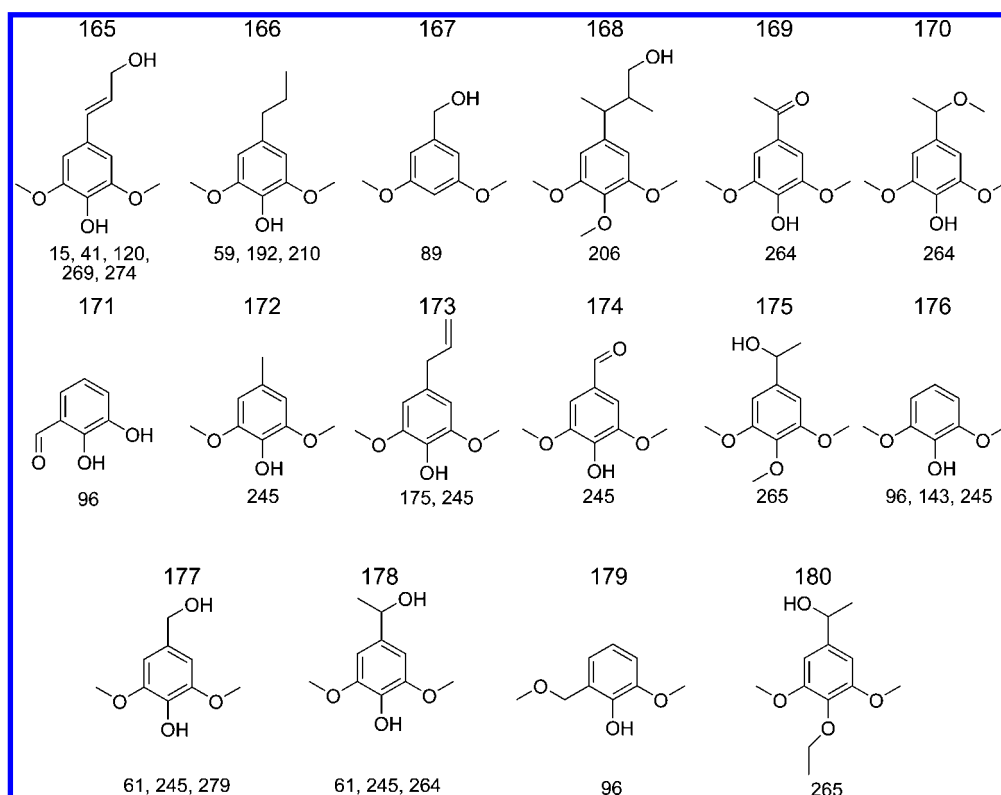
**Repolymerization**

Eckert and co-workers recently reported the use of CO<sub>2</sub> expanded organic solvents to extract high value chemicals, such as vanillin, syringol, and syringaldehyde, from lignin.<sup>77</sup> The advantages of using CO<sub>2</sub> expanded solvents include the ability to tune the product solubility, transportability, and polarity of several standard solvents and that the quantity of solvent required to dissolve a given amount of biomass is reduced.<sup>77</sup> The separation and isolation of product components is facilitated by the ability to decrease component solubility such that the products fall out of solution when desired.<sup>77</sup> Ehara and co-workers used supercritical water to

Ionic liquids have recently become very popular solvents for the dissolution of biomass. Ionic liquids are salts with melting points below an arbitrary set point of 373 K. They often have tunable physical properties based on the choice of cation and anion pair, a negligible vapor pressure, and good thermal stability.<sup>79</sup> In a pioneering study by Rogers and co-workers, several ionic liquids, in particular, 1-butyl-3-methylimidazolium chloride, were found capable of dissolving up to 10 wt % cellulose.<sup>80</sup> Hydrogen bonds formed with nonhydrated Cl<sup>-</sup> ions disrupted the intermolecular hydrogen bonding in the cellulose structure, which allowed the dissolution of the cellulose.<sup>79</sup> Since this study, several researchers have investigated the dissolution of biomass, including lignin, using ionic liquids. Lee and co-workers observed that [EMIM][OAc] was able to selectively extract lignin from wood with less crystalline cellulose remaining.<sup>81</sup> Fort and co-workers used 1-butyl-3-methylimidazolium

Scheme 8. Reaction of Dimethoxy Coniferyl Alcohol Resembling Lignin Model Compounds to Various Products<sup>a</sup>

<sup>a</sup> The number on the arrow refers the reader to the article in which the reaction was reported. We refer to Figure 13 for the model compounds used in these reaction.

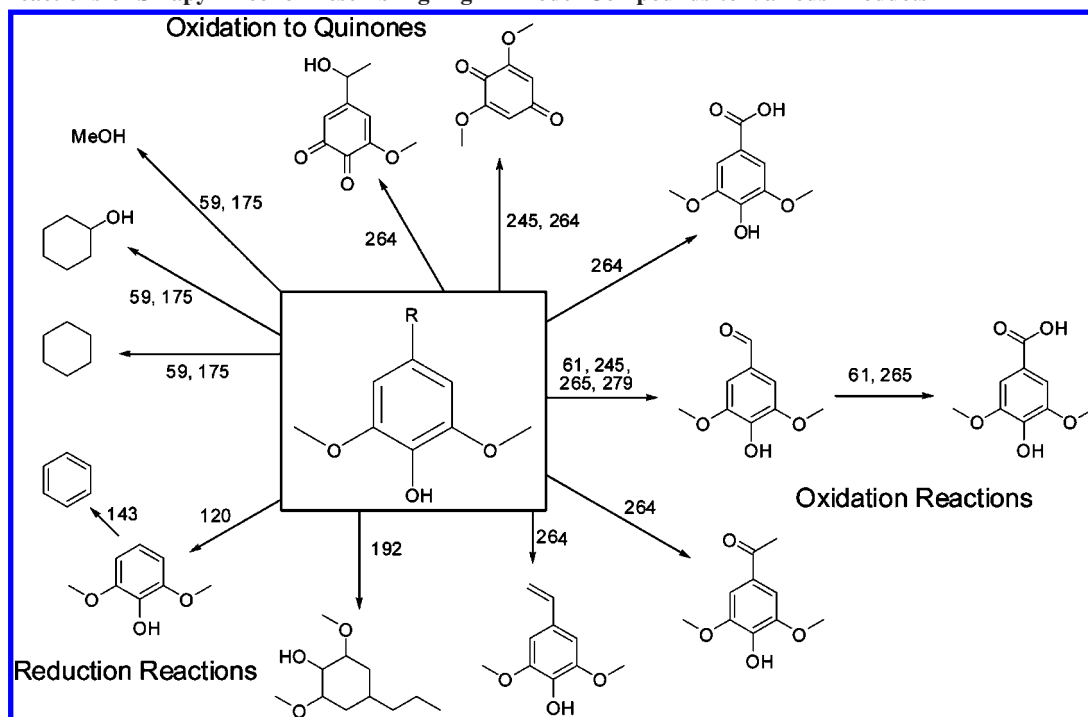


**Figure 14.** Sinapyl alcohol resembling lignin model compounds.

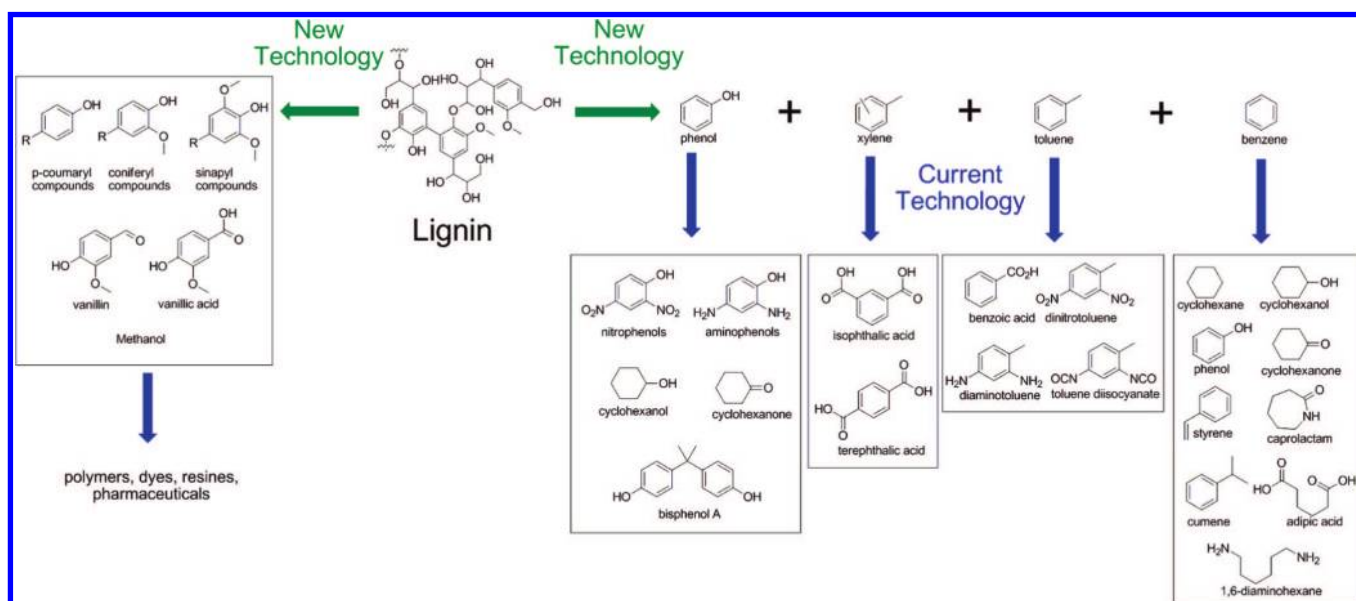
chloride to dissolve wood and followed the dissolution by <sup>13</sup>C NMR spectroscopy. They found that this ionic liquid was capable of dissolving both cellulose and lignin, and they were able to use precipitation solvents to isolate cellulose from the other biomass components.<sup>79</sup> Based on these initial investigations, the use of ionic liquids as biomass solvents has recently attracted considerable interest, and important developments in the use of ionic liquids for biomass

fractionation, analysis, and pollutant removal have been recently achieved. Lignin and wood solubility data for several wood and lignin sources are summarized in Table 3.

Current research focuses include identifying the superior ionic liquids and performing subsequent reactions on the dissolved biomass, ionic liquid recyclability, and acquisition of toxicology data and other industrially relevant parameters. High-throughput screening methods, discussed below, have

Scheme 9. Reactions of Sinapyl Alcohol Resembling Lignin Model Compounds to Various Products<sup>a</sup>

<sup>a</sup> The number on the arrow refers the reader to the article in which the reaction was reported. We refer to Figure 14 for the model compounds used in these reactions.



**Figure 15.** Valuable products potentially obtained from lignin with development and integration of new and current technology.<sup>6,67</sup>

provided insight into the desirable characteristics of ionic liquids. The recyclability of ionic liquids is necessitated by the relatively high ionic liquid price.<sup>82</sup> Other challenges associated with ionic liquids include substrate and product separation from the ionic liquid after reaction, which is necessary both to analyze reaction product mixtures and for industrial chemical purification. Difficulty in separating lignin-derived molecules is particularly acute because  $\pi$ - $\pi$  interactions between the ionic liquid and aromatic moieties often make the aromatic products more soluble in the ionic liquid relative to aliphatic compounds, thus increasing the difficulty of extraction.<sup>83</sup> Nevertheless, typical analytical methods include solute extraction using organic solvents,<sup>83</sup> and techniques to analyze the products dissolved in the ionic

liquids directly are under development and include Uv–vis and infrared spectroscopy, light scattering techniques, NMR spectroscopy, and mass spectrometry, although the latter two techniques often suffer from low solute concentrations relative to the amount of ionic liquid present.<sup>84</sup> Limited data is available on the miscibility of ionic liquids with other solvents and on extraction coefficients of various solute–ionic liquid mixtures; additional knowledge on the solubility of reagents and products is required in order to enable effective product separation and isolation. In general, ionic liquids are immiscible with nonpolar solvents such as diethyl ether and hexanes, whereas low polarity solvents, such as ethylacetate, show variable solubility depending on the properties of the ionic liquid.<sup>83</sup> Polar solvents are frequently miscible with



**Table 3. Lignin Dissolution in Ionic Liquids**

entry	ionic liquid	conditions		weight % loaded	lignin source	solubility	ref
		<i>T</i> (K)	<i>t</i> (h)				
1	[AMIM]Cl	363	12	5	aticel lignin	soluble	73
2	[AMIM]Cl	363	12	5	α-cellulose	soluble	73
3	[AMIM]Cl	363	12	5	spruce	soluble	73
4	[AMIM]Cl	363	12	5	silver fur	soluble	73
5	[AMIM]Cl	363	12	5	common beech	soluble	73
6	[AMIM]Cl	363	12	5	chestnut	soluble	73
7	[AMIM]Cl	353	8	~20	ball-milled southern pine powder	8 wt %	68
8	[AMIM]Cl	383	8	~20	Norway spruce sawdust	8 wt %	68
9	[AMIM]Cl	353	24	~20	Norway spruce sawdust	5 wt %	68
10	[AMIM]Cl	403	8	~20	Norway spruce sawdust TMP	7 wt %	68
11	[AMIM]Cl	383	8	~20	southern pine TMP	2 wt %	68
12	[AMIM]Cl	403	8	~20	southern pine TMP	5 wt %	68
13	[AMIM]Cl	363	24	50	indulin AT (kraft lignin)	30 wt %	81
14	[BMIM]Cl	363	12	5	aticel lignin	soluble	73
15	[BMIM]Cl	363	12	5	α-cellulose	soluble	73
16	[BMIM]Cl	363	12	5	spruce	partially soluble	73
17	[BMIM]Cl	363	12	5	silver fur	partially soluble	73
18	[BMIM]Cl	363	12	5	common beech	partially soluble	73
19	[BMIM]Cl	363	12	5	chestnut	partially soluble	73
20	[BMIM]Cl	348	<i>a</i>	<i>a</i>	residual softwood kraft pulp lignin	13.9 g/L	89
21	[BMIM]Cl	383	8	~20	Norway spruce sawdust	8 wt %	68
22	[BMIM]Cl	403	8	~20	Norway spruce sawdust TMP	7 wt %	68
23	[BMIM]Cl	403	8		southern pine TMP	5 wt %	68
24	[BMIM]Cl	403	15	~20	wood chips	partially soluble	68
25	[BMIM]Cl	363	24	50	indulin AT (kraft lignin)	10 wt %	81
26	[BMIM]Cl	383	16	5	southern yellow pine	52.6 wt %	88
27	[BMIM]Cl/DMSO- <i>d</i> <sub>6</sub>	373	24	5	oak wood chips	~17 wt %	79
28	[BMIM]Cl/DMSO- <i>d</i> <sub>6</sub>	373	24	5	eucalyptus wood chips	~22 wt %	79
29	[BMIM]Cl/DMSO- <i>d</i> <sub>6</sub>	373	24	5	poplar wood chips	~19 wt %	79
30	[BMIM]Cl/DMSO- <i>d</i> <sub>6</sub>	373	24	5	pine wood chips	~21 wt %	79
31	[BMIM][MeSO <sub>4</sub> ]	323	<i>a</i>	<i>a</i>	residual softwood kraft pulp lignin	312 g/L	89
32	[BMIM][MeSO <sub>4</sub> ]	298	<i>a</i>	<i>a</i>	residual softwood kraft pulp lignin	61.8 g/L	89
33	[BMIM]Br	348	<i>a</i>	<i>a</i>	residual softwood kraft pulp lignin	17.5 g/L	89
34	[BMIM][BF <sub>4</sub> ]	363	24	50	indulin AT (kraft lignin)	4 wt %	81
35	[BMIM][PF <sub>6</sub> ]	343–493	<i>a</i>	<i>a</i>	residual softwood kraft pulp lignin	insoluble	89
36	[BMIM][PF <sub>6</sub> ]	363	24	5	indulin AT (kraft lignin)	~0.1 wt %	81
37	[BMIM][CF <sub>3</sub> SO <sub>3</sub> ]	363	24	50	indulin AT (kraft lignin)	50 wt %	81
38	[EMIM]Cl	363	12	5	aticel lignin	soluble	68
39	[EMIM]Cl	363	12	5	α-cellulose	soluble	68
40	[EMIM]Cl	363	12	5	spruce	partially soluble	68
41	[EMIM]Cl	363	12	5	silver fur	partially soluble	68
42	[EMIM]Cl	363	12	5	common beech	partially soluble	73
43	[EMIM]Cl	363	12	5	chestnut	partially soluble	73
44	[EMIM][XS]	443	2	21.5 <sup>b</sup>	sugar cane bagasse	67% <sup>c</sup>	90
45	[EMIM][XS]	453	2	21.5 <sup>b</sup>	sugar cane bagasse	78% <sup>c</sup>	90
46	[EMIM][XS]	463	2	21.5 <sup>b</sup>	sugar cane bagasse	118% <sup>c,d</sup>	90
47	[EMIM][XS]	463	1.5	21.5 <sup>b</sup>	sugar cane bagasse	97% <sup>c</sup>	90
48	[EMIM][XS]	463	1	21.5 <sup>b</sup>	sugar cane bagasse	96% <sup>c</sup>	90
49	[EMIM][XS]	463	0.5	21.5 <sup>b</sup>	sugar cane bagasse	67% <sup>c</sup>	90
50	[EMIM]OAc	363	12	5	aticel lignin	soluble	73
51	[EMIM]OAc	363	12	5	α-cellulose	soluble	73
52	[EMIM]OAc	363	12	5	spruce	soluble	73
53	[EMIM]OAc	363	12	5	silver fur	partially soluble	73
54	[EMIM]OAc	363	12	5	common beech	soluble	73
55	[EMIM]OAc	363	12	5	chestnut	soluble	73
56	[EMIM]OAc	363	24	50	indulin AT (kraft lignin)	30 wt %	81
57	[EMIM]OAc	383	16	5	southern yellow pine	5 wt %	88
58	[EMIM]OAc	383	16	5	red Oak	5 wt %	88
59	[MMIM][MeSO <sub>4</sub> ]	298	<i>a</i>	<i>a</i>	residual softwood kraft pulp lignin	74.2 g/L	89
60	[MMIM][MeSO <sub>4</sub> ]	323	<i>a</i>	<i>a</i>	residual softwood kraft pulp lignin	344 g/L	89
61	[MMIM][MeSO <sub>4</sub> ]	363	24	50	indulin AT (kraft lignin)	50 wt %	81
62	[HMIM][CF <sub>3</sub> SO <sub>4</sub> ]	343	<i>a</i>	<i>a</i>	residual softwood kraft pulp lignin	275 g/L	89
63	[HMIM][CF <sub>3</sub> SO <sub>4</sub> ]	323	<i>a</i>	<i>a</i>	residual softwood kraft pulp lignin	<10 g/L	89
64	[BM <sub>2</sub> IM]Cl	343–373	<i>a</i>	<i>a</i>	residual softwood kraft pulp lignin	14.5 g/L	89
65	[bz <sub>mim</sub> ]Cl	403	8	~20	southern pine TMP	5 wt %	68
66	[bz <sub>mim</sub> ]Cl	403	8	~20	Norway spruce TMP	5 wt %	68
67	[bz <sub>mim</sub> ]Cl	363	24	50	indulin AT (kraft lignin)	10 wt %	81
68	[bz-ome-mim]Cl	403	8	~20	southern pine TMP	5 wt %	68
69	[bz-ome-mim]Cl	403	8	~20	southern pine TMP	2 wt %	68
70	BenzylmimDca	403	8	~20	southern pine TMP	2 wt %	68
71	[BMPY]Cl	363	12	5	aticel lignin	soluble	73
72	[BMPY]Cl	363	12	5	α-cellulose	soluble	73
73	[BMPY]Cl	363	12	5	spruce	not tested	73
74	[BMPY]Cl	363	12	5	silver fur	not tested	73

Table 3. Continued

entry	ionic liquid	conditions		weight % loaded	lignin source	solubility	ref
		<i>T</i> (K)	<i>t</i> (h)				
75	[BMPY]Cl	363	12	5	common beech	not tested	73
76	[BMPY]Cl	363	12	5	chestnut	not tested	73
77	[BMPY][PF <sub>6</sub> ]	343–493	<i>a</i>	<i>a</i>	residual softwood kraft pulp lignin	insoluble	89
78	ECOENG	363	12	5	aticel lignin	soluble	73
79	ECOENG	363	12	5	α-cellulose	soluble	73
80	ECOENG	363	12	5	spruce	partially soluble	73
81	ECOENG	363	12	5	silver fir	partially soluble	73
82	ECOENG	363	12	5	common beech	partially soluble	73
83	ECOENG	363	12	5	chestnut	partially soluble	73

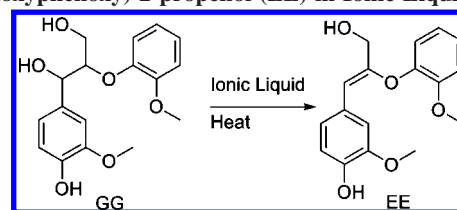
<sup>a</sup> Not specified. <sup>b</sup> Dry basis. <sup>c</sup> As a percentage of original lignin content, corrected for ash content. <sup>d</sup> Higher than theoretical mass maybe partially due to incorporation of xylenesulfonate anion or a cation.

ionic liquids.<sup>83</sup> Brennecke and co-workers demonstrated the possibility of extracting a wide variety of components from ionic liquids using supercritical CO<sub>2</sub>.<sup>85,86</sup> This solvent has shown interesting phase behavior with ionic liquids in that large amounts of CO<sub>2</sub> dissolve in the ionic liquids, but no measurable quantity of ionic liquid dissolved in the CO<sub>2</sub>.<sup>87</sup> An advantage of using supercritical CO<sub>2</sub> as the extraction solvent is that it is also considered an environmentally benign solvent.<sup>87</sup>

The results of high-throughput screening experiments have identified several ionic liquids that readily dissolve lignin and wood. Zavrel and co-workers used a high-throughput method to test 21 ionic liquids for their ability to dissolve cellulose and woody biomass.<sup>73</sup> Of the ionic liquids investigated, 1-ethyl-3-methylimidazolium chloride was found to best dissolve cellulose, while 1-allyl-3-methylimidazolium chloride best dissolved wood chips.<sup>73</sup> In this study, it was suggested that  $\pi$ -electrons in the side chain of the 1-allyl-3-methylimidazolium cation contribute to  $\pi$ - $\pi$  interactions with the aromatic lignin parts and that the anion disrupts the hydrogen bonds found in the lignocelluloses, thereby disrupting the three-dimensional structures and allowing dissolution.<sup>73</sup> It was found also that precipitation of lignocellulosic materials was subsequently possible using various antisolvents. The ability to use high-throughput screening methods to test for biomass reactivity in ionic liquids was also highlighted, especially with enzymes.<sup>73</sup> Sun and co-workers recently investigated the dissolution of southern yellow pine and red oak, achieving nearly complete dissolution of the latter in 16 h.<sup>88</sup> As indicated by the results compiled in Table 3, the properties of the anion are extremely important in the solubility of lignin in ionic liquids. Pu and co-workers specifically investigated the effect of various anions on the solubility of lignin from kraft pulp.<sup>89</sup> They discovered that up to 20 wt % of lignin was soluble using [CF<sub>3</sub>SO<sub>3</sub>]<sup>−</sup> or [MeSO<sub>4</sub>]<sup>−</sup> anions, and for 1-butyl-3-methylimidazolium salts, the order of solubility was [MeSO<sub>4</sub>]<sup>−</sup> > Cl<sup>−</sup>  $\approx$  Br<sup>−</sup>  $\gg$  [PF<sub>6</sub>]<sup>−</sup>.<sup>89</sup> The noncoordinating [PF<sub>6</sub>]<sup>−</sup> anion was essentially ineffective in dissolving lignin.<sup>89</sup> Tan and co-workers observed that 1-ethyl-3-methylimidazolium cation with a mixture of alkylbenzene sulfonate anions (mainly xylenesulfonate) dissolved lignin, and an extraction yield of 93% was attained.<sup>90</sup>

Recent investigations of the use of ionic liquids for lignin dissolution have also focused on the various types of reactions used for the analysis and conversion of lignin to useful chemicals. Kilpeläinen and co-workers used 1-butyl-3-methylimidazolium chloride and 1-allyl-3-methylimidazolium chloride to dissolve Norway spruce sawdust, Norway spruce fibers, and southern pine fibers.<sup>68</sup> The dissolved fibers

**Scheme 10. Thermal Conversion of Guaiacyl- $\beta$ -guaiacyl Ether (GG) to 3-(4-Hydroxyl-3-methoxyphenyl)-2-(2-methoxyphenoxy)-2-propenol (EE) in Ionic Liquids**



were then acetylated to form products that are completely soluble in chloroform, which allowed analysis by <sup>1</sup>H NMR.<sup>68</sup> Sievers and co-workers<sup>91</sup> and Li and co-workers<sup>92</sup> in turn demonstrated the acid hydrolysis of pine wood in ionic liquids with the intent of converting lignocellulosic materials to simpler monosaccharides, which can then be converted to fuels and other chemicals.<sup>91</sup> Kubo and co-workers converted guaiacyl- $\beta$ -guaiacyl ether (GG), which contains the predominant interunit  $\beta$ -O-4 linkage of lignin, to 3-(4-hydroxyl-3-methoxyphenyl)-2-(2-methoxyphenoxy)-2-propenol (EE) by heat treatment (see Scheme 10).<sup>93</sup>

EE is believed to be an unstable intermediate under acidic or alkaline conditions, yet it was successfully isolated in the ionic liquids.<sup>93</sup> Xie and co-workers recently reported the acylation of wood to form highly substituted lignocellulosic esters in ionic liquids using acetyl chloride or benzoyl chloride in the presence of pyridine.<sup>94</sup> Noting that few studies have involved the examination of enzyme-catalyzed oxidative biotransformations in ionic liquids, Sgalla and co-workers investigated the reactivity of horseradish peroxidase in 1-butyl-3-methylimidazolium tetrafluoroborate/water mixtures.<sup>95</sup> Although lower enzymatic activity was observed relative to standard water buffers, the enzyme was still active for the transformation of water-insoluble phenolic compounds into 2,2-bis-(4-phenylphenol), a member of an important group of platform chemicals.<sup>95</sup>

## 6. Catalytic Lignin Transformations

Following the biomass pretreatment, the lignin polymer is susceptible to a wide range of chemical transformations to form valuable chemicals. As indicated above, the fragmentation reactions can be principally divided into lignin cracking or hydrolysis reactions, catalytic reduction reactions, and catalytic oxidation reactions. For lignin reductions, typical reactions involve the removal of the extensive functionality of the lignin subunits to form simpler monomeric compounds such as phenols, benzene, toluene, or xylene. These simple aromatic compounds can then be hydrogenated to alkanes or used as platform chemicals for

use in the synthesis of fine chemicals using technology already developed in the petroleum industry. For lignin oxidations, lignin is converted to more complicated platform chemicals with extensive functionality or converted directly to target fine chemicals (see Figure 5).

## 6.1. Lignin Catalytic Cracking and Hydrolysis

Disruption of the complicated lignin polymer into smaller subunits is an important step for lignin valorization. The smaller subsets better resemble the model compounds and target products depicted above, and they expose various functional groups on the aromatic rings to further catalytic transformations. Amen-Chen and co-workers published a review of the production of monomeric phenols by thermochemical lignin conversion.<sup>12</sup> Several routes to phenolic compounds were described, including the pyrolysis of monomeric, dimeric, and trimeric compounds, in addition to the effects that different conditions have on forming methane, methanol, and various compounds from biomass.<sup>12</sup> Several transition metal catalytic processes were also reviewed, including kraft lignin pyrolysis by  $\text{ZnCl}_2$ .<sup>12</sup> Dorrestijn and co-workers published a review detailing the pyrolysis of lignin with a brief discussion of pyrolysis, catalytic hydrogenation, and oxidation.<sup>62</sup> Britt et al. studied flash vacuum pyrolysis of methoxy-substituted  $\beta$ -O-4 lignin model compounds in order to provide mechanistic insight into the relevant reaction pathways.<sup>96</sup> The reactions were dominated by free radical reactions, molecular rearrangements, and concerted eliminations.<sup>96</sup> Misson and co-workers investigated the pretreatment of empty palm fruit bunches with  $\text{NaOH}$ ,  $\text{H}_2\text{O}_2$ , and  $\text{Ca}(\text{OH})_2$  before catalytic pyrolysis using Al-MCM-41 and H-ZSM-5 to give phenolic yields of 90 and 80 wt % yield, respectively.<sup>97</sup> Li and co-workers studied the depolymerization/repolymerization of lignin during steam treatment of aspen wood.<sup>98</sup> They found that addition of a carbenium ion scavenger, such as 2-naphthol, suppresses the repolymerization reaction to give a more uniform and more easily extractable lignin of low molecular weight.<sup>98</sup> As indicated above, controlling the repolymerization of the monomer is important for selective biomass valorization.

### 6.1.1. Cracking

Cracking is a practice commonly employed in petroleum refineries to convert higher-boiling hydrocarbons into more valuable products by C–C bond cleavage.<sup>99</sup> Fluid catalytic cracking is among the most important of catalytic processes, contributing between 20% and 50% of the blending components in the gasoline pool of a refinery. The process uses highly optimized zeolites as catalysts to achieve the C–C bond cleavage in an acid-catalyzed reaction. In the hydrocracking process, the catalytic cracking of heavy oil fractions is combined with a hydrogenation/hydrogenolysis step; reactions are in this case run under elevated partial hydrogen pressure. The catalysts used in hydrocracking are predominantly bifunctional, combining a support active in cracking with a (noble) metal for the hydrogenation reaction. The hydrogenation catalyst is typically composed of cobalt, tungsten, palladium, or nickel, and the cracking component typically consists of zeolites or amorphous silica–alumina with various compositions.<sup>99</sup> Lignin can also be treated with hydrocracking catalysts, which leads to cleavage of the  $\beta$ -O-4 bond and relatively unstable carbon–carbon bonds.<sup>99</sup>

The resulting low molecular weight aromatic compounds are then susceptible to further conversion to valuable products.

Several catalysts crack lignin into low molecular weight compounds. Huber and Corma included a paragraph on the catalytic cracking of lignin in their review of bio- and petrochemical refineries in which two examples of bio-oil upgrading are described.<sup>35</sup> Sharma and Bakhshi reported on the catalytic cracking of pyrolytic lignin<sup>100</sup> or bio-oil produced by liquefaction<sup>101</sup> using H-ZSM-5 as a catalyst between 613 and 683 K in a fixed bed reactor. The products were distilled, and the maximum amount of organic distillate was 30 wt % of pyrolytic lignin, and nearly 60 wt % of the bio-oil was obtained as useful chemical byproducts.<sup>100</sup> H-ZSM-5 and H-mordenite produced more aromatic than aliphatic hydrocarbons from fast pyrolysis bio-oil, whereas H-Y, silicalite, and silica–alumina produced more aliphatic than aromatic hydrocarbons.<sup>102</sup> H-ZSM-5 was most effective for the production of an organic distillate fraction and aromatic hydrocarbons relative to the other zeolites investigated.<sup>103</sup> Similarly, H-ZSM-5 produced the highest yield of deoxygenated liquid fraction and aromatic and naphthenic compounds relative to other zeolites.<sup>104</sup> Chantal and co-workers used H-ZSM-5 to hydrotreat pyrolytic oil and found that the percentage of coke formed is mostly dependent on the flow rate of the oil whereas the percentage of unreacted tar is a function of both temperature and flow rate.<sup>105</sup> The presence of methanol in the oil decreased coke formation.<sup>105</sup> Gayubo and co-workers investigated the effects of temperature and time on the conversion of model compounds obtained from the flash pyrolysis of vegetable biomass using H-ZSM-5.<sup>106</sup> Alcohols (principally propanol and butanol) transform into gasoline hydrocarbons and light olefins similarly to ethanol and methanol, yet phenol and 2-methoxyphenol were less reactive and led to coke formation.<sup>106</sup>

The product distribution observed in these cracking reactions is thought to result from a series of reactions whereby nonvolatile compounds are first cracked to heavy volatile compounds, which are then subsequently cracked to volatile alkyl aromatics and ultimately to coke and gas.<sup>100</sup> The two general reaction pathways are either thermal, which results in the formation of light and heavy organic compounds and polymerization to form char, or thermocatalytic, which involves a range of processes including deoxygenation, cracking, cyclization, aromatization, isomerization, and polymerization.<sup>102</sup> The performances of the catalysts indicated above are strongly dependent on structural characteristics of the catalyst, including framework and the presence and strength of acid sites. Hydrocarbon formation, for example, occurs more readily with H-ZSM-5 compared with silicalite.<sup>102</sup> These catalysts have similar frameworks but differ in that acid sites are present in the former but absent in the latter.<sup>102</sup> The formation of aromatic compounds and coke is linked to catalyst structure since aromatic products are observed with the zeolite catalysts but only low quantities of aromatics are observed with amorphous silica–alumina, and the effectiveness of the catalysts in reducing coke formation decreased with increasing pore size.<sup>102</sup> Excess water was found to have an adverse effect on catalyst performance by decreasing the number of acid sites in the catalyst.<sup>100</sup> Char and tar formation, which is thought to occur via the polymerization of heavy and nonvolatile bio-oil components, is likely temperature related, and the zeolite catalysts indicated above typically reduce char and tar formation more readily at elevated temperatures.<sup>100,102</sup> Cau-



tion is required, however, to avoid bio-oil decomposition, which is also favored at elevated temperatures.<sup>100</sup>

Other catalysts besides zeolites were also reported to be active for the catalytic cracking of biomass. Sheu and co-workers performed a kinetic study on the upgrading of pine pyrolytic oil produced from southern pine sawdust and bark in a trickle bed reactor using Pt/Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> and sulfided Co–Mo/Al<sub>2</sub>O<sub>3</sub>, Ni–W/Al<sub>2</sub>O<sub>3</sub>, and Ni–Mo/Al<sub>2</sub>O<sub>3</sub>.<sup>107</sup> The reactions were conducted between 623 and 673 K and at 5.17–10.34 MPa.<sup>107</sup> Two models for oxygen removal and for compositional changes in the bio-oil were developed, and it was found that Pt/Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> had the best hydrotreating ability of the catalysts analyzed.<sup>107</sup> Supported or non-supported Pt-modified superacid catalysts, such as Pt/SO<sub>4</sub><sup>2–</sup>/ZrO<sub>2</sub>, Pt/WO<sub>4</sub><sup>2–</sup>/ZrO<sub>2</sub>, or Pt/SO<sub>4</sub><sup>2–</sup>/TiO<sub>2</sub> and similar combinations, were demonstrated as effective hydrocracking catalysts at 623 K and 10.34 MPa H<sub>2</sub>.<sup>108</sup> Products included predominantly C<sub>1</sub>–C<sub>2</sub> alkyl-substituted phenols and methoxyphenols or C<sub>3</sub>–C<sub>4</sub> alkyl-substituted phenols depending on the methanol/lignin ratio in the preceding mild base-catalyzed depolymerization step.<sup>108</sup> UOP LLC patented a process for the treatment of lignin and cellulosic biomass to produce aromatics useful in fuels, as well as chemical precursors for the chemical industry.<sup>109</sup> The lignocellulosic biomass is first dispersed with, for example, glycerol, after which it is treated under a hydrogen atmosphere (573–673 K, 3.3–6.8 MPa H<sub>2</sub>) with a metal-loaded large pore zeolite or a sulfided Ni–Mo hydroprocessing catalyst claimed to produce various phenols and aromatics, among other products.

### 6.1.2. Hydrolysis

Lignin hydrolysis was also the focus of several investigations. Karagoz and co-workers described the use of Rb and Cs carbonate solutions to treat pine sawdust to form phenolic compounds.<sup>110</sup> They found that more oil, consisting of a mixture of oxygenated lignin products, was produced using Rb<sub>2</sub>CO<sub>3</sub> catalysts than Cs<sub>2</sub>CO<sub>3</sub>.<sup>110</sup> The base catalysts hindered char formation and favored the formation of the (methylated) catechols and 2-methoxyphenyl products.<sup>110</sup> Thring explored the depolymerization of Alcell lignin by alkaline hydrolysis.<sup>111</sup> Between 7% and 30% conversion of Alcell lignin was obtained to yield a concentration of 4.4% phenols mostly consisting of syringol (2.4%).<sup>111</sup> Several years later, Miller and co-workers performed alkaline hydrolysis of Alcell lignin using KOH in supercritical methanol or ethanol.<sup>112</sup> Only 7% of the ether-insoluble material was left in the KOH/methanol solution after 10–15 min at 563 K.<sup>112</sup> The reaction was favored by strong bases, and combinations of bases gave either positive synergistic effects, such as with NaOH and Ca(OH)<sub>2</sub>, or negative synergistic effects, such as with LiOH or CsOH with Ca(OH)<sub>2</sub>, as indicated by the relative decrease in insolubles.<sup>112</sup> Model compound studies indicated that the principle route for lignin depolymerization was through solvolysis of the ether linkages.<sup>112</sup> Recently, Nenkova and co-workers described the alkaline depolymerization of technical hydrolysis lignin and poplar wood sawdust.<sup>113</sup> Isolated products from extraction with toluene included several high-value products commonly obtained from lignin oxidation, such as 2-methoxyphenol, 4-hydroxy-3-methoxybenzaldehyde, 2,6-dimethoxyphenol, and 1-(4-hydroxy-3-methoxyphenyl)ethanone.<sup>113</sup>

Several examples of lignin fragmentation by supercritical water were reported. Supercritical water has several advantageous properties that make it suitable for use as a solvent

for lignin valorization. It is completely miscible with light gases, hydrocarbons, and aromatic compounds.<sup>114,115</sup> Reactions with biomass containing relatively high water content are possible without the need to dry the feedstock, and several organic decomposition and formation reactions, such as oxidations and hydrolysis, have been reported to occur without a catalyst.<sup>114,115</sup> In addition, supercritical water has relatively low viscosity, high diffusivity, a dielectric similar to many organic solvents but the advantage of thermal stability.<sup>116</sup> The separation of organic products formed during reactions is conducted with relative ease from the water.<sup>116</sup> The principle disadvantages include the relatively high temperatures and pressures required to reach the supercritical conditions ( $T_c = 647.2$  K,  $P_c = 22.1$  MPa)<sup>101</sup> and that char formation can be problematic. Wahyudiono and co-workers used supercritical water in a batch reactor to decompose the lignin model compound catechol, where it was found that manipulating the temperature and pressure of the supercritical water controlled the reaction rate to forming phenol.<sup>114,115</sup> Watanabe and co-workers used supercritical water as a solvent for the NaOH and ZrO<sub>2</sub> catalyzed partial oxidative gasification of organosolv lignin, where it was found that the presence of both ZrO<sub>2</sub> and NaOH greatly increased the H<sub>2</sub> yield.<sup>117</sup>

## 6.2. Lignin Reduction

The selective catalytic hydrogenation of lignin and its model compounds has been studied for many years and is the subject of several publications. With regard to reductive lignin depolymerization, the emphasis of the reported studies is mainly on the production and upgrading of bio-oils and fuels, although the production of phenols as a chemical commodity is also considered. The replacement of petrochemical-based routes for the production of bulk aromatic compounds, such as benzene, toluene, and xylene (B,T,X), as well as phenol, by renewable routes has nonetheless received relatively little attention.<sup>118</sup> Since approximately 60% of all aromatics produced by a typical integrated chemical production center are first generation unfunctionalized aromatics, the conversion of biomass and lignin in particular to B,T,X therefore deserves more attention.<sup>118</sup>

In this section, we review those studies that are primarily concerned with the production of phenols or aromatics from lignin or lignin model compounds via catalytic hydrogenation or hydrodeoxygenation. The production of monomeric phenols by thermochemical conversion of biomass has already been reviewed and falls beyond the scope of this review.<sup>12</sup>

Most reports on the hydrotreatment of biomass-derived feeds are focused on either bio-oil production or upgrading (hydroprocessing) because chemical conversion is required to turn such bio-oils into useful transportation fuels. Hydrotreatment is then employed to increase the thermal stability and volatility of the oil and to reduce viscosity through oxygen removal and lowering of the molecular weight.<sup>119</sup> Fast pyrolysis studies are generally aimed at the maximum production of liquid products. In this respect, it has been found that reducing conditions, that is, the presence of hydrogen or hydrogen-donating compounds, are beneficial and lead to higher yields and to less coke formation in pyrolysis processes.<sup>120</sup> Studies dealing with the direct conversion of biomass to bio-oils (by fast or slow pyrolysis, liquefaction, etc.), that is, those that do not deal directly with lignin or lignin-related models, are beyond the scope of this review. A recent review on wood/biomass pyrolysis for bio-



oil production is available.<sup>121</sup> For general developments in the field of catalytic hydroprocessing of bio-oils, the reader is referred to work by Elliott<sup>119</sup> or to Briens et al.<sup>122</sup> and Behrend et al.<sup>123</sup> Furimsky has published a review on catalytic hydrodeoxygenation from a broader perspective.<sup>38</sup> An early review on mechanistic aspects, reaction pathways, and kinetics of catalytic hydroprocessing, including hydrodesulfurization, hydrodenitrogenation, and hydrodeoxygenation, is also available.<sup>124</sup> The actual composition of bio-oils is complex, and a multitude of compounds have already been identified.<sup>121</sup> In fact, component analysis and determination of chemical reactivity of the identified components for upgrading purposes is an active field of research. Indeed, some studies are concerned with lignin-related model compounds and aim to further understand the processes governing bio-oil upgrading. As such, they provide important insights into the chemical pathways for the conversion of lignin into valuable chemicals. Most of these efforts are concerned with the hydrotreatment of (a multitude of) oxygen-containing model compounds rather than actual lignin or bio-oil feeds. In terms of catalyst development, an optimal catalyst for the conversion of lignins into phenols or aromatics should have the following characteristics: high conversion at modest temperatures to minimize char formation and competitive thermal condensation reactions, high selectivity to phenols to prevent excessive hydrogen consumption, tolerance to water, the ability to deal with various lignin streams, and possibly the capability for dealkylation (side chain removal).

### 6.2.1. Heterogeneous Catalysis

Early studies on lignin heterogeneous hydrogenation were mainly aimed at structure elucidation of the complex lignin polymer. A catalytic reaction of hardwood lignin with hydrogen was reported by Harris and co-workers as early as 1938, in which lignin was found to react with hydrogen over copper–chromium oxide.<sup>125</sup> The rather harsh hydrogenation conditions led to full reduction of the aromatic rings to yield mainly some monomeric (substituted) propylcyclohexanols and methanol. Other early studies on lignin hydrogenation also included the use of Raney Ni as a catalyst, in which syringol and guaiacol components were isolated.<sup>126,127</sup> Pepper et al. studied the influence of a number of catalysts (Raney Ni, Pd/C, Rh/C, Rh/Al<sub>2</sub>O<sub>3</sub>, Ru/C, Ru/Al<sub>2</sub>O<sub>3</sub>) on softwood lignin (spruce wood) hydrogenation. A significant amount of the original lignin was converted into the monomeric products 4-propylguaiacol and dihydroconiferyl alcohol under mild conditions (3.4 MPa, 468 K), with Rh/C giving the highest yield.<sup>128</sup> The Pd/C-catalyzed reaction yielded mainly dihydroconiferyl alcohol (representing some 24% of the lignin), while 4-propylguaiacol was found in addition to dihydroconiferyl alcohol with Rh/C (together accounting for some 34% of the original lignin). The observed product distribution thus implies that Rh/C is capable also of cleaving other linkages than those cleaved by Pd/C. Reaction conditions such as catalyst loading, hydrogen pressure, and pH of the medium were optimized.<sup>129</sup> The nature of the obtained products was influenced by catalyst loading, because higher loadings resulted in over-hydrogenation and degradation reactions, as well as by variation of the pH. Hardwood lignin (aspen wood), on the other hand, gave mainly the corresponding syringyl and guaiacyl compounds bearing a propyl or propanol group with Rh/C, accounting for about 40 wt % of the original lignin.

These results clearly reflected the differences in building block composition of the hard- and softwood lignin polymers.<sup>130</sup> Since these initial reports, many more examples of catalytic hydrogenation have been reported, and a summary of the catalytic systems used for lignin hydrogenation is given in Table 4.

Workers at the Japanese Noguchi Institute worked on lignin liquefaction for phenol production and discovered an active catalyst in the early 1950s. This discovery led to the patented Noguchi process, in which it was claimed that a mixture of C<sub>6</sub>–C<sub>9</sub> monophenols could be obtained upon hydrogenolysis in yields as high as about 40%.<sup>131</sup> An iron(II) sulfide catalyst with a cocatalyst of at least one sulfide of copper, silver, tin, cobalt, chromium, nickel, zinc, or molybdenum (e.g., Fe–S–Cu–Zn in a ratio of 10:12:1:1) was used, and the reaction was conducted in a solvent such as lignin tars and phenols at 523–723 K with an initial hydrogen pressure of 15.2–45.6 MPa. The high yields of monomeric phenols were in part caused by alkylation of the phenolic solvent during the process, but nonetheless a lignin-derived phenol yield of 21% was obtained. The process was extensively evaluated in a multitude of its variants but suffered from difficulties in reproducibility regarding the production of high yields of monophenols. Although it was concluded that the process remained the best one for lignin liquefaction to that date,<sup>132</sup> the process was economically unattractive because of the kind of lignin used, the relatively low economic value of the monophenol product mixture, and the loss of phenol itself when used as a solvent. Around the same time, Inventa AG patented a similar process consisting of decomposing lignin into distillable products containing a substantial amount of phenols using iron sulfate as the hydrogenation (pre)catalyst.<sup>133</sup>

Urban et al. later claimed a modification and improvement on the Noguchi process, affording up to about 45% cresols and about 65% monophenols from alkali lignin from the kraft process. Cresol yield is substantially increased by the addition of methanol, which is important since cresols might be the source of maximum economic return from the liquefaction of lignin. The catalyst is generated in situ and consists of ferrous sulfide with smaller amounts of other metal sulfides as promoters.<sup>134</sup>

**6.2.1.1. Co–Mo- and Ni–Mo-Based Hydrodeoxygenation Catalysts.** Heterogeneous catalyst systems that have been studied most extensively for lignin hydrogenation are conventional cobalt- and nickel-promoted molybdenum catalysts. Indeed, already in 1970 Alpert and Shuman patented a process for the production of chemicals from lignin using a Co–Mo/Al<sub>2</sub>O<sub>3</sub> catalyst.<sup>135</sup> The initial interest in the hydrocracking and hydrodeoxygenation activity of these catalysts rested on the fact that synthetic oils, either from coal or biomass, can have an oxygen content well in excess of 10% and can even approach 50% for biomass feeds.<sup>38</sup> Application of biomass-derived hydrocarbons requires removal of oxygen from the feed.<sup>123</sup> The well-established hydrotreating catalysts originally developed for the removal of sulfur (HDS) and nitrogen (HDN) from conventional oil feed for purification and upgrading processes proved a useful lead for the removal of oxygen (HDO) from biomass-derived product streams.

Indeed, these conventional catalysts are the most studied systems also for reductive lignin conversion. Elliot published an early study in which a variety of commercial catalysts (Co–Mo, Ni–Mo, Ni–W, Ni, Co, Pd, and Cu–CrO) were

**Table 4. Heterogeneous Catalytic Systems for the Hydrogenation and Hydrodeoxygenation of Lignin (Model Compounds)**

entry	catalyst	support	reaction conditions			lignin (model) compound	major products	conversion (%)	notes	ref
			<i>T</i> (K)	<i>P</i> (MPa)	<i>t</i> (min)					
1	Cu–CrO	none	533	22	1080	lignin	methanol, 4- <i>n</i> -propylcyclohexanol, 4- <i>n</i> -propylcyclohexanediol, glycol	70		125
2	Cu–CrO	none	523	20	300	hydrol lignin	3-cyclohexyl-1-propanol, 4- <i>n</i> -propylcyclohexanol, 3-(4-hydroxycyclohexyl)-1-propanol	12		126
3	Raney Ni	none	446	20	360	maple wood meal	4-ethylsyringol, 4-ethanolsyringol	27		127
4	Raney Ni	none	468	3.4	300	spruce wood meal	dihydroconiferyl alcohol, 4- <i>n</i> -propylguaiaicol	16		128
5	Rh	carbon	468	3.4	300	spruce wood meal	dihydroconiferyl alcohol, 4- <i>n</i> -propylguaiaicol	34		128
6	Rh	Al <sub>2</sub> O <sub>3</sub>	468	3.4	300	spruce wood meal	dihydroconiferyl alcohol, 4- <i>n</i> -propylguaiaicol	13		128
7	Pd	carbon	468	3.4	300	spruce wood meal	dihydroconiferyl alcohol, 4- <i>n</i> -propylguaiaicol	24		128
8	Rh	carbon	468	3.4	300	aspen wood meal	<i>l</i>	<i>l</i>		129
9	FeS <sup>a</sup>	none <sup>c</sup>	523–723	15.2–45.6	60–120	lignin	phenols, benzenes	<i>l</i>	<i>m</i>	131
10	FeS	none <sup>c,d</sup>	648–698	5–15	60	kraft lignin	monophenols C <sub>6</sub> –C <sub>9</sub>	<i>l</i>	<i>n</i>	134
11	Co–Mo	SiO <sub>2</sub> –Al <sub>2</sub> O <sub>3</sub>	573–723	10–20	<i>l</i>	polycyclic aromatics	gasoline hydrocarbons	<i>l</i>		137
12	Ni–Mo	SiO <sub>2</sub> –Al <sub>2</sub> O <sub>3</sub> <sup>c,e,f</sup>	573	5	<i>k</i>	phenol	C <sub>6</sub> hydrocarbons	2		138
13	Ni–Mo	SiO <sub>2</sub> –Al <sub>2</sub> O <sub>3</sub> <sup>c,e,f</sup>	598	5	<i>k</i>	phenol	C <sub>6</sub> hydrocarbons	17		138
14	Ni–Mo	SiO <sub>2</sub> –Al <sub>2</sub> O <sub>3</sub> <sup>c,e,f</sup>	598	5	<i>k</i>	<i>o</i> -cresol	phenol/C <sub>7</sub> hydrocarbons	26		138
15	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c</sup>	573	5	250	4-methylphenol	toluene	100		139
16	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	598	6.9	101	4-methylguaiaicol	toluene, cresol isomers, methylcatechol	98		140
17	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	573	6.9	344	4-methylcatechol	toluene, cresol, alkylphenol, methylcyclohexane	99		140
18	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	573	6.9	240	eugenol	propylcyclohexane, propylphenol, propylguaiaicol, propylcatechol	100		140
19	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	573	6.9	254	vanillin	methylcyclohexane, methylcatechol, cresol	98		140
20	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	573	6.9	443	<i>o,o</i> -biphenol	biphenyl, cyclohexylbenzene, dibenzofuran, 2-phenylphenol	92		140
21	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	573	6.9	361	<i>o</i> -hydroxydiphenylmethane	benzene, cyclohexane, toluene, phenol, diphenylmethane	100		140
22	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	573	6.9	379	phenylether	benzene, cyclohexane, phenol	98		140
23	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	523–598	3.4	400–600	anisole	phenol, benzene, cyclohexane	100		141
24	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	523	3.4	1200	guaiaicol	catechol, phenol, benzene, cyclohexane	100		141
25	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c</sup>	548–598	5	<i>l</i>	<i>o</i> -methoxyphenol	phenols, dioxygen compounds, other hydrocarbons	23–99		142
26	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c</sup>	548–598	5	<i>l</i>	<i>m</i> -methoxyphenol	phenols, dioxygen compounds, other hydrocarbons	27–95		142
27	Ni–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c</sup>	723	2.8	<i>l</i>	catechol	phenol, benzene, cyclohexane	98		143
28	Ni–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c</sup>	673	2.8	<i>l</i>	guaiaicol	benzene, toluene	98		143
29	Ni–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c</sup>	673	2.8	<i>l</i>	syringol	benzene, toluene, trimethylbenzene	98		143
30	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	553	7	150	4-methylacetophenone	ethylmethylbenzene	100	<i>o</i>	144
31	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	553	7	150	guaiaicol	phenol, catechol	57	<i>o</i>	144
32	Ni–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	553	7	150	4-methylacetophenone	ethylmethylbenzene	100	<i>o</i>	144
33	Ni–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	553	7	150	guaiaicol	phenol, catechol	65	<i>o</i>	144
34	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c</sup>	553	7	<i>l</i>	4-methylacetophenone	ethylmethylbenzene	<i>l</i>		145
35	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c</sup>	553	7	<i>l</i>	guaiaicol	phenols, catechol, hydrocarbons	<i>l</i>		145
36	Co–Mo	carbon <sup>c,h</sup>	553	7	180	4-methylacetophenone	ethylmethylbenzene	100		147
37	Co–Mo	carbon <sup>c,h</sup>	553	7	180	guaiaicol	catechol, phenol	35		147
38	Co–Mo	carbon <sup>c,h</sup>	553	7	<i>l</i>	guaiaicol	phenol, benzene, cyclohexane	<i>l</i>		148
39	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,f,g</sup>	573	5	<i>l</i>	anisole	phenol, <i>o</i> -cresol, benzene	77		151
40	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,f,g</sup>	573	5	<i>l</i>	anisole	phenol, <i>o</i> -cresol, benzene	50	<i>p</i>	151
41	Ni–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,f,g</sup>	573	5	<i>l</i>	anisole	phenol, <i>o</i> -cresol	91		151
42	Ni–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,f,g</sup>	573	5	<i>l</i>	anisole	phenol, cyclohexane, <i>o</i> -cresol	69	<i>p</i>	151
43	Co–Mo	MgO <sup>c</sup>	623	5	60	phenol	cyclohexylaromatics	17		152
44	Co–Mo–P	MgO <sup>c</sup>	723	5	60	phenol	benzene, cyclohexylaromatics	90		152
45	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	673	6.9	<i>l</i>	cresols	toluene, methylcyclohexane	<i>l</i>		153
46	Fe <sub>2</sub> O <sub>3</sub>	none <sup>c</sup>	723	9.8	50	dimeric species	benzenes, monophenols, dimers	3–100		154
47	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub> <sup>c</sup>	723	9.8	50	dimeric species	benzenes, monophenols, dimers	12–100		154
48	Ni–Mo	Al <sub>2</sub> O <sub>3</sub>	723	9.8	50	dimeric species	benzenes, monophenols, dimers	36–100		154
49	Mo	TiO <sub>2</sub> <sup>c</sup>	723	9.8	50	dimeric species	benzenes, monophenols, dimers	36–100		154
50	Ni–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g,i</sup>	573–723	3.4	<i>l</i>	4-propylguaiaicol	propylphenols, ethylphenols, cresols, phenol	50–100	<i>q</i>	156
51	Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	523–723	3.4	<i>l</i>	4-propylguaiaicol	propylphenols, propylbenzenes, propylhexane, dealkylated products	50–100	<i>q</i>	156
52	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	673–723	7	5–60	organosolv lignin	insoluble residue	<i>l</i>		156
53	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	673–723	7	60	organosolv lignin	insoluble residue/phenols	<i>l</i>	<i>r</i>	156
54	M <sup>b</sup> or M <sup>b</sup> –Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	623	13.7	<i>l</i>	diphenyl ether and naphthalene mixture	phenol, benzene, cyclohexane, tetralin, decalin	<i>l</i>		155
55	Mo	Al <sub>2</sub> O <sub>3</sub>	613–723	3.4–17	<i>l</i>	depolymerized lignin	phenol, cresols, alkylphenols, alkylbenzenes	<i>l</i>		157
56	Co–Mo	Al <sub>2</sub> O <sub>3</sub>	623–648	10–15	<i>l</i>	depolymerized lignin	toluene, ethylbenzene, xylenes, trimethylbenzenes, alkylbenzenes	<i>l</i>		158
57	Mb–Mo	Al <sub>2</sub> O <sub>3</sub>	473–573	3.5–13.8	5–15	depolymerized lignin	phenols	<i>l</i>		155
58	Ni–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c</sup>	673/648	10/18	<i>l</i>	organocell lignin	phenol, cresols, alkylphenols, xylanols, guaiaicol	<i>l</i>	<i>s</i>	161
59		zeolite A	648	10	<i>l</i>	organocell lignin	phenol, cresols, alkylphenols, xylanols, guaiaicol	<i>l</i>	<i>s</i>	161

Table 4. Continued

entry	catalyst	support	reaction conditions			lignin (model) compound	major products	conversion (%)	notes	ref
			<i>T</i> (K)	<i>P</i> (MPa)	<i>t</i> (min)					
60	Pd	activated charcoal	653	10	15	organocell lignin	oils	15		162
61	Fe <sub>2</sub> O <sub>3</sub>	none	653	10	15	organocell lignin	oils	17		162
62	Raney Ni	none	653	10	15	organocell lignin	oils	53		162
63	Ni–Mo	SiO <sub>2</sub> –Al <sub>2</sub> O <sub>3</sub>	653	10	15	organocell lignin	oils	53		162
64	Ni–Mo	zeolite	653	10	15	organocell lignin	oils	17		162
65	Ni–Mo	SiO <sub>2</sub> –Al <sub>2</sub> O <sub>3</sub> or zeolite <sup>j</sup>	673	10	40	organocell or kraft lignin	oils	49–71		163
66	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	523	7.5	<i>l</i>	phenol	benzene, cyclohexane	<i>l</i>	<i>t</i>	164
67	Ni–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	523	7.5	<i>l</i>	phenol	benzene, cyclohexane	<i>l</i>	<i>t</i>	164
68	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	613–628	7	<i>l</i>	4-methylphenol	toluene, methylcyclohexane	80–100		165
69	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	523	1.5	<i>l</i>	phenol	benzene	36		166
70	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	573	1.5	<i>l</i>	phenol	benzene cyclohexane/hexene	71		166
71	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	523	1.5	<i>l</i>	anisole	<i>o</i> -cresol, xylene, phenol, benzene	88		166
72	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	573	1.5	<i>l</i>	anisole	toluene, phenol, benzene, <i>o</i> -cresol	97		166
73	Ni–Mo–P	Al <sub>2</sub> O <sub>3</sub> <sup>c</sup>	623	3.5	<i>l</i>	benzofuran	dihydrobenzofuran, ethylphenol, phenol ethylbenzene, toluene, benzene			167
74	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	583	7	<i>l</i>	benzofuran	ethylphenol, ethylbenzene ethylcyclohexene, ethylcyclohexane			168
75	Ni–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	633	2	<i>l</i>	benzofuran	cyclohexane, ethylcyclohexane	99	<i>u</i>	169
76	Ni–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>g</sup>	453	5.5	<i>l</i>	benzofuran	octahydrobenzofuran, ethylcyclohexane dihydrobenzofuran	97 (25% HDO)		170
77	Ni–Mo–P	Al <sub>2</sub> O <sub>3</sub> <sup>c</sup>	613	7	<i>l</i>	benzofuran	dihydrobenzofuran, ethylphenol, phenol	48		171
78	Ni–Mo–P	Al <sub>2</sub> O <sub>3</sub>	613	7	<i>l</i>	benzofuran	ethylphenol, phenol, ethylcyclohexane	81	<i>v</i>	171
79	Co–Mo	none <sup>c</sup>	563–613	2–10	<i>k</i>	thiophenes, indoles, phenols	cyclohexanes	<i>l</i>		172
80	Co–Mo	SiO <sub>2</sub> <sup>c</sup>	563–613	2–10	<i>k</i>	furanes, phenols	cyclohexanes	<i>l</i>		172
81	Ni–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c</sup>	523–663	7	<i>l</i>	dibenzofuran	cyclohexane, methylcyclopentane cyclopentane, benzene, methylcyclohexane	100		173
82	Co–Mo	Al <sub>2</sub> O <sub>3</sub> <sup>c</sup>	523–663	7	<i>l</i>	dibenzofuran	cyclohexane, methylcyclopentane cyclopentane, benzene, methylcyclohexane	100	<i>w</i>	173
83	Mo <sub>2</sub> N		723	0.1	<i>l</i>	benzofuran	benzene, toluene, ethylbenzene	35		174
84	Mo <sub>2</sub> N		723	0.1	<i>l</i>	benzothiophene	ethylbenzene	40		174
85	Mo <sub>2</sub> N		723	0.1	<i>l</i>	indole	toluene, benzene, ethylbenzene	20		174
86	Pd	carbon	523	5	30	phenol	cyclohexanol, cyclohexane	100		175
87	Pd	carbon	523	5	30	4- <i>n</i> -propylguaiacol	cycloalkanes, cycloalcohols, methanol	100	<i>x</i>	175
88	Pd	carbon	523	5	30	4-allylguaiacol	cycloalkanes, cycloalcohols, methanol	99	<i>x</i>	175
89	Pd	carbon	523	5	30	4-acetylguaiacol	cycloalkanes, cycloalcohols, methanol	100	<i>x</i>	175
90	Pd	carbon	523	5	30	4-allylsyringol	cycloalkanes, cycloalcohols, methanol	92	<i>x</i>	175
91	Ni–W	SiO <sub>2</sub> –Al <sub>2</sub> O <sub>3</sub> <sup>c</sup> SiO <sub>2</sub> –Al <sub>2</sub> O <sub>3</sub> –PO <sub>4</sub> <sup>c</sup>	573–723	3.5–24	<i>l</i>	lignin	phenolics	<i>l</i>	<i>y</i>	176
92	Rh	SiO <sub>2</sub>	573	1	<i>l</i>	anisole	<i>l</i>	30		177
93	Rh–Co	Al <sub>2</sub> O <sub>3</sub>	573	1	<i>l</i>	anisole	<i>l</i>	75		177
94	Rh–Co	SiO <sub>2</sub>	573	1	<i>l</i>	anisole	<i>l</i>	79		177
95	Rh–Co	SiO <sub>2</sub>	573	1	<i>l</i>	anisole	<i>l</i>	81		177
96	Co	SiO <sub>2</sub>	573	1	<i>l</i>	anisole	<i>l</i>	6		177
97	Rh	ZrO <sub>2</sub>	573	1	<i>l</i>	anisole	<i>l</i>	91		177
98	Rh	CeO <sub>2</sub>	573	1	<i>l</i>	anisole	<i>l</i>	95		177
99	Ni	SiO <sub>2</sub>	573	1	<i>l</i>	anisole	<i>l</i>	46		177
100	Ni	Cr <sub>2</sub> O <sub>3</sub>	573	1	<i>l</i>	anisole	<i>l</i>	16		177
101	Ni	Al <sub>2</sub> O <sub>3</sub>	573	1	<i>l</i>	anisole	<i>l</i>	95		177
102	Ni	ZrO <sub>2</sub>	573	1	<i>l</i>	anisole	<i>l</i>	69		177
103	Ni–Cu	Al <sub>2</sub> O <sub>3</sub>	573	1	<i>l</i>	anisole	<i>l</i>	99		177
104	Ni–Cu	ZrO <sub>2</sub>	573	1	<i>l</i>	anisole	<i>l</i>	60		177
105	Ni–Cu	CeO <sub>2</sub>	573	1	<i>l</i>	anisole	<i>l</i>	100		177
106	Pd	carbon 473	6.9	<i>l</i>	guaiacol	volatile	hydrocarbons, cyclohexanediol 2-methoxycyclohexanol	66		178
107	Ru	carbon	473	6.9	<i>l</i>	guaiacol	2-methoxycyclohexanol, cyclohexanol	100		178
108	Pt	carbon	473	4	240	lignin	monomers, dimers	42		59
109	Pd	carbon	523	4	30–120	monomers, dimers	alkanes, methanol	95–100	<i>x</i>	59
110	V	Al <sub>2</sub> O <sub>3</sub> <sup>c,g</sup>	623	<i>l</i>	<i>l</i>	guaiacol	(methylated) phenol	100	<i>z</i>	180
111	Mo	none	673	7–10	65	lignin	oils	<i>l</i>		182

<sup>a</sup> With cocatalyst. <sup>b</sup> M = Ru, Co, Cu, Ir, Re, Pd, Fe, Rh, Pt, or Ni. <sup>c</sup> Sulfided. <sup>d</sup> Promoter can be used. <sup>e</sup> Amorphous. <sup>f</sup> Pellets. <sup>g</sup>  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. <sup>h</sup> Several carbon supports tested. <sup>i</sup> Phosphorus doped. <sup>j</sup> With CrO on alumina. <sup>k</sup> Continuous flow. <sup>l</sup> Not specified. <sup>m</sup> Several solvents can be used. <sup>n</sup> Phenol is solvent and later lignin tars. <sup>o</sup> Reaction mixture with three substrates. <sup>p</sup> Pyridine poisoned. <sup>q</sup> Dimethyldisulfide in feed. <sup>r</sup> Flow experiment, products removed. <sup>s</sup> Lignin was mixed with different lignin-derived slurry oils. <sup>t</sup> Inhibited by H<sub>2</sub>S. <sup>u</sup> Lower pressure and temperature, less hydrogenation. <sup>v</sup> H<sub>2</sub>S in feed. <sup>w</sup> 1/3 active as Ni–Mo. <sup>x</sup> H<sub>3</sub>PO<sub>4</sub>/H<sub>2</sub>O. <sup>y</sup> Addition of lower aliphatic alcohols increases phenolics yield. <sup>z</sup> In the presence of  $\alpha$ -terpinene.

screened for phenol hydrogenation/hydrodeoxygenation activity; the sulfided Co–Mo catalyst provided the best results, giving the highest yield of benzene (34%) at 673 K.<sup>136</sup> The superiority of the Co–Mo system in terms of hydrodeoxygenation

activity would later be confirmed in many of the earlier studies. With the aim of obtaining high-quality gasoline, an advanced process concept was eventually developed by the same group in which hydroxyaromatic compounds were



converted into single-ring aromatics by dehydroxylation while avoiding ring saturation.<sup>137</sup>

In general, two separate routes can be discerned if one aims for the production of valuable bulk chemicals from lignin. In the first route, various (oxygenated) aromatics can be produced by depolymerization of lignin itself. In this case, the product stream can still have a fairly high oxygen content and products will generally resemble the original building blocks of lignin, that is, consist of molecules containing substituted phenol, guaiacyl, and syringyl moieties (see Figure 13, **129**, and Figure 14, **176**, for guaiacyl and syringyl structures, respectively). In the second route, catalyst systems can also be developed for the conversion and further upgrading of the product streams of already degraded lignin. Irrespective of the way in which the macromolecule was decomposed, these systems should be able to convert mixtures of the smaller oxygenated aromatic fragments into alkylated benzenes and phenol. It is important to note that the goal is to keep the aromaticity of the feed intact in contrast to hydrodesulfurization and hydrodenitrogenation, in which the heteroatom is usually removed after full hydrogenation of the aromatic component. Many of the studies on model compounds that mimic those bio-oil components that need to be deoxygenated for stabilization purposes are relevant with respect to the second route and will also be discussed below.

Initial studies focused on the hydrogenolysis and hydrocracking of the carbon–oxygen bond of simple aromatic model compounds, such as phenol, *o*-cresol (Figure 12, **101**), anisole (Figure 12, **86**), and guaiacol.<sup>138,139</sup> Basic aspects of (substituted) phenol HDO were noted. First of all, the reaction can take two paths, because HDO can be accomplished by either direct deoxygenation of phenol leading to aromatics or ring hydrogenation followed by deoxygenation, the latter route being favored at higher pressures. The position of substituents on the ring also influenced reactivity, because *ortho*-substitution led to lower activity, which was ascribed to steric hindrance.<sup>139</sup>

Bredenberg et al. reported that phenol and *o*-cresol proved to be quite stable under mild hydrocracking conditions (sulfided Ni–Mo/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalyst, 523–623 K, 5 MPa H<sub>2</sub>). A strong influence of temperature not only on conversion but also on product selectivity was observed for guaiacol. Depending on the temperature chosen, guaiacol was mainly converted into phenol (at more elevated temperatures) or catechol (Figure 13, **130**), illustrating the possibility for control over selectivity in this process. Anisole mainly yielded phenol, *o*-cresol, and 2,6-dimethylphenol with constant selectivities over a 523–573 K temperature range. Oxygen-free aromatics only appeared at higher temperatures (over 573 K). The lower reactivity of guaiacol compared with anisole was attributed to a stronger interaction between the substrate and the support. At higher temperatures rapid deactivation of the catalyst was observed, thought to be caused by the large amounts of water released, the loss of sulfur, and excessive coke formation. Below 523 K, catalyst activity remained constant for over 50 h, though.<sup>138</sup> These and other studies demonstrated the feasibility of oxygen removal at conditions far less than required for thermal fragmentation and deoxygenation.<sup>140</sup>

Similar observations were made by Hurff and Klein for a sulfided Co–Mo/Al<sub>2</sub>O<sub>3</sub> catalyst (at 523 K, 3.45 MPa H<sub>2</sub>) as guaiacol conversion also mainly yielded catechol and phenol, after a primary demethylation reaction was followed by

dehydroxylation. Further hydrodeoxygenation of phenol yielded benzene and cyclohexane.<sup>141</sup> Anisole gave phenol as the only primary product, with subsequent conversion to benzene and cyclohexane. No ring methylation was reported in this case. Guaiacol disappearance was much faster than anisole decomposition, indicating that the electronic effect of the *ortho*-methoxy substituent is stronger than any steric hindrance it may cause. Guaiacol was also found to be more prone to coke formation than anisole. At a slightly higher temperature and pressure (598 K, 5 MPa H<sub>2</sub>), excellent conversion of guaiacol and good selectivity for phenols (77%) were reported. In this case, the hydrodeoxygenation reaction was found to coincide with significant ring methylation.<sup>142</sup> A strong temperature dependence was observed as catechol rather than phenol became the major product at 548 K. A comparison between the different methoxyphenol isomers led to the suggestion that the different reactivities are the result of different adsorption modes on the catalyst surface, with the guaiacol isomer adsorbed in an inclined rather than flat mode.

Kallury et al. tested the hydrodeoxygenation activity of a Ni–Mo/Al<sub>2</sub>O<sub>3</sub> catalyst on a number of substrates, including phenol, catechol, guaiacol, and syringol.<sup>143</sup> Catechol proved to be more reactive than phenol itself at 623 K, with loss of one hydroxyl group to give phenol as the major product. The addition of methanol to the reaction mixture resulted in significant amounts of ring-methylated products. The addition of methanol and of water was, however, found to limit the activity of the catalyst. The deactivating effect was suggested to arise from competitive adsorption and blocking of the active sites. Water formation was also thought to be responsible for the reduced deoxygenation ability, associated with the molybdenum sites, of the catalyst over several runs. Interestingly, the hydrogenation properties of the catalyst, evidently due to nickel, were not affected. The results obtained with guaiacol resembled those of catechol. Alkylated phenols are also detected without the addition of methanol, which again illustrates that cleavage of the aryl methyl ethers is a facile process. Syringol is equally reactive and demethylation and dehydroxylation proved rather efficient. The ring hydrogenation activity of the Ni–Mo catalysts was only limited at 623 K under these conditions.<sup>143</sup>

It was noted that the studies of Bredenberg and Kallury were done with poorly sulfided catalysts and therefore might not present optimal results.<sup>144</sup> Laurent et al. attempted to address this issue by reporting a comparison of the HDO of guaiacol with both Co–Mo and Ni–Mo catalysts.<sup>144</sup> Importantly, they found that the alumina support itself also showed catalytic activity, because 37% of the guaiacol substrate was converted to catechol with alumina alone.<sup>144</sup> A comparison was made between Co–Mo and Ni–Mo catalysts using a mixture of reagents typical of bio-oil composition, which included guaiacol. The results confirmed that catechol was formed first as the primary product, followed by dehydroxylation to phenol (573 K, 7 MPa H<sub>2</sub>). No significant methylation was observed in this study, however. A higher activity was found for the Ni–Mo catalyst, but the Co–Mo catalysts showed a higher selectivity for the production of catechol and phenol.<sup>144</sup> Indeed, side reactions are more pronounced with the Ni–Mo catalyst, which was also reflected by a poorer mass balance at similar conversion. The impossibility to close the material balance for both catalysts was attributed to the formation of heavy products or coke. Given the propensity of guaiacol and



catechol-like compounds to form polycondensation products and coke along with the relatively strong interaction of these compounds with the common alumina support, other neutral supports such as carbon and silica were subsequently tested as well.<sup>145</sup> Although both alternative supports show 3–6 times lower activity compared with alumina, further confirming the involvement of acid sites in guaiacol conversion, the carbon-supported catalyst produced phenol faster than the alumina-supported one, resulting in a phenol/catechol ratio seven times greater than that for the alumina-supported catalyst.<sup>145</sup> The latter result indicates that phenol might be produced directly from guaiacol with this catalyst by elimination of the methoxyl group. Furthermore, the results clearly indicated that coking of guaiacol takes place on the acid sites on alumina. On the other hand, guaiacol conversion was lower for the silica- and carbon-supported catalysts, confirming that acid sites are involved also in the steps leading to product formation. The involvement of acid sites is further corroborated by the fact that guaiacol conversion is highly inhibited by ammonia.<sup>146</sup> De la Puente et al. noticed negligible coke formation also on an activated carbon-supported Co–Mo catalyst. Activated carbons differing in the nature and amount of functional groups on the surface were tested, but rather similar results were obtained in the guaiacol HDO reactions. Moderate conversions of guaiacol (35% at 553 K, 7 MPa H<sub>2</sub>) led predominantly to the formation of catechol and, to a lesser extent, phenol.<sup>147</sup> The phenol/catechol ratio was found to depend on the extent of oxygen-functionalization of the amphoteric support. The nonmodified, least acidic carbon gave a higher yield of phenol, further confirming the involvement of acid-sites in the guaiacol-to-catechol-to-phenol route, but not in the direct conversion of guaiacol to phenol. Ferrari et al. showed that the nature of the carbon support and the impregnation order of the metals (Co–Mo or Mo–Co) both have an influence on catalyst activity and selectivity in the hydrodeoxygenation of various substrates, but no clear trends emerged for guaiacol hydrodeoxygenation.<sup>148</sup>

Support effects in hydrotreating catalysts are well-known and have been extensively studied for hydrodesulfurization and hydrogenation processes.<sup>149</sup> For these hydrotreating catalysts, it has been well-established that the use of supports other than alumina, for example, carbon, titania, mixed oxides, zeolites, or clays, can lead to enhanced catalytic properties. For hydrodeoxygenation purposes, this topic has been less well explored.

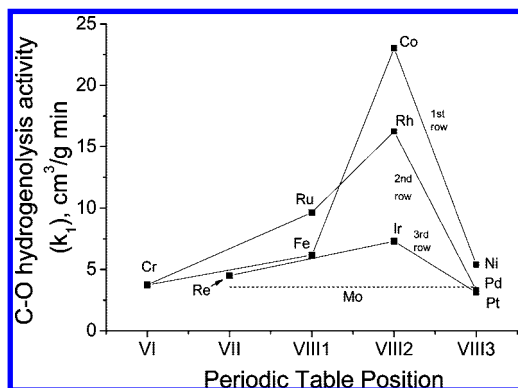
The origin of the almost exclusive use of alumina as support can be ascribed to its very good textural and mechanical properties and its relatively low cost.<sup>149</sup> It is well-known, however, and clearly confirmed by the previously discussed results that the support is not an inert carrier and that other supports should be explored as well. An additional reason for the use of alternative supports, in particular with respect to the conditions encountered in HDO, is the possible instability of alumina in the presence of high levels of water.<sup>150</sup> Alumina is known to be metastable under hydrothermal conditions, for instance, and partially transforms into boehmite under processing conditions. A limited number of studies on support influence on HDO activity and selectivity have been reported. For instance, the (Lewis) acidity of the alumina support was shown to be an important characteristic for the observed demethylation activity with the (substituted) guaiacol substrates. In addition to this reaction taking place on the metal, it is also thought to occur on the support surface

(albeit via a different mechanism). Indeed, anisole demethylation activity (and subsequent ring methylation of the phenol product) could be partly blocked by selective poisoning of the acid sites of the support with pyridine.<sup>151</sup> The hydrodeoxygenation and hydrogenation selectivity was not markedly affected, however.

MgO was also tested as a support for Co–Mo catalysts,<sup>152</sup> with the aim of promoting the dispersion of the (acidic) MoO<sub>3</sub> precursor on the basic support and inhibiting coke formation. Hydrotreatment of phenol was conducted using a sulfided Co–Mo/MgO catalyst in supercritical hexane (623–723 K, 5 MPa H<sub>2</sub>). Additionally, phosphorus-doped analogues (Co–Mo–P/MgO) were also tested. Phosphorus doping has been commonly used in attempts to improve the activity of MoS<sub>2</sub>-based hydrotreating catalysts in hydrodenitrogenation and hydrodesulfurization studies, but information on its effect on Co–Mo catalysts for hydrodeoxygenation is limited. Both systems proved to be effective for phenol hydrodeoxygenation, with Co–Mo–P/MgO giving superior activity and yielding mainly benzene and some cyclohexyl aromatics as the products. The MgO-supported catalysts also showed good resistance to coking.<sup>152</sup>

Petrocelli et al. expanded the scope of hydrodeoxygenation of lignin model compounds by studying the hydrotreatment of 4-methylguaiacol, 4-methylcatechol, eugenol (Figure 13, **126**), vanillin (Figure 13, **124**), *o,o'*-biphenol (Figure 9, **40**), *o*-hydroxydiphenylmethane, and phenyl ether over a sulfided Co–Mo/Al<sub>2</sub>O<sub>3</sub> catalyst (at 523–598 K, 6.9 MPa H<sub>2</sub>). The latter three substrates mimic some of the thermally more stable linkages found in lignin.<sup>140</sup> For the monoaromatic compounds, hydrodeoxygenation proceeded predominantly by demethylation followed by dehydroxylation to a monohydroxyl-substituted intermediate, which finally undergoes dehydroxylation to an aromatic hydrocarbon; saturation is observed, but only to a minor extent. The methyl and propyl substituents of the reactants and products appeared to be quite stable. This observation is in agreement with previous findings of Odebunmi et al. after hydrodeoxygenation of cresol using a Co–Mo/Al<sub>2</sub>O<sub>3</sub> catalyst.<sup>153</sup> Encouragingly, the results show that substituted guaiacols and catechols readily react to form thermally stable phenols during hydrodeoxygenation at 573 K, with possible yields of total single-ring phenols of about 60%. Importantly, char formation was greatly reduced in comparison to pyrolysis. Reasonable activity was observed toward hydrocracking of the interaromatic ring bonds in the diaromatic substrates with dehydroxylation both preceding and following breakage of the interunit link, although the C–C bond in *o,o'*-biphenol proved stable under the conditions employed.

Koyama reported an extensive comparison of iron and molybdenum catalysts in the hydrogenation of various model compounds containing different kinds of ether bonds. The hydrocracking of lignin model dimers using Fe<sub>2</sub>O<sub>3</sub>–S, Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>–S, NiO–MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, and MoO<sub>3</sub>/TiO<sub>2</sub>–S between 613 and 723 K was described.<sup>154</sup> The Mo catalysts significantly increased the bond cleavage between the aromatic rings of 4-hydroxydiphenylether, diphenylether, and diphenylmethane, whereas the Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>–S catalysts only slightly promoted bond cleavage between the aromatics of these compounds.<sup>154</sup> The higher activity of the molybdenum-based catalysts led to the conclusion that these catalysts are more likely to give higher monophenol and benzene yields in lignin hydrocracking processes.<sup>154</sup>



**Figure 16.** Variation in C–O hydrogenolysis activity ( $k_1$ ) for M–Mo/Al<sub>2</sub>O<sub>3</sub> catalysts as a function of periodic table position of M, adapted from Shabtai et al.<sup>155</sup>

Shabtai et al. presented a thorough investigation into the activities of first, second, and third-row transition metals as possible promoters for supported molybdenum sulfide catalysts.<sup>155</sup> Although their initial interest was in the preparation of new catalysts with improved hydrodeoxygenation activity for coal- and peat-derived liquids, the hydrodeoxygenation results of the model compounds studied are also relevant for lignin product streams. The systematic study consisted of C–O bond hydrogenolysis of diphenyl ether of a series of sulfided M–Mo/Al<sub>2</sub>O<sub>3</sub> catalysts (M = Cr, Fe, Co, Ni, Ru, Rh, Pd, Ir, or Pt, at 623 K, 13.8 MPa H<sub>2</sub>). The corresponding M/Al<sub>2</sub>O<sub>3</sub> catalysts (i.e., without molybdenum) were also tested. The Co–Mo, Rh–Mo, and Ru–Mo catalysts showed the highest hydrogenolysis activity, in that order, although considerable ring hydrogenation activity was also observed with Co–Mo (see Figure 16). The Ru–Mo catalyst provided the highest selectivity for hydrogenolysis. The Ni–Mo catalyst yielded the lowest hydrogenolysis selectivity, mainly because of high ring hydrogenation activity.

Ratcliff et al. studied a sulfided Co–Mo/Al<sub>2</sub>O<sub>3</sub> catalyst for the hydrodeoxygenation of both model compounds and organosolv lignin in a batch reactor with the aim of converting the obtained (substituted) phenols into phenyl methyl ethers, which can be blended into gasoline.<sup>156</sup> Various parameters were tested and 1-methylnaphthalene was used as the solvent, which, it was later discovered, acted as a reagent rather than as an inert solvent. Phenol yield, although low overall (10 wt %), could be considerably improved if the reaction was carried out under flow rather than batch conditions. A significant amount of char was formed as well in all the lignin hydrodeoxygenation experiments (14 wt % of lignin charged). The model compound 4-propylguaiacol could, depending on the temperature used, be converted into catechols (<573 K), phenols, or saturated and aromatic hydrocarbons (>673 K). The use of a Ni–Mo catalyst on a more acidic support, a phosphated alumina, resulted in higher dealkylation activity and subsequently higher yields of cresols and phenol.

Related to this study is a patented hydrocracking process in which kraft lignin is used to produce monoaromatic phenol-containing products from lignin-containing feedstocks. The Hydrocarbon Research Institute's (HRI) lignol process combines a hydrotreatment step in an ebullated catalyst bed reactor with a subsequent thermal dealkylation step. Using a catalyst comprised of an (Co- or Ni-promoted) iron or molybdenum oxide on alumina, a 37.5% yield of phenols is claimed (wt % based on organic content of

lignin).<sup>157</sup> The yield of monophenols by the HRI process is quite high and corresponds to approximately 60% of the aromatic rings making up the lignin molecule. It exceeds the conversion obtained in the Noguchi process, although the HRI results have not been independently confirmed.

Shabtai et al. patented a two-stage, catalytic reaction process for the conversion of lignin into a reformulated hydrocarbon gasoline product with a controlled amount of aromatics.<sup>158</sup> The (wet) lignin material is first subjected to a base-catalyzed depolymerization step in a supercritical alcohol, followed by a two-step hydroprocessing reaction to produce the reformulated hydrocarbon gasoline mixture. Of particular interest, the first hydroprocessing treatment of the depolymerized lignin products, primarily methoxy-substituted alkylphenols, entails an exhaustive dehydrodeoxygenation using a sulfided Co–Mo/Al<sub>2</sub>O<sub>3</sub> catalyst system. The hydrodeoxygenation step (at 623–648 K, 9.7–15.2 MPa H<sub>2</sub>) yields mainly a mixture of alkylated benzenes but hardly any benzene (undesired for gasoline applications because it is a known carcinogen) itself. In yet another patent, lignin is also subjected to a base-catalyzed partial depolymerization first, followed by stabilization through partial hydrodeoxygenation using a sulfided catalyst system M–Mo supported on Al<sub>2</sub>O<sub>3</sub> or on activated carbon (M = Co, Rh, Pd, Ru, or Pt). These catalysts, which were already demonstrated to be effective C–O bond<sup>155</sup> and C–N bond<sup>159</sup> hydrogenolysis catalysts, were also used as lignin hydrocracking/ring hydrogenation catalysts.<sup>158</sup> Shabtai et al. reported conversion of over 95% of methoxyphenols and benzenediols to phenol-based products having a single oxygen moiety. Finally, the product is converted to biofuel via further refining steps.<sup>160</sup> A general drawback of processes such as those mentioned above is that they suffer from coke formation, which limits the capacity and lifetime of the catalyst and can cause blocking of the reactor.<sup>120</sup>

Meier et al. subjected organocell lignin to catalytic hydrocracking using a lignin-derived slurry oil with the objective of maximizing phenol yields.<sup>161</sup> Up to 12.8 wt % of a mixture of monophenols and little coke formation was obtained using a spent, conventional Ni–Mo hydrocracking catalyst. Of the parameters studied, hydrogen pressure proved the most important. A number of lignins were also subjected to catalytic hydropyrolysis using various different catalysts in a gas–solid type reaction to exclude any influence of the solvent or pasting oil on the origin of the degradation products. Of the catalysts tested, Ni–Mo/Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> and Pd/C gave the highest yields of liquid products (oil) and the least amount of char formation. The Ni–Mo catalyst gave the best results in terms of phenol production, while mostly alkylated cyclohexanones were obtained with Pd/C.<sup>162</sup>

Several different catalysts were studied in the conversion of five different softwood and hardwood kraft lignins and one softwood organocell lignin into oil-like products. Highest yields were obtained for the organocell lignin with a catalyst mixture of sulfided Ni–Mo/Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> resulting in at most 10 wt % of the lignin feedstock converted into alkylbenzenes and phenols, in addition to unidentified products.<sup>163</sup>

In some cases, the low sulfur content of bio-oils or lignin product streams demands the addition of a sulfiding agent to the feed to maintain the sulfidation degree and consequently the activity of the catalysts.<sup>38</sup> The addition of the sulfiding agent affects the hydrodeoxygenation process and differences have been observed for different classes of

substrates on how particular pathways and catalyst activity are influenced by such additives. Whereas a promoting effect was observed for aliphatic oxygenates, hydrodeoxygenation activity of phenolic compounds was generally found to be suppressed on sulfided Ni–Mo and Co–Mo catalysts.<sup>139,164–166</sup> The addition of H<sub>2</sub>S, for instance, suppressed direct hydrogenolysis of phenol due to competitive adsorption.<sup>164</sup> Şenol et al. compared the influence of increasing concentrations of H<sub>2</sub>S on phenol hydrodeoxygenation with both sulfided Co–Mo and Ni–Mo catalysts under identical conditions.<sup>164</sup> On both catalysts, the HDO conversion of phenol decreased with increasing H<sub>2</sub>S concentration in the feed. Hydrodeoxygenation of phenols is generally accepted to proceed via two parallel reaction pathways: the direct hydrogenolysis route involving cleavage of the C–O bond giving aromatic products, or ring hydrogenation prior to C–O bond cleavage (hydrogenation–hydrogenolysis) yielding saturated hydrocarbons. The yields of both aromatics and saturated hydrocarbons dropped upon introduction of H<sub>2</sub>S, but not to the same extent. The decrease in molar ratio of aromatics to saturated hydrocarbons was minor with the Ni–Mo catalyst, indicating that both pathways were equally affected. The addition of H<sub>2</sub>S to phenol hydrodeoxygenation over a sulfided Co–Mo/Al<sub>2</sub>O<sub>3</sub>, on the other hand, suppressed the direct hydrogenolysis route but not the combined hydrogenation–hydrogenolysis route. This observation supports the idea that the two reactions take place at different sites. Although only a minor pathway in the absence of H<sub>2</sub>S, the latter route thus becomes more important with increasing concentrations of the sulfiding agent as the direct hydrogenolysis route becomes increasingly blocked. The inhibiting effect of H<sub>2</sub>S was interpreted in terms of competitive adsorption of phenol and H<sub>2</sub>S on the catalytic sites, that is, coordinatively unsaturated sites associated with the MoS<sub>2</sub> phase. Interestingly, the addition of H<sub>2</sub>S did not solve the deactivation problem of the sulfided Co–Mo catalyst, hinting at the influence of the formation of coke and high molecular weight compounds on catalyst performance.<sup>166</sup> Laurent et al. also noted that hydrogenolysis was affected more than hydrogenation upon addition of H<sub>2</sub>S for both Co–Mo and Ni–Mo catalysts.<sup>165</sup> As expected, the Co–Mo catalyst activity is more sensitive to H<sub>2</sub>S as the dominant hydrogenolysis pathway becomes inhibited. It was also noted that the activity and selectivity of Co–Mo and Ni–Mo catalysts in 4-methylphenol hydrodeoxygenation was not substantially affected by the presence of added water. Pretreatment of a sulfided Ni–Mo catalyst with water under hydrotreating conditions did, however, result in a loss of two-thirds of the initial activity after 60 h, but the hydrogenolysis/hydrogenation selectivity remained unchanged. Partial recrystallization of the support into a hydrated boehmite phase was observed together with partial oxidation of the nickel sulfide phase into oxidized nickel species.<sup>150</sup>

Benzofuran (Figure 10, 68) has been used as a common probe molecule to evaluate catalyst performance in hydrodeoxygenation reactions, and various studies using Ni–Mo or Co–Mo catalysts have been reported, with the former being more active for this substrate.<sup>167–173</sup> As indicated above, the reduced benzofuran derivative, 2,3-dihydrobenzofuran, resembles some of the cyclic ethers found in lignin and is therefore studied as a model compound of this linkage. Different hydrodeoxygenation routes have been suggested depending on the catalyst and conditions used, but ethylcyclohexane is commonly obtained as the major product.

Product distribution was found to depend strongly on temperature and hydrogen pressure employed. For sulfided Ni–Mo/Al<sub>2</sub>O<sub>3</sub>, for instance, hydrogenation of the benzofuran heterocycle to 2,3-dihydrobenzofuran is followed by hydrogenolysis, producing 2-ethylphenol. Further hydrogenation/dehydroxylation leads to loss of aromaticity and ethylcyclohexane formation but only at higher temperatures. A reduced Ni–Mo catalyst showed much higher hydrogenation activity, which resulted in ring saturation being favored over the hydrogenolysis route.<sup>169,170</sup> The activity of Mo<sub>2</sub>N for benzofuran hydrodeoxygenation has also been investigated, and molybdenum nitride was found to be an effective catalyst as rapid hydrogenation of the heterocyclic ring, followed by hydrogenolysis of the ether and release of the heteroatom yielded a mixture of alkylated aromatics, that is, benzene, toluene, and ethylbenzene in approximately equal amounts.<sup>174</sup>

Interesting effects of adding H<sub>2</sub>S to the feed for the sequential deoxygenation of benzofuran and its products were observed with Co–Mo and Ni–Mo catalysts. The addition of H<sub>2</sub>S was found to have a major influence on benzofuran hydrodeoxygenation over sulfided Ni–Mo–P/Al<sub>2</sub>O<sub>3</sub>, as benzofuran conversion increased significantly giving 2-ethylphenol as the major product.<sup>171</sup> The influence on each individual step of the reaction pathway was more subtle, however. Both Bunch et al. and Romero et al. found, for instance, that while H<sub>2</sub>S promoted the conversion of dihydrobenzofuran to 2-ethylphenol, it inhibited the conversion of 2-ethylphenol to ethylbenzene.<sup>169–171</sup> These phenomena can be explained by the role of H<sub>2</sub>S in filling vacancies in the MoS<sub>2</sub> phase, leading to an interconversion of direct deoxygenation sites to hydrogenation sites.<sup>171</sup>

#### 6.2.1.2. Nonconventional Hydrodeoxygenation Catalysts.

Some disadvantages that are associated with conventional hydrodeoxygenation catalysts are possible contamination of products by incorporation of sulfur, rapid deactivation by coke formation, and potential poisoning by water. These issues arise especially with biomass feedstocks and thus have prompted efforts to explore alternative hydrogenation catalysts.<sup>175</sup>

Thring et al. used a Ni–W/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalyst for hydrocracking of solvolysis (Alcell) lignin in the presence of tetralin, a hydrogen donor solvent at little or no hydrogen pressure. Reaction conditions were deemed insufficient to degrade the lignin to liquid and gaseous products, because conversion did not exceed 50% at the highest severity conditions. Recondensation appeared to dominate hydrocracking, which was attributed to insufficient amounts of hydrogen atoms released by the solvent to stabilize the lignin fragments. Recondensation poses a general problem in lignin degradation, as mentioned previously. Size exclusion chromatography studies showed that lignin was nevertheless increasingly depolymerized, but yields of monomeric products were very low.<sup>99</sup> A patent by Engel et al. claimed that hydrocracking of kraft lignin afforded phenolics in high yields using a supported Ni–W catalyst. Using a mildly acidic support and various additives, high yields of phenols and cresols were obtained.<sup>176</sup>

In search of a stable and active nonsulfided hydrodeoxygenation catalyst, which would dispense with the need to possibly add a sulfur source to the feed and give less rise to coking, Yakovlev et al. tested a number of metals and supports for anisole hydrodeoxygenation activity. The support was again found to play a major role, and zirconia and ceria, which can have a valence change under hydrodeoxy-



genation conditions, proved the most effective because of possible additional activation of oxy-compounds on the support surface. Various supported rhodium catalysts performed well with good selectivity for aromatic products in some cases. The influence of the support was clearly illustrated by a comparison of Ni–Cu/ZrO<sub>2</sub> and Ni–Cu/CeO<sub>2</sub>, because the former gave mostly aromatic products and the latter full conversion to cyclohexane.<sup>177</sup>

Elliott et al. reported on the use of Ru/C and Pd/C for the catalytic hydroprocessing of guaiacol (among others), which was used as a chemical model for bio-oil. The supported platinum-group catalysts are known to be more active than the sulfided Mo-based ones and can therefore be used at lower temperatures, and nonalumina supports such as carbon or TiO<sub>2</sub> avoid water instability associated with Al<sub>2</sub>O<sub>3</sub>.<sup>178</sup> The Ru-catalyzed reactions of guaiacol yield methoxycyclohexanol and cyclohexanediols at 423 K, cyclohexanol at 473 K, and gasification products at temperatures exceeding 523 K. In contrast, Pd-catalyzed reactions yield methoxycyclohexanone at 423 K, cyclohexanol and cyclohexane at 523 K, and cyclohexane and a considerable amount of methanol at temperatures exceeding 573 K.<sup>176</sup> Although different products are obtained for the two different metals, substrate hydrogenation and loss of aromaticity rather than hydrodeoxygenation is observed for both. Similarly, Zhao et al. recently showed that a combination of Pd/C (or Pt/C, Ru/C, or Rh/C) and a mineral acid could completely convert phenolic bio-oil components (phenols, guaiacols, and syringols) to cycloalkanes and methanol, that is, full hydrogenation and deoxygenation was achieved.<sup>175</sup> No direct hydrogenolysis of phenol to benzene was observed. This result is in stark contrast with sulfided Co–Mo catalysts, which mainly yield benzene with little formation of cyclohexane from phenol. Guaiacol and syringol substrates showed fast ring hydrogenation before removing oxygen functional groups to form cycloalkanes with high selectivity.

De Wild et al. recently reported on the hydrotreatment of a pyrolytic lignin oil fraction obtained from Alcell lignin using a Ru/C hydrogenation catalyst. Full reduction of the aromatic compounds was observed; cycloalkanes, alkyl-substituted cyclohexanols, cyclohexanol, and linear alkenes were identified as the major products. This fast and full hydrogenation led to the conclusion that Ru/C is too active a catalyst for the desired conversion of the pyrolytic lignin oil to low molecular weight phenolics.<sup>179</sup>

A two-step process for the selective degradation of actual wood lignin over noble-metal catalysts has also been communicated. In a first step, catalytic cleavage of the C–O–C bonds (without disrupting the C–C linkages) in white birch wood lignin was achieved using a series of active carbon supported catalysts, that is, Ru/C, Pd/C, Rh/C, and Pt/C, under modest H<sub>2</sub> pressures and using acidified, near-critical water as the solvent. The Pt/C catalyst gave the best results, and four monomers, namely, guaiacylpropane, syringylpropane, guaiacylpropanol, and syringylpropanol, were identified as the main constituents of the product stream. Combined total yields of monomer and dimer products reached about 45 (close to the calculated theoretical maximum) and 12 wt %, respectively. In a second step, the products could be further hydrogenated over Pd/C with excellent yields to the corresponding fully saturated hydrocarbons for eventual application in transportation fuel production.<sup>59</sup>

In an alternative approach, Filley et al. reported the reductive deoxygenation of guaiacol (as well as catechol) in the presence of the cheap reductant  $\alpha$ -terpinene catalyzed by vanadium on alumina at atmospheric pressure. Phenol and methyl-substituted phenols were obtained in high yields and with excellent selectivity.<sup>180</sup> Nickel boride was also communicated as an effective catalyst for the preparation of 4-ethylguaiacol and 4-ethylsyringol from various wood meals at 453 K and 13 MPa H<sub>2</sub> in basic medium.<sup>181</sup> The nickel boride catalyst was generated within the wood structure by impregnating the wood with a nickel salt, followed by reaction with sodium borohydride. Yields of phenolics of up to 69% showed that this catalyst system might provide an easy to prepare, nonpyrophoric, and cheaper alternative to noble metal catalysts such as rhodium or palladium. In a somewhat similar approach, Oasmaa and Johansson impregnated kraft pine lignin with an aqueous solution of ammonium heptamolybdate and hydrotreated after drying at 8 MPa H<sub>2</sub> and 723 K, with or without additives such as sodium hydroxide or carbon disulfide. High yields (61% of the original lignin) of low molecular weight oils were obtained, consisting mainly of phenols, benzenes, naphthalenes, and cyclohexanes. The catalyst remained in the solid residue and was easily separated.<sup>182</sup>

As mentioned above, dihydrobenzofuran is studied as a model compound for some of the cyclic ether structures that can be found in lignin. A Cu-doped Mg–Al mixed metal oxide was found to transfer H<sub>2</sub> equivalents from methanol to dihydrobenzofuran under supercritical conditions leading first to hydrogenolysis of the ether bond and subsequently to hydrogenation of the aromatic ring, resulting in the formation 2-ethylcyclohexanol. Significant amounts of methylethylcyclohexanols were also found in the product mixture. Methanol served as a relatively inexpensive source of in situ production of H<sub>2</sub> equivalents in this reaction.<sup>57</sup>

Finally, BASF has recently patented the use of supported or unsupported transition-metal carbides, tungsten carbide, in particular, for the hydrogenation of lignin in a single stage process under relatively mild conditions (403–463 K, 7–14 MPa H<sub>2</sub>). The catalyst can cope with both sulfur-rich and sulfur-poor lignin streams to yield mainly a mixture of low molecular weight oligomers, consisting of, for example, dimers and trimers of coniferyl and coumaryl alcohols.<sup>183</sup>

### 6.2.2. Electrocatalysis

For efficient lignin degradation by a hydrogenation process, hydrogenolysis of the ether bonds needs to be much faster than the hydrogenation of the aromatic rings. Some efforts have been aimed at achieving this by electrocatalytic hydrogenation instead of the more classical hydrogenation routes. Chemisorbed hydrogen, generated in situ on the electrocatalyst surface by water electrolysis, reacts with the adsorbed organic substrate, bypassing the kinetic barrier related to low solubility of hydrogen and to its dissociative adsorption. The reactions can be carried out at relatively low pressures and temperatures with possibly fewer or no side reactions. Electrocatalytic hydrogenation is, therefore, expected to be more selective than catalytic hydrogenation.<sup>184</sup> Competing hydrogen evolution can, however, significantly hamper hydrogenation activity. A summary of electrocatalytic lignin hydrogenation reactions is given in Table 5. Mahdavi et al. evaluated the potential of electrocatalytic hydrogenation by studying some model compounds in aqueous ethanol, using Raney-Ni electrodes. Highly selective



**Table 5. Electrocatalytic Systems for the Hydrogenation of Lignin Model Compound**

entry	electrocatalyst/ electrode	solution	<i>T</i> (K)	<i>I</i> (mA)	<i>Q</i> <sup>a</sup> (F mol <sup>-1</sup> )	substrate	products	conversion (%)	ref
1	Raney Ni	EtOH-H <sub>2</sub> O/NaCl	323	20	2	α-O-4 dimer	<i>b</i>	70–100	184
2	Pd/C, Pd/Al <sub>2</sub> O <sub>3</sub>	1 M NaOH	323	5	6	4-O-5 dimer	phenol, 4-phenyloxyphenol	<i>b</i>	185
3	Raney Ni	1 M NaOH	323	5	6	4-O-5 dimer	phenol, cyclohexanol	<i>b</i>	185
4	Raney Ni	1 M NaOH	323	5–20	18	β-O-4 dimer	guaiacol, α-methylvanillin, 4-ethylphenol, acetovanillone	100	186

<sup>a</sup> Charge corresponding to the number of moles of electrons per mole of substrate. <sup>b</sup> Not specified.

**Table 6. Homogeneous Catalytic Systems for the Hydrogenation of Lignin (Model Compounds)**

entry	catalyst	reaction conditions			substrate	products	conversion (%)	notes	ref
		<i>T</i> (K)	<i>P</i> (MPa)	<i>t</i> (min)					
1	(1,5-hexadiene)RhCl dimer <sup>d</sup>	<i>g</i>	0.1	<i>h</i>	phenol	cyclohexanol	<i>h</i>		190
2	colloidal rhodium	<i>g</i>	5	<i>h</i>	methylanisole	methylcyclohexane, 1-methyl-2-methoxycyclohexane, <sup><i>i</i></sup> methylcyclohexanone	100		191
3	[(1,5-C <sub>6</sub> H <sub>10</sub> )RhCl] <sub>2</sub> <sup>b</sup>	<i>g</i>	0.1	3000	propylphenol	<i>cis</i> -4-propylcyclohexanol, <i>trans</i> -4-propylcyclohexanol, 4-propylcyclohexanone	100		192
4	[(1,5-C <sub>6</sub> H <sub>10</sub> )RhCl] <sub>2</sub> <sup>b</sup>	<i>g</i>	0.1	3000	2-methoxy-4-propylphenol	<i>cis</i> -2-methoxy- <i>cis</i> -4-propylcyclohexanol, <i>cis</i> -2-methoxy- <i>trans</i> -4-propylcyclohexanol	100		192
5	[(1,5-C <sub>6</sub> H <sub>10</sub> )RhCl] <sub>2</sub> <sup>b</sup>	<i>g</i>	1.4	3000	2,6-dimethoxy-4-propylphenol	<i>cis</i> -2,6-methoxy-4-propylcyclohexanol	100		192
6	rhodium nanoparticles <sup>c</sup>	293	0.1	1500	anisole	methoxycyclohexane	100		193
7	rhodium nanoparticles <sup>c</sup>	294	0.2	1500	phenol	cyclohexanol	100		193
8	oxo-trirhodium(III)acetate <sup>d</sup>	313	0.1	<i>h</i>	anthracene	1,2,3,4-tetrahydroanthracene, 1,2,3,4,5,6,7,8-octahydroanthracene	<i>h</i>	<i>j</i>	194
9	[(C <sub>6</sub> H <sub>6</sub> ) <sub>4</sub> Ru <sub>4</sub> H <sub>4</sub> ]Cl <sub>2</sub> <sup>e</sup>	363	6	14	acetophenone	methylcyclohexylketone, phenylethanol, cyclohexylethanol	64		195
10	[(C <sub>6</sub> H <sub>6</sub> ) <sub>4</sub> Ru <sub>4</sub> H <sub>4</sub> ]Cl <sub>2</sub> <sup>e</sup>	363	6	14	anisole	methoxycyclohexane	22		195
11	[(C <sub>6</sub> H <sub>6</sub> ) <sub>4</sub> Ru <sub>4</sub> H <sub>4</sub> ]Cl <sub>2</sub> <sup>e</sup>	363	6	20	methylbenzoate	methylcyclohexanoate	66		195
12	[Ru(C <sub>5</sub> H <sub>5</sub> )Cl(TPPDS) <sub>2</sub> ] <sup>e</sup>	378	9.7	180	toluene	probably methylcyclohexane	65		196
13	rhodium nanoparticles <sup>f</sup>	348	4	600	4-methoxyphenol	4-methoxycyclohexanol, 1-methoxy-4-cyclohexenol	21		197
14	rhodium nanoparticles <sup>f</sup>	348	4	600	4-propylphenol	4-propylcyclohexanol, 4-propylcyclohexanone, 1-propane-4-cyclohexenol	11		197
15	NaBH <sub>4</sub> + I <sub>2</sub>	<i>g</i>	5	<i>h</i>	ethanol organosolv lignin	lower <i>M<sub>w</sub></i> lignin (12% decrease)	<i>h</i>	<i>k</i>	198
16	RuCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub>	<i>g</i>	5	<i>h</i>	ethanol organosolv lignin	lower <i>M<sub>w</sub></i> lignin	<i>h</i>	<i>l</i>	198

<sup>a</sup> With phase transfer catalyst. <sup>b</sup> With Bu<sub>4</sub>NHSO<sub>4</sub> phase transfer agent. <sup>c</sup> Stabilized by surfactant. <sup>d</sup> Active after reduction with H<sub>2</sub>. <sup>e</sup> Biphasic conditions. <sup>f</sup> In ionic liquids. <sup>g</sup> Room temperature. <sup>h</sup> Not specified. <sup>i</sup> Two isomers. <sup>j</sup> Extremely air sensitive. <sup>k</sup> Most completely soluble product. <sup>l</sup> More hydroxyl groups.

cleavage of various model compounds could be achieved by optimizing substrate concentration, current density, and temperature, illustrating the feasibility of the approach.<sup>184</sup> The electrocatalytic hydrogenolysis of 4-phenoxyphenol, a model for the 4-O-5 type linkages found in lignin, was tested using a number of different catalysts. Raney Ni and Pd supported on alumina or carbon showed high efficiencies of electrohydrogenolysis to phenol.<sup>185</sup> Several phenolic lignin model compounds that included β-O-4 linkages were also subjected to electrocatalytic hydrogenation using Raney Ni and Pd-based electrodes. The ether bonds were readily cleaved at room temperature in basic aqueous medium to give a mixture of phenolic compounds.<sup>186</sup> No study on the electrocatalytic hydrogenation of lignin, rather than its models, has been reported to date.

### 6.2.3. Homogeneous Catalysis

Compared with the number of heterogeneous catalysts developed for lignin reduction, relatively few examples of homogeneous catalysts for lignin reduction have been reported. A summary of the homogeneous catalyst systems is given in Table 6. The most relevant studies were conducted by Hu and co-workers, who reported that a di-μ-chloro-bis(η<sup>4</sup>-1,5-hexadiene)-dirhodium(I) complex effectively cata-

lyzed the hydrogenation of the lignin model compounds 4-propylphenol, eugenol, 1,2-dimethoxy-4-propylbenzene, and 2,6-dimethoxy-4-propylphenol at 298 K in a two-phase hexane/aqueous medium.<sup>187</sup> The complex preferentially hydrogenated double bonds followed by aromatic rings and carbonyl groups in the model compounds. Similar results were also obtained with colloidal rhodium complexes in aqueous ethanol.<sup>188</sup>

In contrast to the work of Hu and co-workers, who used lignin model compounds, the focus of other studies of homogeneous hydrogenation catalysts has centered on simple arene compounds, which otherwise lack the ether linkages or the functional groups found in lignin. Since the hydrogenation of aromatic compounds that do not resemble lignin is beyond the scope of this review, only a few recent examples of homogeneous hydrogenation catalysts are given. The following complexes show arene hydrogenation activity but have not yet been analyzed in terms of the ability to disrupt the specific linkages in lignin. The most useful application of these catalysts is for the hydrogenation of highly degraded aromatic hydrocarbons with limited functionalities such as those indicated in Figure 15. A review on soluble transition-metal nanoclusters used for the hydrogenation of arenes was published by Widegren and Finke.<sup>189</sup>

Although a majority of the examples involve simple arenes such as benzene, several references describe the hydrogenation of compounds resembling lignin model compounds. Several examples were provided of the Rh-catalyzed hydrogenation of the aromatic ring of 4-methylanisole,<sup>190</sup> 2-methylanisole,<sup>191</sup> 2,6-dimethoxy-4-propylphenol,<sup>192</sup> or *m*-cresol.<sup>193</sup> The clusters showed high selectivity for the formation of the all-*cis* diastereomers,<sup>189</sup> which could have important implications if these catalysts are employed for the selective hydrogenation of lignin. Advantages of using nanoclusters over heterogeneous catalysts include the relative ease of study because of solubility and lack of support, good activity under mild conditions, and high ligand-modified selectivity.<sup>189</sup> The primary disadvantages include poor thermal stability since the bulk metal is thermodynamically more stable, separation problems commonly associated with homogeneous catalysts, and possible catalyst precipitation, especially with changes in solvent polarity.<sup>189</sup> Lamping and co-workers used  $\mu_3$ -oxotrirhodium acetate to hydrogenate several aromatic compounds such as benzene, toluene, and phenol at 298–353 K in dimethylformamide.<sup>194</sup> The Rh(III) cluster hydrogenated anthracene with a maximum turnover frequency of  $\sim 3.2 \times 10^{-3} \text{ s}^{-1}$  but was extremely air-sensitive; however, the SiO<sub>2</sub>-supported Rh<sub>3</sub>O analogue was stable in air.<sup>194</sup> Plasseraud reported the hydrogenation of several benzene derivatives using  $[(\eta^6\text{-C}_6\text{H}_6)_4\text{Ru}_4\text{H}_6]\text{Cl}_2$  clusters at 363 K and 6 MPa H<sub>2</sub>.<sup>195</sup> Although these clusters hydrogenated toluene with a maximum turnover frequency of  $6.9 \times 10^{-2} \text{ s}^{-1}$ , they were considerably less effective for functionalized aromatics, such as those found in the lignin polymer. Reduced activity, for example, was obtained for anisole hydrogenation (turnover frequency of  $4.6 \times 10^{-3} \text{ s}^{-1}$ ) and reduced selectivity if other reducible functionality exists on the arene.<sup>195</sup> Suárez and co-workers reported the hydrogenation of toluene, benzene, and *m*-xylene using  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{TPPDS})_2]$  where TPPDS =  $\text{P}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4\text{SO}_3^-)_2$  at 378 K and 9.65 MPa H<sub>2</sub><sup>196</sup> in a biphasic *n*-heptane/water medium. In this experiment, the complex was dissolved in the water phase, which could be reused several times with little loss in activity.<sup>196</sup> Zhao and co-workers described the use of Rh nanoparticles dispersed in an ionic-liquid-like copolymer, poly[(*N*-vinyl-2-pyrrolidone)-*co*-(1-vinyl-3-butylimidazolium chloride)] for the hydrogenation of several aromatic compounds.<sup>197</sup> The products were readily separated from the reaction medium without contamination of the catalyst.<sup>197</sup> Recently, in their efforts to produce ethanol and other high value chemicals from lignin, Nagy and co-workers demonstrated the use of the common hydrogenation catalyst Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub> for the hydrogenation of organosolv lignin.<sup>198</sup> This catalyst, along with Raney Ni, Pt/C, and NaBH<sub>4</sub>/I<sub>2</sub>, could cleave 4-O-5 and aryl-O-aliphatic linkages to yield products with decreased oxygen functionality.<sup>198</sup>

### 6.3. Lignin Oxidation

Whereas reductive reactions tend to disrupt and remove functionality in lignin to produce simpler phenols, oxidation reactions tend to form more complex aromatic compounds with additional functionality. Many of these chemicals either serve as platform chemicals used for subsequent organic synthesis, or they serve as target fine chemicals themselves. The catalytic processes involved in the oxidation of lignin, including their historical development in the paper pulping industry, are considered below.

#### 6.3.1. Heterogeneous Catalysis

Heterogeneous oxidative catalysts have played an important role in the pulp and paper industry as a means to remove lignin and other compounds from wood pulps in order to increase the quality of the final paper product. Table 7 lists a summary of lignin heterogeneous oxidation catalysts, reaction conditions, and results. The first examples include photocatalytic oxidation catalysts, which were designed to remove lignin from paper industry wastewater streams. The most common catalysts involve TiO<sub>2</sub><sup>199</sup> or supported precious metals, such as Pt/TiO<sub>2</sub>,<sup>200</sup> which were found to efficiently degrade lignin using ultraviolet light. The addition of small quantities of Fe<sup>2+</sup> provided an increase in lignin photooxidation efficiency using TiO<sub>2</sub> catalysts.<sup>201</sup> The use of UV light was necessary to displace the valence-band electrons in the TiO<sub>2</sub>, which was necessary to initiate the oxidation.<sup>199</sup> Other examples include Ni/MgO catalysts used in the gasification of lignin to H<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub>,<sup>116</sup> or methylrhodium trioxide catalysts immobilized on poly(4-vinyl pyridine) or polystyrene.<sup>202</sup> The latter catalyst was found to oxidize phenolic, nonphenolic, monomeric, and dimeric lignin model compounds in addition to sugar cane lignin and red spruce kraft lignin for treatment of kraft pulp.<sup>202,203</sup> Vanillyl and veratryl alcohol were oxidized to the acids, aldehydes, and quinones in up to 49% yield with the balance forming polymeric products.<sup>202,203</sup> Herrmann and co-workers also applied methylrhodium trioxide in the presence of H<sub>2</sub>O<sub>2</sub> for the oxidation of isoeugenol (Figure 13, **121**) and *trans*-ferulic acid (Figure 13, **115**) to produce vanillin.<sup>204</sup> The catalyst was found to cleave the C–C double bond to yield either the aldehyde or the acid depending on the reaction conditions. The catalyst was found to deactivate through the formation of a perhenate species after 1000 to 2000 cycles, but a one-pot method to reactivate the catalyst was described.<sup>205</sup> Sales and co-workers recently investigated the applicability of Pd/Al<sub>2</sub>O<sub>3</sub> catalysts for the oxidative conversion of alkaline lignin extracted from sugar cane bagasse in both batch slurry and continuous fluidized-bed reactors.<sup>206</sup> Approximately 0.56 g of vanillin and 0.50 g of syringaldehyde were obtained from 30 g of lignin at 393 K after 2 h.<sup>189</sup> Bhargava and co-workers described the catalytic wet oxidation of ferulic acid using single-metal (Cu), bimetal (Cu–Ni, Cu–Co, and Cu–Mn), and multimetal (Cu–Ni–Ce) alumina-supported catalysts, Cu and Cu–Mn kaolin-supported catalysts, and multimetal oxide (Cu–Co–Mn and Cu–Fe–Mn) catalysts.<sup>207</sup> Cu–Ni–Ce/Al<sub>2</sub>O<sub>3</sub> catalysts were most active but were susceptible to catalyst leaching.<sup>207</sup> Cu–Mn/Al<sub>2</sub>O<sub>3</sub> was the most stable and was second to Cu–Ni–Ce/Al<sub>2</sub>O<sub>3</sub> in terms of activity of the nine catalysts studied.<sup>207</sup> Citing the desire to replace “toxic” metal ions (i.e., Sr, Ce, Co, and Mn) in perovskite-type oxides with “nontoxic” iron to avoid environmental pollution, Zhang and co-workers recently reported the use of the perovskite-type oxide LaFe<sub>1-x</sub>Cu<sub>x</sub>O<sub>3</sub> ( $x = 0, 0.1, 0.2$ ) for the wet aerobic oxidation of lignin.<sup>208</sup> Improvements in aromatic aldehyde yields and conversion were reported, and the catalyst was stable after a series of successive recycling.<sup>208</sup>

#### 6.3.2. Electrocatalysis

Several electrochemical studies have been conducted relating to the decomposition of lignin on various electrodes. Pardini and co-workers studied the anodic oxidation of lignin model compounds in methanol and observed the cleavage

**Table 7. Heterogeneous Catalytic Systems for the Oxidation of Lignin (Model Compounds)**

entry	catalyst	oxidant	solvent	reaction conditions			lignin/model compound	products	yield (%)	conversion (%)	notes	ref
				<i>T</i> (K)	<i>P</i> (MPa)	<i>t</i> (h)						
1	TiO <sub>2</sub>	<i>a</i>	H <sub>2</sub> O	293	<i>a</i>	6	alkali lignin	<i>a</i>	<i>a</i>		<i>e</i>	199
2	TiO <sub>2</sub>	<i>a</i>	H <sub>2</sub> O	293	<i>a</i>	6	humic acid	<i>a</i>	<i>a</i>		<i>e</i>	199
3	TiO <sub>2</sub>	<i>a</i>	H <sub>2</sub> O	<i>a</i>	<i>a</i>	1	Aldrich commercial lignin powder	<i>a</i>	<i>a</i>			200
4	Pt/TiO <sub>2</sub>	<i>a</i>	H <sub>2</sub> O	<i>a</i>	<i>a</i>	1	Aldrich commercial lignin powder	<i>a</i>	<i>a</i>			200
5	Fe <sup>2+</sup> /TiO <sub>2</sub>	<i>a</i>	H <sub>2</sub> O	293	<i>a</i>	0.25	Aldrich synthetic lignin	<i>a</i>	<i>a</i>		<i>e</i>	201
6	Pd/Al <sub>2</sub> O <sub>3</sub>	O <sub>2</sub>	NaOH/H <sub>2</sub> O <sup>b</sup>	373–413	0.2–1	2.5	alkaline lignin from sugar bagasse	vanillin	<i>a</i>			206
7	Ni/MgO	<i>a</i>	H <sub>2</sub> O <sup>c</sup>	673	<i>a</i>	2	organosolv lignin	syringaldehyde	<i>a</i>			116
								<i>p</i> -hydroxybenzaldehyde	<i>a</i>			
								carbon gases	45.4			
								hydrogen	99.2			
8	CH <sub>3</sub> ReO <sub>3</sub>	H <sub>2</sub> O <sub>2</sub>	CH <sub>3</sub> COOH	<i>d</i>	<i>a</i>	<i>a</i>	hydrolytic sugar cane ligin	THF insolubles	74.0			202, 203
								aliphatic OH	0.921			
								syringol OH	0.29			
								guaiacyl OH	0.354			
9	CH <sub>3</sub> ReO <sub>3</sub>	H <sub>2</sub> O <sub>2</sub>	CH <sub>3</sub> COOH	<i>d</i>	<i>a</i>	<i>a</i>	red spruce kraft lignin	<i>p</i> -hydroxy phenyl OH	0.548			202, 203
								COOH	1.26			
								aliphatic OH	0.904			
								syringol OH	0.984			
10	CH <sub>3</sub> ReO <sub>3</sub>	H <sub>2</sub> O <sub>2</sub>	CH <sub>3</sub> COOH	<i>d</i>	<i>a</i>	<i>a</i>	hardwood organosolvent lignin	guaiacyl OH	0.606			202, 203
								<i>p</i> -hydroxy phenyl OH				
								COOH	0.535			
								aliphatic OH	0.528			
11	CH <sub>3</sub> ReO <sub>3</sub>	H <sub>2</sub> O <sub>2</sub>	CH <sub>3</sub> COOH	<i>d</i>	<i>a</i>	<i>a</i>	vanillyl alcohol	syringol OH	0.289			202, 203
								guaiacyl OH	0.173			
								<i>p</i> -hydroxy phenyl OH				
								COOH	1.504			
12	CH <sub>3</sub> ReO <sub>3</sub>	H <sub>2</sub> O <sub>2</sub>	CH <sub>3</sub> COOH	<i>d</i>	<i>a</i>	<i>a</i>	veratryl alcohol	see schemes <sup>f</sup>				202, 203
13	CH <sub>3</sub> ReO <sub>3</sub>	H <sub>2</sub> O <sub>2</sub>	CH <sub>3</sub> COOH	<i>d</i>	<i>a</i>	<i>a</i>	$\beta$ -O-4 model compounds	see schemes <sup>f</sup>				202, 203
14	CH <sub>3</sub> ReO <sub>3</sub>	H <sub>2</sub> O <sub>2</sub>	CH <sub>3</sub> COOH	<i>d</i>	<i>a</i>	<i>a</i>	$\alpha$ -1 model compounds	see schemes <sup>f</sup>				202, 203
15	CH <sub>3</sub> ReO <sub>3</sub>	H <sub>2</sub> O <sub>2</sub>	<i>tert</i> -butanol	333	<i>a</i>	10	isoeugenol/trans-ferulic acid	vanillin		100		204
16	Cu–Ni–Ce/Al <sub>2</sub> O <sub>3</sub>	O <sub>2</sub>	H <sub>2</sub> O	373	0.173 (O <sub>2</sub> )	2	ferulic acid	degraded products	<i>a</i>			207
17	Cu–Mn/Al <sub>2</sub> O <sub>3</sub>	O <sub>2</sub>	H <sub>2</sub> O	373	0.173 (O <sub>2</sub> )	2	ferulic acid	degraded products	<i>a</i>			207
18	LaFe <sub>1-x</sub> Cu <sub>x</sub> O <sub>3</sub> ( <i>x</i> = 0,0.1,0.2)	O <sub>2</sub>	NaOH/H <sub>2</sub> O <sup>b</sup>	373	0.2 (O <sub>2</sub> )	3	enzymatic hydrolysis of steam-explosion cornstalks	<i>p</i> -hydroxybenzaldehyde			10–20	208
									vanillaldehyde		10–20	
									syringaldehyde		10–20	

<sup>a</sup> Not specified. <sup>b</sup> 2 mol/L. <sup>c</sup> Supercritical. <sup>d</sup> Room temperature. <sup>e</sup> UV light, 360 nm. <sup>f</sup> Too many products to concisely summarize. See schemes or refer to original work.

of the C<sub>α</sub>–C<sub>β</sub> bond through the formation of radical cations.<sup>209</sup> In this study, it was shown that oxidation peak potentials as determined by cyclic voltametry are influenced by substrate structure but not solution pH.<sup>192</sup> Parpot and co-workers investigated the electrochemical oxidative degradation of kraft lignin in batch and flow cells on Pt, Au, Ni, Cu, DSA–O<sub>2</sub>, and PbO<sub>2</sub> anodes.<sup>210</sup> Vanillin was produced from the lignin but required continuous extraction to prevent its further oxidation.<sup>210</sup> El-Ashtouky and co-workers performed the electrochemical decolorization of wastewater effluent stream using a lead sheet anode, although the products formed during the treatment were not determined.<sup>211</sup>

### 6.3.3. Homogeneous Catalysis

The oxidation of lignin by homogeneous catalysts represents one of the most promising approaches toward the production of fine chemicals from lignin and lignin pulp streams. Several homogeneous catalysts that are capable of performing selective oxidation of lignin have been reported in the literature. Homogeneous catalysts offer several advantageous properties that make them particularly suitable for lignin oxidation, especially the ability to use a wide range of ligands, the electronic and steric properties of which drastically influence the activity, stability, and solubility of the catalyst. It thus becomes possible to tune the reactivity and selectivity of the homogeneous catalyst to the oxidation of specific lignin linkages or functionalities with appropriate

choice of ligands. Given the complicated structure and wide distribution of linkages in lignin, the ability to tune a homogeneous catalyst to form robust catalysts, as demonstrated effectively by Collins in the development of iron tetraamido macrocyclic ligand (TAML) complexes,<sup>212</sup> that specifically disrupt targeted linkages or perform oxidations of specific functionalities while leaving other groups intact is important for the rational valorization of lignin to high-value products.

Generally, the homogeneous catalysts used for lignin oxidation can be subdivided into six categories depending on the ligand set employed. The first category, which consists of the metalloporphyrins, involves catalysts formed from the metalation of the porphyrin with transition metal salts.<sup>213</sup> As discussed below, the porphyrin provides several opportunities to attach functional groups, such as halogens or sulfonate groups, to alter the electronic characteristics of the catalyst, which in turn enhances the stability and solubility of the catalyst. The second group involves Schiff-base catalysts, especially Co(salen), which are typically simpler structurally and synthetically than the porphyrin ligands and have displayed activity in alcohol oxidation. The third group involves complex and often highly developed nonporphyrinic or Schiff-base catalysts, such as the extremely robust iron tetraamido macrocyclic ligand (TAML), manganese 1,4,7-trimethyl-1,4,7-triazacyclononane (TACN), or manganese 1,2-bis-(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethane (DTNE)



complexes, which were historically used extensively as wood pulp bleaching catalysts. The fourth category includes polyoxometalates, which involve polyatomic clusters of early transition metal oxy anions and were also originally used as wood pulp bleaching catalysts. The fifth category involves simple metal salts. The sixth category involves miscellaneous catalysts that employ various ligand systems.

**6.3.3.1. Biomimetic Catalysts.** The development of several homogeneous catalysts used for lignin transformation and degradation was inspired by examples of efficient catalyst systems capable of such transformations already found in Nature. Indeed, the motivation for using several metalloporphyrin complexes originated from the desire to mimic the activity of the heme cofactor found at the active sites of the enzymes lignin peroxidase or manganese-dependent peroxidase, which are found in white rot fungi.<sup>214,215</sup> The fungi are involved in lignin biodegradation (rotting) and are capable of breaking down this highly recalcitrant material completely into carbon dioxide and water. The enzymes involved are known to preferentially degrade lignin from wood over cellulose and other polysaccharides, which is of considerable interest to the paper pulping industry as indicated above.<sup>216</sup> The study of iron and manganese porphyrin lignin oxidation catalysts originated in an effort to better understand the mechanism by which these enzymes degraded lignin,<sup>216</sup> and several investigators noted that iron porphyrin catalysts were able to cleave the  $C_{\alpha}-C_{\beta}$  bond and oxidize lignin model compounds in analogy to ligninase enzymes.<sup>217,218</sup> In fact, in many catalytic cycles involving Fe porphyrin catalysts, the formation of a highly reactive oxo-iron(IV) porphyrin  $\pi$ -cation radical is invoked, similar to the species also observed in the catalytic cycle of the enzymatic reactions.<sup>219,220</sup> It should be noted, however, that the inaccessibility of the enzyme active site for the large lignin substrate precludes direct interaction with the high-valent oxidant, and enzymatic reactions most likely initially proceed by generating freely diffusing strong-oxidant mediators that attack lignin, such as the veratryl alcohol radical cation or Mn(III).<sup>221</sup> Nevertheless, the structural similarities between the active site of the enzyme and metalloporphyrin complexes prompted the search for biomimetic metal porphyrin catalysts capable of selectively degrading lignin.<sup>222,223</sup>

**6.3.3.1.1. Metalloporphyrin Catalysts.** Metalloporphyrin complexes are well-known to engage in selective oxidations of hydrocarbons such as alkene oxidation to form epoxides<sup>220,224</sup> or alkanes to form aldehydes or alcohols.<sup>225</sup> In addition to iron-containing porphyrins that resemble the heme group found in several enzymes,<sup>223</sup> such as cytochrome P-450,<sup>225,226</sup> metalloporphyrins of the transition metals Mn, Ru,<sup>227</sup> and Co<sup>227,228</sup> have found use as oxidation catalysts to form valuable products from hydrocarbon feed stocks. Similarly, the use of metal porphyrin complexes as selective oxidation catalysts is becoming increasingly important for the conversion of lignin to valuable products.<sup>225</sup> Early studies in the subject focused on the ability of the metal porphyrin complex to act as a bleaching agent for pulp mill decolorization and pollutant removal.<sup>229</sup> That is, the value of the catalyst was judged on the ability to remove lignin from the stream without regard to the products formed from the lignin reaction. For example, Paszczynski et al. extended the use of the various transition metal porphyrins that were found active in disrupting the bonds typically found in lignin<sup>217,218</sup> to wood chips.<sup>216</sup> They noted that the complex successfully bleached kraft lignin but gave no indication of the products

formed as a result of the oxidation.<sup>216</sup> Because of its structure and properties, the presence of lignin in a cellulose stream inhibits the degradation of cellulose;<sup>69</sup> thus, the degradation and removal of lignin from the carbohydrate component of wood is a critical step in the pulp and paper industry.<sup>60</sup> However, as described above, lignin constitutes a significant fraction of biomass,<sup>230</sup> and the potential to convert it to useful chemicals, such as vanillin or other aromatic compounds,<sup>231</sup> has motivated recent efforts to develop metalloporphyrin catalysts that perform selective oxidation of lignin beyond its simple removal from paper pulps.

Several metal porphyrin catalysts were found to be capable of performing the oxidation of lignin and lignin model compounds.<sup>225</sup> Crestini and Tagliatesta provide an extensive review on the oxidation of lignin and lignin model compounds using metalloporphyrin complexes.<sup>232</sup> A summary of the metalloporphyrin-catalyzed reactions is given in Table 8. Structures of several porphyrin- and phthalocyanine-based catalysts are depicted in Figure 17. Table 9 lists the oxidation of the lignin model compound veratryl alcohol to veratryl aldehyde, depicted in Scheme 11, using metal porphyrin complexes as a catalyst.

Relatively high conversions were obtained at elevated temperatures with Co porphyrin and  $O_2$ , corresponding to approximately 26 catalyst turnovers (entry 1) and at room temperature with Fe (entries 2–6) and Mn complexes (entry 7) and  $H_2O_2$ . High conversions of veratryl alcohol were also observed with both free and ion-exchange resin-immobilized Fe(TPPS) (entries 8–13) and Mn(TPPS) (entries 14–18) complexes, achieving 67% veratryl alcohol conversion ( $\sim 25$  catalyst turnovers) using  $KHSO_5$  as an oxidant after 1 min.<sup>233</sup> In addition to veratryl alcohol, porphyrin catalysts were also found to be capable of oxidizing other lignin model compounds. Shimada and co-workers used a tetraphenylporphyrinatoiron(III) chloride complex in the presence of *tert*-butylhydroperoxide to perform the C–C bond cleavage of the model compound 1,2-diarylpropene-1,3-diol at 293 K.<sup>218</sup> The principle products of the oxidation included 3-methoxy-4-ethoxybenzaldehyde (54% yield on the oxidant), and formaldehyde (see Scheme 12).<sup>218</sup>

Zhu and Ford described the oxidation of lignin model compounds using iron(III) and manganese(III) meso-tetraphenylporphyrin and phthalocyanine complexes.<sup>234</sup> Artaud and co-workers described the oxidation of  $\alpha,\beta$ -diarylpropane lignin dimer model compounds using an iron porphyrin catalyst.<sup>235</sup> The metal porphyrin was found to oxidize the  $\alpha,\beta$ -diarylpropane through four primary reactions including  $C_{\alpha}-C_{\beta}$  propyl side chain cleavage, phenyl- $C_{\alpha}$  bond cleavage, oxidation of the dimethoxyaryl nucleus to form quinone, and opening of the dimethoxyaryl ring to form a muconic acid dimethyl ester.<sup>235</sup>

Several catalysts that resemble porphyrins were also active for lignin oxidation. Robinson and co-workers reported the activity of trisodium tetra-4-sulfonatophthalocyanineiron(III), the ligand of which is closely related to the naturally occurring porphyrin structure, for the oxidation of several simple lignin model compounds (see Scheme 13).<sup>236</sup> The catalyst oxidized the benzylic hydroxyl groups in 2-hydroxyethyl apocynol; however, the extent of oxidation did not increase upon addition of oxygen because of increased complex degradation.<sup>236</sup>

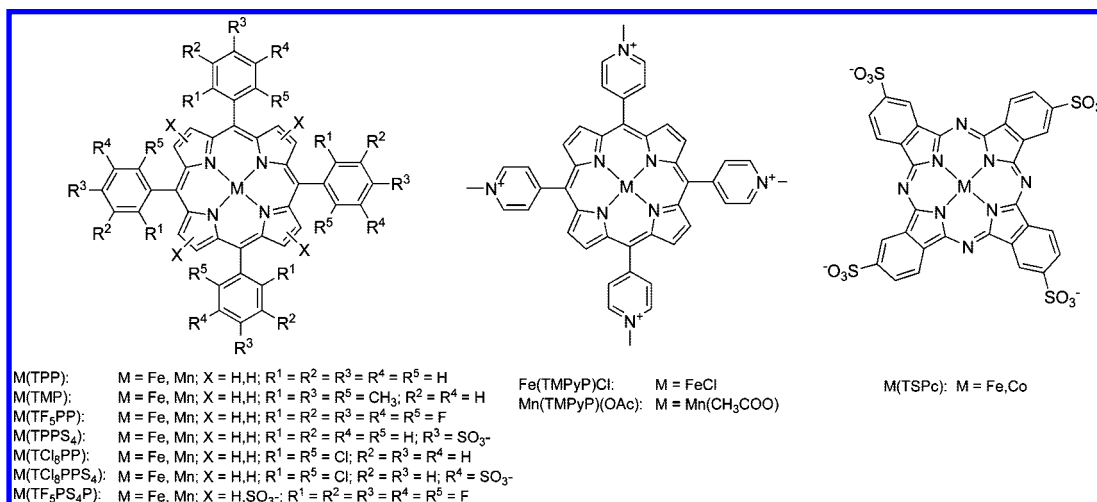
A significant disadvantage of using the porphyrin complexes is the susceptibility to degradation in the presence of excess oxidant, particularly  $H_2O_2$ , or through the formation



Table 8. Metalloporphyrin Catalytic Systems for the Oxidation of Lignin (Model Compounds)

entry	catalyst	oxidant	solvent	reaction conditions			lignin/model compound	products	yield (%)	conversion (%)	notes	ref
				T (K)	P (MPa)	t (h)						
1	Mn(TSPc)Cl	<i>a</i>	<i>c</i>	rt	<i>h</i>	1	veratryl alcohol	veratraldehyde	29		<i>k</i>	229
2	Mn(TSPc)Cl	<i>t</i> -BuOOH	<i>c</i>	rt	<i>h</i>	1	veratryl alcohol	veratraldehyde		16	<i>k</i>	229
3	Mn(TSPc)Cl	H <sub>2</sub> O <sub>2</sub>	<i>c</i>	rt	<i>h</i>	1	veratryl alcohol	veratraldehyde		10	<i>k</i>	229
4	Mn(TSPc)Cl	NaClO	<i>c</i>	rt	<i>h</i>	1	veratryl alcohol	veratraldehyde		6	<i>k</i>	229
5	Mn(TSPc)Cl	PhIO	<i>c</i>	rt	<i>h</i>	1	veratryl alcohol	veratraldehyde		9	<i>k</i>	229
6	Mn(TSPc)Cl	KHSO <sub>5</sub>	<i>c</i>	rt	<i>h</i>	1	veratryl alcohol	veratraldehyde		2	<i>k</i>	229
7	Fe(TSPc)Cl	<i>a</i>	<i>c</i>	rt	<i>h</i>	1	veratryl alcohol	veratraldehyde		16	<i>k</i>	229
8	Fe(TSPc)Cl	<i>t</i> -BuOOH	<i>c</i>	rt	<i>h</i>	1	veratryl alcohol	veratraldehyde		3	<i>k</i>	229
9	Fe(TSPc)Cl	H <sub>2</sub> O <sub>2</sub>	<i>c</i>	rt	<i>h</i>	1	veratryl alcohol	veratraldehyde		1	<i>k</i>	229
10	Fe(TSPc)Cl	NaClO	<i>c</i>	rt	<i>h</i>	1	veratryl alcohol	veratraldehyde		1	<i>k</i>	229
11	Fe(TSPc)Cl	PhIO	<i>c</i>	rt	<i>h</i>	1	veratryl alcohol	veratraldehyde		4	<i>k</i>	229
12	Fe(TSPc)Cl	KHSO <sub>5</sub>	<i>c</i>	rt	<i>h</i>	1	veratryl alcohol	veratraldehyde	<i>i</i>		<i>k</i>	229
13	Mn(TSPc)Cl <sub>2</sub>		<i>c</i>	rt	<i>h</i>	1	$\beta$ -O-4 model compounds	see Scheme			<i>k</i>	229
14	Mn(TSPc)Cl <sub>2</sub>		<i>c</i>	rt	<i>h</i>	1	$\beta$ -1 model compounds	see Scheme			<i>k</i>	229
15	Fe(TSPc)Cl	<i>t</i> -BuOOH	H <sub>2</sub> O <sup>d</sup>	reflux	<i>h</i>	24	kraft softwood pulp	<i>h</i>			<i>l</i>	216
16	Fe(TF5PP)Cl	<i>t</i> -BuOOH	H <sub>2</sub> O <sup>d</sup>	reflux	<i>h</i>	24	birch wood chips	<i>h</i>			<i>m</i>	216
17	Fe(TPP)Cl	<i>t</i> -BuOOH	CH <sub>2</sub> Cl <sub>2</sub>	rt	<i>h</i>	48	$\beta$ -1 model compounds	see Scheme				218
18	CoTSPc	O <sub>2</sub>	<i>e</i>	358	0.1 (O <sub>2</sub> )	12	veratryl alcohol	veratraldehyde		100		234
19	CoTSPc	O <sub>2</sub>	H <sub>2</sub> O	358	0.1 (O <sub>2</sub> )	5	4-hydroxy-3-methoxytoluene	2,2'-dihydroxy-3,3'-dimethoxy-5,5'-dimethylbiphenyl		100		234
20	CoTSPc	O <sub>2</sub>	H <sub>2</sub> O	358	0.1 (O <sub>2</sub> )	5	3,4-dimethoxytoluene	none		0		234
21	FeTSPc	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O	343	<i>h</i>	1	veratryl alcohol	veratraldehyde	11			234
22	Fe(TF5PP)Cl	H <sub>2</sub> O <sub>2</sub>	CH <sub>3</sub> CN/CH <sub>2</sub> Cl <sub>2</sub>	rt	<i>h</i>	<i>h</i>	$\beta$ -1 model compounds	quinones	12			235
23	Fe(TF <sub>3</sub> PS <sub>4</sub> P)Cl	<i>b</i>	H <sub>2</sub> O	rt	<i>h</i>	<i>h</i>	1,2-dimethoxyarenes	aldehydes (see Scheme)				235
24	Fe(TSPc)Cl	NaOH/H <sub>2</sub> O <sup>f</sup>		408	0.1 (N <sub>2</sub> )	2	2-hydroxyethyl apocynol	acetovanillone (25%)	25			236
25	Fe(TSPc)Cl	NaOH/H <sub>2</sub> O <sup>f</sup>		408	0.1 (N <sub>2</sub> )	2	veratrylglycol- $\beta$ -guaiacyl ether	2-methoxyphenol	26			236
26	Rh(TSPP)	NaOH/H <sub>2</sub> O <sup>f</sup>		408	0.1 (N <sub>2</sub> )	2	veratrylglycol- $\beta$ -guaiacyl ether	3,4-dimethoxyacetophenone	6			236
27	Fe(TF <sub>3</sub> PP)Cl	H <sub>2</sub> O <sub>2</sub>	<i>g</i>	298	<i>h</i>	3	veratryl alcohol	acetovanillone	7			236
28	Fe(TF <sub>3</sub> PP)Cl	H <sub>2</sub> O <sub>2</sub>	<i>g</i>	298	<i>h</i>	3	veratrylaldehyde	2-methoxyphenol	28			236
29	Fe(TF <sub>3</sub> PP)Cl	H <sub>2</sub> O <sub>2</sub>	<i>g</i>	298	<i>h</i>	3	veratric acid	3,4-dimethoxyacetophenone	6			236
30	Fe(TF <sub>3</sub> PP)Cl	H <sub>2</sub> O <sub>2</sub>	<i>g</i>	298	<i>h</i>	3	isovanillyl alcohol	acetovanillone	7			236
31	Fe(TF <sub>3</sub> PP)Cl	H <sub>2</sub> O <sub>2</sub>	<i>g</i>	298	<i>h</i>	3	vanillyl alcohol	acetovanillone	7			236
32	Fe(TF <sub>3</sub> PP)Cl	H <sub>2</sub> O <sub>2</sub>	<i>g</i>	298	<i>h</i>	3	1,2,3-trimethoxybenzene	2-methoxyphenol	28			236
33	Fe(TF <sub>3</sub> PP)Cl	H <sub>2</sub> O <sub>2</sub>	<i>g</i>	298	<i>h</i>	3	ferulic acid	3,4-dimethoxyacetophenone	6			236
34	Fe(TF <sub>3</sub> PP)Cl	H <sub>2</sub> O <sub>2</sub>	<i>g</i>	298	<i>h</i>	3	veratrole	acetovanillone	17			236
35	Fe(TF <sub>3</sub> PP)Cl	H <sub>2</sub> O <sub>2</sub>	<i>g</i>	298	<i>h</i>	3	4-methoxybenzyl alcohol	<i>h</i>		~70		241
36	Fe(TF <sub>3</sub> PP)Cl	H <sub>2</sub> O <sub>2</sub>	<i>g</i>	298	<i>h</i>	3	3,4,5-trimethoxybenzyl alcohol	<i>h</i>		~30		241
37	Mn(TSPP)Cl	H <sub>2</sub> O <sub>2</sub>	<i>g</i>	298	<i>h</i>	0.5	veratryl alcohol	veratraldehyde	<i>j</i>	~50		241

<sup>a</sup> 4'-Methoxyacetophenone. <sup>b</sup> Magnesium monoperoxyphthalate. <sup>c</sup> Aqueous phosphate buffer. <sup>d</sup> Deionized. <sup>e</sup> Carbonate/bicarbonate, 0.39 M. <sup>f</sup> 1 mol/L. <sup>g</sup> pH 3 buffer solution. <sup>h</sup> Not specified. <sup>i</sup> Trace. <sup>j</sup> Michaelis–Menten kinetics ( $k_{cat} = 18.6 \pm 0.9$  min,  $K_M = 5.5 \pm 0.9$  mM). <sup>k</sup> pH 10. <sup>l</sup> Kappa number reduced to 1.5. <sup>m</sup> 25.7% loss of lignin.



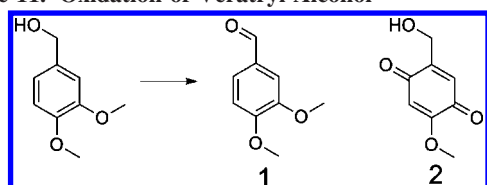
**Figure 17.** Structures and designations of reported porphyrin and phthalocyanine catalysts used for lignin oxidation.

**Table 9. Metal Porphyrin Catalytic Systems for the Oxidation of Veratryl Alcohol to Veratryl Aldehyde**

entry	catalyst	time (min)	temp (K)	oxidant	yield (%)		ref
					1	2	
1	Co(TSPc)	300	358	O <sub>2</sub>	76–78		234
2	Fe(TPPS <sub>4</sub> )-H <sub>2</sub> O	360	<i>a</i>	H <sub>2</sub> O <sub>2</sub>	27	3	242
3	Fe(TPPS <sub>4</sub> )-[BMIM][PF <sub>6</sub> ]	360	<i>a</i>	H <sub>2</sub> O <sub>2</sub>	54	6	242
4	Fe(TPPS <sub>4</sub> )-[BMIM][PF <sub>6</sub> ]-NMI	360	<i>a</i>	H <sub>2</sub> O <sub>2</sub>	69	8	242
5	Fe(TCl <sub>6</sub> PPS <sub>4</sub> )-H <sub>2</sub> O	360	<i>a</i>	H <sub>2</sub> O <sub>2</sub>	71	9	242
6	Fe(TCl <sub>6</sub> PPS <sub>4</sub> )-[BMIM][PF <sub>6</sub> ]	360	<i>a</i>	H <sub>2</sub> O <sub>2</sub>	83	12	242
7	MnTPPS/IPS	120	293	H <sub>2</sub> O <sub>2</sub>	89.7		243
8	Fe(TPPS)	1	<i>a</i>	H <sub>2</sub> O <sub>2</sub>	5		233
9	Fe(TPPS)-imidazole	1	<i>a</i>	H <sub>2</sub> O <sub>2</sub>	7		233
10	Fe(TPPS)	1	<i>a</i>	KHSO <sub>5</sub>	67		233
11	Fe(TPPS)-imidazole	1	<i>a</i>	KHSO <sub>5</sub>	65		233
12	Fe(TPPS)-Ad	1	<i>a</i>	H <sub>2</sub> O <sub>2</sub>	6		233
13	Fe(TPPS)-Ad	1	<i>a</i>	KHSO <sub>5</sub>	50		233
14	Mn(TPPS)	1	<i>a</i>	H <sub>2</sub> O <sub>2</sub>	2		233
15	Mn(TPPS)-imidazole	1	<i>a</i>	H <sub>2</sub> O <sub>2</sub>	7		233
16	Mn(TPPS)-imidazole	1	<i>a</i>	KHSO <sub>5</sub>	67		233
17	Mn(TPPS)-Ad-imidazole	1	<i>a</i>	H <sub>2</sub> O <sub>2</sub>	9		233
18	Mn(TPPS)-Ad-imidazole	1	<i>a</i>	KHSO <sub>5</sub>	61		233

<sup>a</sup> Room temperature.

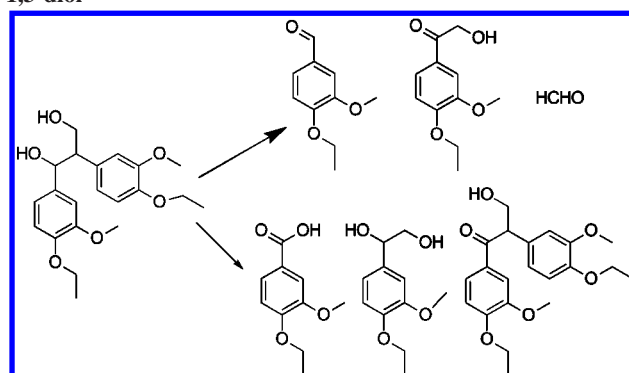
**Scheme 11. Oxidation of Veratryl Alcohol**



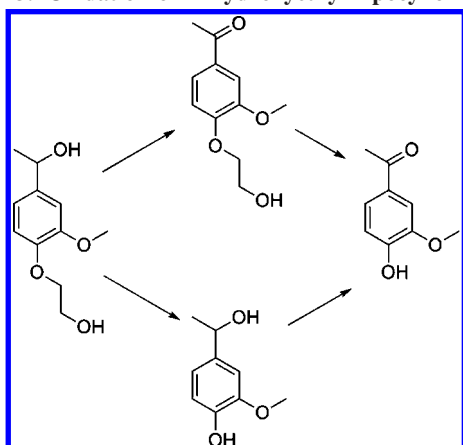
of catalytically inactive  $\mu$ -oxo species.<sup>60</sup> In order to improve the stability, chloro substituents were added to the porphyrin ring to increase the steric bulk and improve the porphyrin resistance to oxidation.<sup>222</sup> In addition, the chlorines on the porphyrins increased the catalyst efficiency by altering the redox potential of the metal center.<sup>222</sup> The favorable results given by the presence of chlorine in the porphyrin periphery prompted the incorporation of other substituents, such as fluoro<sup>226</sup> or sulfonato<sup>219,229</sup> groups, which improved catalytic activity, resistance to oxidation, and solubility. The incorporation of a variety of ring substituents, including both cationic<sup>237</sup> and anionic groups,<sup>238</sup> or axial ligands is possible, making the metalloporphyrin a highly tunable catalyst, especially when coupled with the different properties that arise given the choice of metal center.<sup>60</sup>

Despite the demonstrated efficiency of using metalloporphyrins for lignin oxidation, a large hindrance to the

**Scheme 12. C–C Bond Cleavage of 1,2-Diarylpropene-1,3-diol<sup>218</sup>**



development of metalloporphyrins for industrial scale lignin oxidation to useful chemicals is the expense associated with the complexes, especially given catalyst degradation and loss. In order to address these challenges, recent metalloporphyrin research has transitioned to the development and implementation of immobilization techniques to improve catalyst stability and recyclability. Crestini and co-workers immobilized metalloporphyrins of manganese on smectite clay montmorillonite in order to mimic the polypeptide envelope

Scheme 13. Oxidation of 2-Hydroxyethyl Apocynol<sup>236</sup>

that protects the catalyst center of natural enzymes.<sup>239</sup> The presence of the montmorillonite clay prevents the formation of  $\mu$ -oxo species and allows facile recovery and recycling of the porphyrin catalyst.<sup>239</sup> Similar metalloporphyrin immobilization was demonstrated to occur on a variety of polymers. Naik et al. demonstrated the immobilization of iron and cobalt porphyrin complexes on polystyrene for the oxidation of alcohols, achieving a turnover frequency of  $0.18 \text{ s}^{-1}$  for 1785 total turnovers in the oxidation of benzyl alcohol to benzaldehyde.<sup>240</sup> These results contrast with other previously reported systems, which often exhibit lower rates and turnover numbers ranging between 10 and 100. Zucca and co-workers recently demonstrated the immobilization of Fe(III)-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin on a pyridyl-functionalized poly(vinyl alcohol).<sup>241</sup> The latter complex was demonstrated as an active oxidation catalyst for lignin-type model compounds. Kumar and co-workers also recently demonstrated the immobilization of Fe porphyrins used for the oxidation of the model lignin compound veratryl alcohol in ionic liquids.<sup>242</sup> The metalloporphyrin catalysts in the ionic liquid demonstrated higher catalytic activity when compared with similar complexes in aqueous solutions. Zucca and co-workers recently immobilized a Mn(III)–porphyrin complex to imidazole-bearing silica and similarly used this catalyst to oxidize veratryl alcohol using  $\text{H}_2\text{O}_2$ .<sup>243</sup> These findings have important implications for the further development of lignin oxidation catalysts, especially given the favorable dissolution characteristics of lignin in ionic liquids.

**6.3.3.2. Metallo-salen Catalysts.** Cobalt(salen) complexes, where salen = [*N,N'*-bis(salicylidene)ethane-1,2-diaminato], are emerging as promising lignin oxidation catalysts. Gupta and co-workers reviewed the use of polymer-supported Schiff base complexes, including Co(salen), for lignin model compound oxidations.<sup>244</sup> A summary of metallo-salen-catalyzed lignin oxidation reactions is given in Table 10. The structures of Co(salen) and related complexes are depicted in Figure 18.

The efficiency of Co(salen) to oxidize lignin originates from the ability to form cobalt–superoxo complexes and dimeric peroxo complexes upon exposure to molecular oxygen. These reactive species are effective oxidants, and several studies have indicated the potential use of Co(salen) as a lignin oxidation catalyst. Bozell and co-workers demonstrated that Co(salen) was effective for the oxidation of the phenolic groups of aromatic compounds to form benzoquinones in up to 90% yield in 18 h.<sup>245</sup> Drago and co-workers demonstrated that Co(salen) complexes in the

presence of molecular oxygen rapidly oxidized lignin and the lignin model compound, isoeugenol, to vanillin.<sup>246</sup> The Co(salen) complexes have several advantages over the metalloporphyrin complexes discussed above in that they are often cheaper, easier to synthesize, and relatively stable. Alterations of the salen ligand, such as the addition of sulfonato groups to the salen, are readily achieved and can alter the properties of the catalyst in terms of solubility and reactivity for lignin oxidation.<sup>247</sup> In analogy to the immobilization of the metalloporphyrins, Badamali and co-workers recently immobilized Co(salen) on SBA-15 and demonstrated its effective oxidation of the lignin model compound apocynol (Figure 13, **122**) using microwave heating.<sup>248</sup> Kervinen and co-workers studied the Co(salen)-catalyzed oxidation of veratryl alcohol using in situ UV–vis, ATR-IR, and Raman spectroscopy.<sup>249,250</sup> Typical turnover frequencies for these Co(salen) complexes typically range between  $2.8 \times 10^{-3}$  and  $4.1 \times 10^{-3} \text{ s}^{-1}$  with total turnover numbers around 300.<sup>251</sup> Canevali and co-workers studied the oxidative degradation of several lignin model compounds using Co(salen).<sup>252</sup> Investigation by electron paramagnetic resonance spectroscopy revealed that two phenoxy cobalt radicals are involved in the oxidation mechanism of phenolic compounds.<sup>252</sup> In addition to investigating Co(salen) complexes, Haikarainen and co-workers used Cu-, Fe-, and Mn-triphenylphosphonium-decorated salen complexes (Figure 18) for the oxidation of coniferyl alcohol, noting that Mn and Co showed different regioselectivity relative to the enzyme horseradish peroxidase.<sup>63</sup> Relatively few investigations on Co(salen) complexes for the oxidation of lignin itself have been conducted, and according to Badamali and co-workers, the complexes need to be studied in greater detail.<sup>248</sup>

### 6.3.3.3. Metallo-TAML, -DTNE, and -TACN Catalysts.

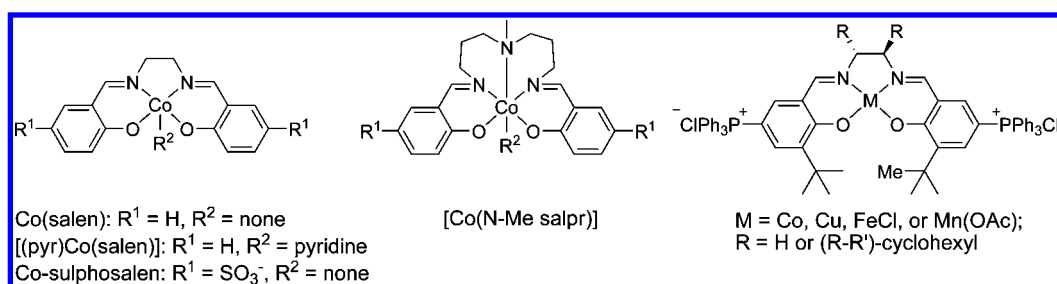
In a concerted effort spanning nearly three decades, Collins and co-workers developed a series of iron–TAML complexes, where TAML stands for tetraamido macrocyclic ligand, that were demonstrated as active, selective, and extremely robust oxidation catalysts.<sup>212,253</sup> The ligands in these TAML catalysts were designed in a four-step iterative process in which the ligand structure was designed to be resistant to oxidative degradation, after which it was oxidized until decay occurred. The products were characterized in order to identify the vulnerable site on the catalyst, and finally the ligand was modified to make the weak site more robust.<sup>212,254</sup> Although not yet applied specifically to the valorization of lignin or lignin-based model compounds, a  $\mu$ -oxo-bridged diiron(IV)–TAML complex was shown to selectively oxidize aromatic alcohols, such as benzyl, 4-chlorobenzyl, 4-nitrobenzyl, 4-methoxybenzyl, and cinnamyl alcohols, to the corresponding aldehydes.<sup>255</sup> Chen and co-workers demonstrated the use of  $[(\text{Me}_4\text{DTNE})\text{Mn}(\text{IV})_2(\mu\text{-O})_3](\text{ClO}_4)_2$ , where DTNE is 1,2-bis-(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethane, or  $[(\text{Me}_3\text{TACN})\text{Mn}(\text{IV})_2(\mu\text{-O})_3](\text{PF}_6)_2$ , where TACN is 1,4,7-trimethyl-1,4,7-triazacyclononane, and  $\text{H}_2\text{O}_2$  to bleach pine kraft-AQ pulp, noting that this catalyst was more effective for delignification of softwood pulps over hardwood pulps.<sup>256–258</sup> Table 11 summarizes the use of Mn-DTNE and Mn-TACN catalysts for pulp delignification. The structures of these complexes are depicted in Figure 19.

Cui and co-workers reported that  $[(\text{Me}_4\text{DTNE})\text{Mn}(\text{IV})(\mu\text{-O})_3\text{Mn}(\text{IV})](\text{ClO}_4)_2$  readily oxidized several lignin model compounds with hydrogen peroxide to aldehydes, epoxides,

**Table 10. Metallosalen Catalytic Systems for the Oxidation of Lignin (Model Compounds)**

entry	catalyst	oxidant	solvent	reaction conditions			lignin/model compound	products	yield (%)	conversion (%)	ref
				<i>T</i> (K)	<i>P</i> (MPa)	<i>t</i> (h)					
1	[(pyr)Co(salen)]	O <sub>2</sub>	MeOH	<i>c</i>	0.345	17	syringyl alcohol	2,6-dimethoxybenzoquinone	88		245
2	[Co(N-Me salpr)]	O <sub>2</sub>	MeOH	<i>c</i>	0.345	17	syringaldehyde	2,6-dimethoxybenzoquinone	0		245
3	[(pyr)Co(salen)]	O <sub>2</sub>	MeOH	<i>c</i>	0.345	17	syringyl alcohol	2,6-dimethoxybenzoquinone	71		245
4	[Co(N-Me salpr)]	O <sub>2</sub>	MeOH	<i>c</i>	0.345	17	syringaldehyde	2,6-dimethoxybenzoquinone	0		245
5	Co(salen)	O <sub>2</sub>	MeOH	<i>c</i>	0.345	17	syringaldehyde	2,6-dimethoxybenzoquinone	72		245
6	[Co(N-Me salpr)]	O <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	<i>c</i>	0.345	17	vanillyl alcohol	2-methoxybenzoquinone	43		245
7	Co-sulphosalen	O <sub>2</sub>	toluene	298	0.518	2	isoeugenol	vanillin	27.9 <sup>f</sup>		246
8	Co-sulphosalen	O <sub>2</sub>	H <sub>2</sub> O <sup>a</sup>	363	0.8	3	2,2'-biphenol	<i>e</i>		6	247
9	Co-sulphosalen	O <sub>2</sub>	H <sub>2</sub> O <sup>a</sup>	363	0.8	3	veratryl alcohol	veratraldehyde			247
10	Co(salen)/SBA-15	H <sub>2</sub> O <sub>2</sub>	CH <sub>3</sub> CN	<i>d</i>	<i>e</i>	0.5	apocynol	acetovanillone	11 <sup>g</sup>		248
								2-methoxyquinone	9 <sup>g</sup>		
11	Co(salen)/SBA-15	H <sub>2</sub> O <sub>2</sub>	CH <sub>3</sub> CN	<i>d</i>	<i>e</i>	0.66	apocynol	<i>e</i>	<i>h</i>		248
12	Co(salen)	O <sub>2</sub>	NaOH/H <sub>2</sub> O <sup>b</sup>	353	0.1		veratryl alcohol	<i>e</i>			249
13	Co(salen)	O <sub>2</sub>	NaOH/H <sub>2</sub> O <sup>b</sup>	353	0.1	28	veratryl alcohol	veratraldehyde	43		250
14	Co(salen)	O <sub>2</sub>	CHCl <sub>3</sub>	298	1	0.5	coniferyl alcohol model	3,4-dimethoxybenzaldehyde		60	252
15	Co(salen)	O <sub>2</sub>	CHCl <sub>3</sub>	298	1	0.5	β-O-4 model compounds	quinones (see scheme)		90	252
16	Co(salen)	O <sub>2</sub>	CHCl <sub>3</sub>	298	1	0.5	β-5 model compounds	see scheme		99	252

<sup>a</sup> alkaline. <sup>b</sup> 2 mol/L. <sup>c</sup> Room temperature. <sup>d</sup> 300 W microwave. <sup>e</sup> Not stated. <sup>f</sup> 562 turnovers. <sup>g</sup> 88% total lignin degradation. <sup>h</sup> 100% lignin degradation. N-Me salpr = bis(salicylidene-γ-iminopropyl)methylamine.

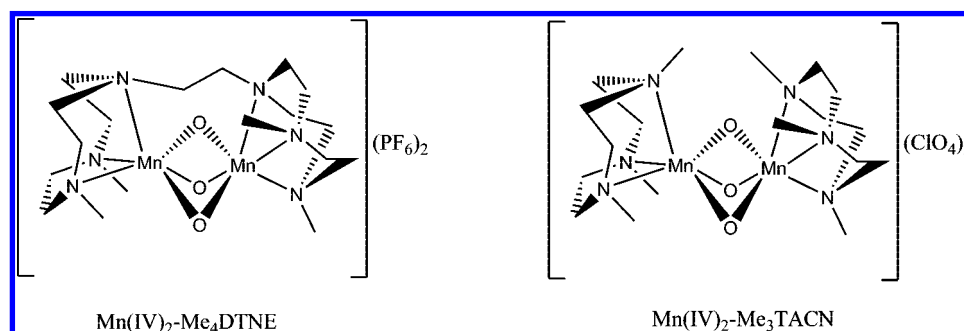
**Figure 18.** Structure of Co(salen) and related complexes.**Table 11. 1,2-Bis-(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethane or 1,4,7-Trimethyl-1,4,7-triazacyclononane Catalytic Systems for Delignification**

entry	catalyst	oxidant	solvent	reaction conditions		lignin/model compound	delignification (%)	ref
				<i>T</i> (K)	<i>t</i> (min)			
1	Mn(IV)–Me <sub>3</sub> TACN	H <sub>2</sub> O <sub>2</sub>	acetone	313	60	1-(3,4-dimethoxyphenyl)ethanol	95	256
2	Mn(IV)–Me <sub>4</sub> DTNE	H <sub>2</sub> O <sub>2</sub>	acetone	353	60	1-(3,4-dimethoxyphenyl)ethanol	43	256
3	Mn(IV)–Me <sub>4</sub> DTNE	H <sub>2</sub> O <sub>2</sub>	water	353	120	pine kraft-AQ pulp	43	257
4	Mn(IV)–Me <sub>3</sub> TACN	H <sub>2</sub> O <sub>2</sub>	water	333	120	pine kraft-AQ pulp	43.8	258
5	Mn(IV)–Me <sub>4</sub> DTNE	H <sub>2</sub> O <sub>2</sub>	acetone	323	10	1-(3,4-dimethoxyphenyl)ethanol	~50	259
6	Mn(IV)–Me <sub>4</sub> DTNE	H <sub>2</sub> O <sub>2</sub>	acetone	313	5	1-(3,4-dimethoxyphenyl)-1-propene	~90	259
7	Mn(IV)–Me <sub>4</sub> DTNE	H <sub>2</sub> O <sub>2</sub>	acetone	323	10	( <i>E</i> )-1,2-diphenylethene	~40	259

and alcohols.<sup>259</sup> This catalyst preferentially epoxidated C–C double bonds conjugated with aromatic moieties.<sup>259</sup>

**6.3.3.4. Polyoxometalate-Based Catalysts.** The development of polyoxometalates (POMs) for use as delignification catalysts originated with the objective to replace the chlorine-based pulp bleaching processes, which resulted in the accumulation of chlorine in the local environment, with environmentally benign oxidation processes.<sup>31</sup> Gaspar and

co-workers published a review of polyoxometalates for delignification that highlighted the general properties and factors influencing catalytic activity.<sup>41</sup> The distinctive properties of polyoxometalates constitute the principle factors of their design. Polyoxometalates consist of both primary and secondary heteroatoms, where the former determines the structure and the latter, typically transition metal ions, may be substituted without change of structure.<sup>41</sup> These properties

**Figure 19.** Structures of [(Me<sub>4</sub>DTNE)Mn(IV)<sub>2</sub>(μ-O)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> and [(Me<sub>3</sub>TACN)Mn(IV)<sub>2</sub>(μ-O)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub>.



**Table 12. Polyoxometalate Catalytic Systems for Oxidation of Lignin**

entry	catalyst	oxidant	solvent	reaction conditions			lignin/model compound	products	conversion (%)	ref
				<i>T</i> (K)	<i>P</i> (MPa)	<i>t</i> (h)				
1	SiW <sub>11</sub> Mn(III)	O <sub>2</sub>	<i>a</i>	383	0.5	2	eucalypt kraft pulp	<i>a</i>	59 <sup>g</sup>	261
2	BW <sub>11</sub> Co(III)	O <sub>2</sub>	<i>a</i>	383	0.5	2	eucalypt kraft pulp	<i>a</i>	36 <sup>g</sup>	261
3	SiW <sub>11</sub> Co(III)	O <sub>2</sub>	<i>a</i>	383	0.5	2	eucalypt kraft pulp	<i>a</i>	62 <sup>g</sup>	261
4	SiW <sub>11</sub> Ru(IV)	O <sub>2</sub>	<i>a</i>	383	0.5	2	eucalypt kraft pulp	<i>a</i>	51 <sup>g</sup>	261
5	PW <sub>11</sub> Ru(IV)	O <sub>2</sub>	<i>a</i>	383	0.5	2	eucalypt kraft pulp	<i>a</i>	48 <sup>g</sup>	261
6	HPA-5-Mn(II)	O <sub>2</sub>	<i>a</i>	373	0.5	2	eucalypt kraft pulp	<i>a</i>	76 <sup>g</sup>	262
7	α-[SiVW <sub>10</sub> O <sub>40</sub> ] <sup>5-</sup>	<i>a</i>	buffer <sup>b</sup>	363	<i>a</i>	1	lodgepole pine milled wood lignin	<i>a</i>		263
8	Na <sub>5(+1.9)</sub> [SiV <sub>1(-0.1)</sub> MoW <sub>10(+0.1)</sub> ]	<i>a</i>	buffer <sup>b</sup>	438	<i>a</i>	1	3,4-dimethoxy acetophenone	<i>a</i>	<i>h</i>	265
9	Na <sub>5(+1.9)</sub> [SiV <sub>1(-0.1)</sub> MoW <sub>10(+0.1)</sub> ]	<i>a</i>	buffer <sup>b</sup>	453	<i>a</i>	1	3,4,5-trimethoxy acetophenone	3,4,5-trimethoxybenzaldehyde	<i>i</i>	265
10	Na <sub>5(+1.9)</sub> [SiV <sub>1(-0.1)</sub> MoW <sub>10(+0.1)</sub> ]	<i>a</i>	buffer <sup>b</sup>	453	<i>a</i>	1	1-(4-hydroxy-3,5-dimethoxyphenyl)-ethanone	<i>a</i>	<i>j</i>	265
11	H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	O <sub>2</sub>	H <sub>2</sub> O/CH <sub>3</sub> OH	443	0.5	0.33	kraft lignin	vanillin	5.18	267
12	HPA-5-Mn(II)	O <sub>2</sub>	CH <sub>3</sub> CN	363	0.5	0.5	eucalypt kraft pulp	several aromatic compounds		268
13	LaMnO <sub>3</sub>	O <sub>2</sub>	NaOH/H <sub>2</sub> O <sup>c</sup>	493	0.5	3	<i>d</i>	<i>p</i> -hydroxybenzaldehyde	1.7	269
14	LaMnO <sub>3</sub>	O <sub>2</sub>	NaOH/H <sub>2</sub> O <sup>c</sup>	493	0.5	3	<i>d</i>	vanillin	~4	269
15	LaMnO <sub>3</sub>	O <sub>2</sub>	NaOH/H <sub>2</sub> O <sup>c</sup>	493	0.5	3	<i>d</i>	syringaldehyde	~4	269
16	LaCoO <sub>3</sub>	O <sub>2</sub>	NaOH/H <sub>2</sub> O <sup>c</sup>	493	0.5	3	<i>d</i>	<i>p</i> -hydroxybenzaldehyde	2.2	270
17	LaCoO <sub>3</sub>	O <sub>2</sub>	NaOH/H <sub>2</sub> O <sup>c</sup>	493	0.5	3	<i>d</i>	vanillin	~4	270
18	LaCoO <sub>3</sub>	O <sub>2</sub>	NaOH/H <sub>2</sub> O <sup>c</sup>	493	0.5	3	<i>d</i>	syringaldehyde	~2.4	270
19	H <sub>2</sub> MoO <sub>4</sub>	H <sub>2</sub> O <sub>2</sub>	CH <sub>3</sub> COOH/H <sub>2</sub> O	503	<i>a</i>	2	larch wood delignification	<i>e</i>		271
20	Fe <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	H <sub>2</sub> O <sub>2</sub>	CH <sub>3</sub> COOH/H <sub>2</sub> O	503	<i>a</i>	2	larch wood delignification	<i>f</i>		271

<sup>a</sup> Not specified. <sup>b</sup> Sodium acetate. <sup>c</sup> 2 mol/L. <sup>d</sup> Enzymatic hydrolysis of steam-explosion cornstalks. <sup>e</sup> Lignin completely removed from stream. <sup>f</sup> Two percent lignin remaining in stream. <sup>g</sup> Kappa number reduction. <sup>h</sup> Rate constant = 17.2 × 10<sup>-3</sup> s<sup>-1</sup>. <sup>i</sup> Rate constant = 16.80 × 10<sup>-3</sup> s<sup>-1</sup>. <sup>j</sup> Rate constant = 12.30 × 10<sup>-3</sup> s<sup>-1</sup>.

allow release and substitution of the secondary heteroatom with ions that give the polyoxometalate desirable redox characteristics, that is, thermodynamic conditions such that the POMs have higher redox potentials than lignin but lower than molecular oxygen.<sup>41,260</sup> In addition to choice of transition metal, the choice of countercation determines the solubility of the POM, which has important ramifications for industrial utilization of these catalysts.<sup>41,260</sup> With appropriate choice of countercation, the POMs are selectively soluble in water, polar organic solvents, or nonpolar solvents.<sup>41,260</sup> A summary of POM-catalyzed lignin oxidation reactions is given in Table 12. Several POMs, including transition metal polyoxotungstates containing Mn(III), Co(III), or Ru(IV)<sup>261</sup> and heteropolyanion-5 consisting of [PMo<sub>(12-n)</sub>M<sub>n</sub>O<sub>40</sub>]<sub>(3+n)</sub><sup>-</sup> where M is Mn(II)<sup>262</sup> or V(V),<sup>31</sup> were shown to be effective catalysts for the degradation of lignin in *Eucalyptus globulus* kraft pulps. Kim and co-workers demonstrated the oxidation of milled wood lignin by α-[SiVW<sub>10</sub>O<sub>40</sub>]<sub>5</sub><sup>-</sup>.<sup>263</sup> Investigation by <sup>13</sup>C NMR of the lignin before and after reaction indicated that POM oxidation leads to degradation of the β-O-4 linkages.<sup>263</sup> The oxidation of several lignin model compounds was conducted with an emphasis on the structural effects of the model compounds on the kinetics.<sup>264</sup> Yokoyama and co-workers performed kinetic experiments using POMs of composition Na<sub>5(+1.9)</sub>[SiV<sub>1(-0.1)</sub>MoW<sub>10(+0.1)</sub>] for the oxidation of 1-(3,4,5-trimethoxyphenyl)ethanol to the corresponding aldehydes.<sup>265</sup> They observed a rate constant of 16.80 s<sup>-1</sup> at 453 K, an activation energy of 68.4 kJ mol<sup>-1</sup>, and frequency factor of 1.28 × 10<sup>6</sup> s<sup>-1</sup> for the reaction of 1-(3,4,5-trimethoxyphenyl)ethanol to 1-(3,4,5-trimethoxyphenyl)ethanal.<sup>265</sup>

Similarly to the case of metalloporphyrins, the original objective for the design of POMs focused on the ability to selectively degrade lignin rather than cellulose and other materials in the paper industry. That is, active catalysts rapidly oxidized lignin to carbon dioxide and water with minimal degradation of the polysaccharides, leaving a lignin-free white pulp suitable for paper production.<sup>31,261,262,266</sup>

Recently, the use of POMs for the selective oxidation of kraft pulps to chemicals was also reported.<sup>267</sup> Kraft lignin from spruce wood was oxidized by H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> in the presence of oxygen and either methanol or ethanol to produce vanillin, methyl vanillate, ethyl vanillate, and other monomeric products.<sup>267</sup> The methanol and ethanol were added to prevent recondensation of the lignin fragments.<sup>267</sup> Gaspar and co-workers performed the oxidative delignification of homovanillyl alcohol, homoveratryl alcohol, and lignin from *Eucalyptus globulus* using Mn(II)-substituted heptamolybdopentavanadophosphate polyanions, which yielded several simpler substituted aromatic compounds.<sup>268</sup> The catalytic wet oxidation of steam-exploded cornstalk lignin to form *p*-hydroxybenzaldehyde, vanillin, and syringaldehyde from the coniferyl, sinapyl, and *p*-coumaryl alcohols was also recently reported using perovskite-type oxides including LaMnO<sub>3</sub><sup>269</sup> and LaCoO<sub>3</sub>.<sup>270</sup> Kuznetsov and co-workers demonstrated that soluble redox catalysts (H<sub>2</sub>MoO<sub>4</sub> or Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>) can be used to obtain high-quality cellulose from wood in a one-step acetic acid–H<sub>2</sub>O<sub>2</sub> medium.<sup>271</sup>

**6.3.3.5. Simple Metal Salt-Based Catalysts.** Several studies have demonstrated the reactions of lignin or lignin model compounds using simple metal salt catalysts in the presence of oxygen. The development of these catalysts originated with hydrocarbon oxidation catalysts, particularly for the selective oxidation of aromatic hydrocarbons such as *p*-xylene to form terephthalic acid, which is an important platform chemical for the production of, for instance, the plastic poly(ethylene terephthalate).<sup>272</sup> Since aromatic units constitute a significant proportion of lignin structure, the use of these oxidation catalysts to valorize lignin in kraft pulp was a logical extension of the hydrocarbon oxidation catalysts. A summary of lignin or lignin model compound oxidations by these catalysts is presented in Table 13. Co(III) and Mn(III) oxidative degradation of lignin was described to yield benzoic acids.<sup>12</sup> The production of aromatic ketones and aldehydes from lignin using CuO, CuSO<sub>4</sub>, FeCl<sub>3</sub>, and

Table 13. Simple Metal Salt and Miscellaneous Catalytic Systems for Oxidation of Lignin (Model Compounds)

entry	catalyst	oxidant	solvent	reaction conditions			lignin/model compound	products	yield (%)	conversion (%)	ref
				T (K)	P (MPa)	t (h)					
1	Co(OAc) <sub>2</sub> /Mn(OAc) <sub>2</sub>	O <sub>2</sub>	CH <sub>3</sub> COOH	443	3.45 <sup>d</sup>	3	(1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol)	3,4-dimethoxybenzaldehyde	22.9		273
2	Co(OAc) <sub>2</sub> /Mn(OAc) <sub>2</sub>	O <sub>2</sub>	CH <sub>3</sub> COOH	443	3.45 <sup>d</sup>	3	(1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol)	3,4-dimethoxybenzoic acid	33.2		273
3	Co(OAc) <sub>2</sub> /Mn(OAc) <sub>2</sub>	O <sub>2</sub>	CH <sub>3</sub> COOH	443	3.45 <sup>d</sup>	3	(1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol)	guaiacol	7.1		273
4	Co(OAc) <sub>2</sub> /Mn(OAc) <sub>2</sub> /HBr	O <sub>2</sub> <sup>b</sup>	CH <sub>3</sub> COOH	323	ns	5	(2-methoxyphenoxy)propane-1,3-diol) sugar cane straw bagasse	$k^e = 9.90 \times 10^{-2} \text{ h}^{-1}$ ; $k^e = 56.61 \times 10^{-2} \text{ h}^{-1}$			274
5	Co(OAc) <sub>2</sub> /Mn(OAc) <sub>2</sub> /HBr	O <sub>2</sub> <sup>b</sup>	CH <sub>3</sub> COOH	353	r	5	sugar cane straw bagasse	$k^e = 6.20 \times 10^{-2} \text{ h}^{-1}$ ; $k^e = 14.83 \times 10^{-2} \text{ h}^{-1}$			274
6	Co(OAc) <sub>2</sub> /Mn(OAc) <sub>2</sub> /HBr	O <sub>2</sub> <sup>b</sup>	CH <sub>3</sub> COOH	388	r	5	sugar cane straw bagasse	$k^e = 1.10 \times 10^{-2} \text{ h}^{-1}$ ; $k^e = 10.61 \times 10^{-2} \text{ h}^{-1}$			274
7	Co(OAc) <sub>2</sub> /Mn(OAc) <sub>2</sub> /HBr	O <sub>2</sub> <sup>b</sup>	CH <sub>3</sub> COOH	383	r	10	acetosolv eucalyptus wood pulp	vanillin and vanillic acid/ vanillin and vanillic acid <sup>f</sup>	0.38 <sup>g</sup>		275
8	Co(OAc) <sub>2</sub> /Mn(OAc) <sub>2</sub> /HBr	O <sub>2</sub> <sup>b</sup>	CH <sub>3</sub> COOH	383	r	10	acetosolv sugar cane bagasse pulp	vanillin and vanillic acid <sup>f</sup>	0.05 <sup>g</sup>		275
9	Co(OAc) <sub>2</sub> /Mn(OAc) <sub>2</sub> /HBr	O <sub>2</sub> <sup>b</sup>	CH <sub>3</sub> COOH	383	r	10	acetone/water/FeCl <sub>3</sub> -lignin	vanillin and vanillic acid <sup>f</sup>	0.45 <sup>g</sup>		275
10	Co(OAc) <sub>2</sub> /Mn(OAc) <sub>2</sub> /HBr	O <sub>2</sub> <sup>b</sup>	CH <sub>3</sub> COOH	383	r	10	organocell softwood mixture pulp	vanillin and vanillic acid <sup>f</sup>	0.84 <sup>g</sup>		275
11	Co(OAc) <sub>2</sub> /Mn(OAc) <sub>2</sub> / Zr(OAc) <sub>4</sub> /HBr	O <sub>2</sub>	CH <sub>3</sub> COOH	353	r	r	4-hydroxybenzaldehyde	no reaction			61
12	Co(OAc) <sub>2</sub> /Mn(OAc) <sub>2</sub> /HBr	O <sub>2</sub>	CH <sub>3</sub> COOH	353	r	r	3-methoxy-4-acetoxybenzaldehyde	3-methoxy-4-acetoxybenzoic acid; $k^e = 81 \times 10^{-5} \text{ s}^{-1}$			61
13	Co(OAc) <sub>2</sub> /Mn(OAc) <sub>2</sub> /HBr	O <sub>2</sub>	CH <sub>3</sub> COOH/ (CH <sub>3</sub> CO) <sub>2</sub> O	353	r	r	4-methoxytoluene	4-methoxybenzoic acid; $k^e = 27 \times 10^{-5} \text{ s}^{-1}$			61
14	Co(OAc) <sub>2</sub> /Mn(OAc) <sub>2</sub> / Zr(OAc) <sub>4</sub> /HBr	O <sub>2</sub>	CH <sub>3</sub> COOH/ (CH <sub>3</sub> CO) <sub>2</sub> O	368	r	r	3-methoxy-4-acetoxytoluene	3-methoxy-4-acetoxybenzoic acid; $k^e = 7.2 \times 10^{-5} \text{ s}^{-1}$			61
15	Co(OAc) <sub>2</sub> /Mn(OAc) <sub>2</sub> / Zr(OAc) <sub>4</sub> /HBr	air	CH <sub>3</sub> COOH	453	13.8	2	organosolv mixed hardwood lignin	syringic/vanillic acid	10.9 <sup>h</sup>		61
16	Co(OAc) <sub>2</sub> /Mn(OAc) <sub>2</sub> / Zr(OAc) <sub>4</sub> /HBr	air	CH <sub>3</sub> COOH	413	6.9	2	lignosulfonic acid, sodium salt	syringic/vanillic acid	0.2		61
17	Co(OAc) <sub>2</sub> /Mn(OAc) <sub>2</sub> / Zr(OAc) <sub>4</sub> /HBr	air	CH <sub>3</sub> COOH	413	6.9	2	hydrolytic lignin	syringic/vanillic acid	7.53		61
18	Mn(OAc) <sub>3</sub>	air	CH <sub>3</sub> CN/H <sub>2</sub> O	q	r	2	guaiacol	polyguaiacol	88		276
19	Mn(OAc) <sub>3</sub>	air	dioxane/H <sub>2</sub> O	q	r	2	guaiacol	polyguaiacol	60		276
20	Mn(OAc) <sub>3</sub>	air	CH <sub>3</sub> OH/water	q	r	2	guaiacol	polyguaiacol	25		276
21	CuSO <sub>4</sub>	O <sub>2</sub>	NaOH/water	383–433	0.2	1	softwood lignosulfonates	vanillin	14.7 <sup>i</sup>		277
22	CuSO <sub>4</sub> /FeCl <sub>3</sub>	O <sub>2</sub>	c	433	1.38	0.33	yellow poplar wood chips	total lignin		62.9	278
								vanillin		3.7	
								syringaldehyde		7.7	
								acetovanillone		0.5	
								acetosyringone		2.4	
23	CuSO <sub>4</sub> /FeCl <sub>3</sub>	O <sub>2</sub>	c	443	1.38	0.33	yellow poplar wood chips	total lignin		70.3	278
								vanillin		4.7	
								syringaldehyde		8.8	
								acetovanillone		0.7	
								acetosyringone		2	
24	CuSO <sub>4</sub> /FeCl <sub>3</sub>	O <sub>2</sub>	c	453	1.38	0.33	yellow poplar wood chips	total lignin		77.8	278
								vanillin		4.3	
								syringaldehyde		8.4	
								acetovanillone		0.8	
								acetosyringone		2.6	
25	Mn(OAc) <sub>3</sub>	O <sub>2</sub>	CH <sub>3</sub> COOH	343	1	1	syringyl alcohol	syringaldehyde	30		279
26	Cu(OH) <sub>2</sub>	O <sub>2</sub>	c	433	0.15	1	vanillideneacetone	vanillin	60		280
27	Cu(OH) <sub>2</sub>	O <sub>2</sub>	c	433	0.2	0.66	fir wood by sulfite pulping	vanillin	13.9 <sup>j</sup>		280
28	MnSO <sub>4</sub>	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O/H <sub>2</sub> SO <sub>4</sub>	373	6–18	1	rice straw	vanillin	r		281
29	NaBr, TEMPO <sup>o</sup>	NaClO	H <sub>2</sub> O	r	r	r	softwood thermomechanical kraft pulp	r	k		282

Table 13. Continued

entry	catalyst	oxidant	solvent	reaction conditions			lignin/model compound	products	yield (%)	conversion (%)	ref
				T (K)	P (MPa)	t (h)					
30	CuO	O <sub>2</sub>	c	453	1.52	2	hardwood kraft lignin	syringaldehyde vanillin	3.5 1.1		283
								syringic acid vanillic acid	1.5 0.75		
31	CoO	O <sub>2</sub>	c	453	1.52	2	hardwood kraft lignin	syringaldehyde vanillin	2.5 0.9		283
								syringic acid vanillic acid	1.2 0.27		
32	none	m	buffer <sup>p</sup>	294	r	r	erythro/threo β-O-4 model compounds	erythro degradation threo degradation	38 82		284
33	none	n	buffer <sup>p</sup>	294	r	r	erythro/threo β-O-4 model compounds	erythro degradation threo degradation	56 59		284
34	none	o	buffer <sup>p</sup>	294	r	r	erythro/threo β-O-4 model compounds	erythro degradation threo degradation	25 66		284
35	l	r	r	r	r	20	veratryl alcohol	veratraldehyde	16		285
36	Ru(CN) <sub>6</sub> <sup>4+</sup>	r	r	r	r	20	veratryl alcohol	veratraldehyde	99		285
37	[Cu(phen)(OH) <sub>2</sub> ]	O <sub>2</sub>	alkaline water	353	1	1	veratryl alcohol	veratraldehyde	~20		286

<sup>a</sup>TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxyl radical. <sup>b</sup>60 mL/min. <sup>c</sup>Alkaline solution. <sup>d</sup>4% O<sub>2</sub>. <sup>e</sup>Rate constants. <sup>f</sup>Oxidized lignin also observed. <sup>g</sup>Weight percent. <sup>h</sup>Given in g/L of 180 g/L spent liquor. <sup>i</sup>Given in g/L. <sup>k</sup>Kappa number = ~0.5. <sup>j</sup>Tris-(4,4'-dimethyl-2,2',2'-bipyridine)iron(II). <sup>m</sup>Cerium ammonium nitrate. <sup>n</sup>Fenton's reagent. <sup>o</sup>Lead tetraacetate. <sup>p</sup>Sodium acetate. <sup>q</sup>Room temperature. <sup>r</sup>Not stated.

Fe<sub>2</sub>O<sub>3</sub> and the production of monomeric phenols using Co, Fe, and Rh were also described.<sup>12</sup> DiCosimo and Szabo performed the single-electron oxidation of the lignin model compound 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-propane-1,3-diol (Figure 8, 4) using Co(II) acetate and Mn(II) acetate, where the oxidation occurred principally through cleavage of the C<sub>α</sub>–C<sub>β</sub> bond.<sup>273</sup> Labat and co-workers demonstrated the oxidation of lignin from sugar cane straw and bagasse, obtained from ethanol–water pulping, using cobalt(II)acetate/manganese(II)acetate/HBr solutions.<sup>274</sup> The kinetics and activation energy of the lignin oxidation were calculated using UV–visible spectroscopy.<sup>274</sup> Goncalves and Schuchardt performed the oxidation of lignins obtained from the organosolv pulping of eucalyptus wood, sugar cane bagasse, and a softwood mixture using HBr, Co(II), and Mn(II) as catalysts, obtaining vanillin, vanillic acid, and oxidized lignin that remained in solution.<sup>275</sup> Parteneheimer recently demonstrated the oxidation of lignin from wood and bagasse to over 18 valuable products using Mn(II)acetate/Co(II)acetate/Zr(IV)acetate/HBr catalyst solution.<sup>61</sup> Nearly 10.9 wt % of the lignin was converted to aromatic products such as vanillin, vanillic acid, syringaldehyde, and syringic acid.<sup>61</sup> A principle advantage of using this oxidation catalyst system is that the process is already used industrially and the engineering challenges such as corrosion, catalyst recycling, and efficient mixing have already been solved.<sup>61</sup>

Other metal salt solutions besides Mn(II)/Co(II) combinations have been used to catalyze lignin oxidation reactions. Hwang and co-workers demonstrated the use of Mn(III) acetate as a polymerization catalyst of guaiacol to polyguaiacol,<sup>276</sup> and a mechanistic study using CuSO<sub>4</sub> demonstrated the role of the metal in lignin oxidation to vanillin.<sup>277</sup> Xiang and Lee demonstrated the oxidation of yellow poplar wood chips using CuSO<sub>4</sub> and FeCl<sub>3</sub> at 433–453 K.<sup>278</sup> The primary identifiable products consisted of aromatic aldehydes, ketones, and acids, with the yield of vanillin and syringaldehyde approximately 15%.<sup>278</sup> Other complexes have also been reported as active oxidation catalysts. Sugimoto and co-workers investigated the oxidation of syringyl alcohol to syringaldehyde using Mn(III) acetate and molecular oxygen.<sup>279</sup> Further mechanistic investigations were performed by Tarabanko and co-workers using copper oxide as a catalyst.<sup>280</sup> Borthakur patented a process for the oxidation of rice straw to form vanillin. The ferulic acid groups found in this renewable resource are converted with hydrogen peroxide using manganese sulfate hydrate with a Co, Ni, or Cu cocatalyst.<sup>281</sup> Okita and co-workers used catalytic amounts of NaBr and 2,2,6,6-tetramethylpiperidine-1-oxyl-radical to perform the oxidation of a softwood thermomechanical pulp.<sup>282</sup> The process almost completely oxidized the lignin and hemicelluloses to provide water-soluble compounds.<sup>282</sup> Bhargava and co-workers investigated several homogeneous and heterogeneous catalysts for ferulic acid catalytic wet oxidation.<sup>207</sup> The order of activity for the homogeneous catalysts was Cu<sup>2+</sup> > Fe<sup>2+</sup> > Mn<sup>2+</sup> > Ce<sup>2+</sup> > Bi<sup>2+</sup> > Co<sup>2+</sup> > Zn<sup>2+</sup> > Mg<sup>2+</sup> > Ni<sup>2+</sup>.<sup>207</sup> Finally, Villar and co-workers used Cu(II) and Co(II) salts in the presence of molecular oxygen to oxidize hardwood kraft lignin in alkaline medium to produce syringaldehyde, vanillin, and other acids.<sup>283</sup>

**6.3.3.6. Miscellaneous Catalyst Systems.** Bohlin and co-workers performed a direct comparison between enzymatic (i.e., lignin peroxidase, laccase) and nonenzymatic catalysts (Fenton's reagent, lead tetraacetate) and noted differences in lignin oxidation selectivity with respect to the ability of

the catalyst to oxidize the erythro or the threo form of the  $\beta$ -O-4 linkage in softwood.<sup>284</sup> Rochefort and co-workers performed a study in which hexacyanoruthenate(II) or tris-(4,4'-dimethyl-2,2'-bipyridine)iron(II) was used in the presence of an electron transport mediator, such as 1-hydroxybenzotriazole, to oxidize veratryl alcohol to veratryl aldehyde. The electron transport mediator aided in the oxidation of the lignin model compounds, and the activity of the system was compared with the electrochemical oxidation and enzymatic oxidation of the model compounds.<sup>285</sup> Recently, Korpi and co-workers reported the oxidation of veratryl alcohol to veratryl aldehyde using Cu(II) sulfate and 1,10-phenanthroline (phen) in alkaline, aqueous solutions.<sup>286</sup> The [Cu(phen)(OH)<sub>2</sub>] complex was formed in situ and involved a catalytic cycle in which two [Cu(phen)(OH)<sub>2</sub>] were reduced to two [Cu(phen)(OH)] by the aldehyde, and molecular oxygen and water reoxidized the complex in the presence of OH<sup>−</sup> ions.<sup>286</sup>

## 7. Concluding Remarks

Lignin is an important component of biomass from which several useful chemicals can be produced as indicated by the work initiated in the second half of the last century and the renewed interest today. Lignin valorization constitutes an important component of the modern biorefinery scheme, and the structure and composition of lignin offer unique routes to produce several fine and bulk chemicals. In the preceding sections, we have presented the different approaches and strategies currently available for catalytic lignin valorization. Generally, lignin reduction catalytic systems produce bulk chemicals with reduced functionality, whereas lignin oxidation catalytic systems produce fine chemicals with increased functionality.

Considerable effort has already been devoted to developing a wide variety of catalytic routes specifically for lignin oxidation and reduction, yet several issues are apparent after review of these processes. First, there is a general lack of detailed information regarding the performance of catalysts on the valorization of actual lignin streams. This lack of information originates with the analytical challenges associated with the native lignin polymer itself, the influence of different pretreatments on this structure,<sup>287–290</sup> and the wide variety of compounds obtainable from lignin degradation. Moreover, lignin streams could contain proteins, inorganic salts, and other potential poisons that generally complicate catalysis. Although important for understanding the chemistry of the lignin polymer and the possible chemicals obtainable from its conversion, a majority of the reported catalytic systems involve the use of pure lignin model compounds that are free from these complicating factors. Since catalyst materials will eventually encounter these factors in an operational biorefinery, obtaining performance information with these factors is important for the development of effective catalysts suitable for use in practical biorefineries. In addition, we advocate the use of the most relevant model compounds (i.e., those with appropriate functionality in positions resembling the conferyl or sinapyl alcohols) for the development of catalytic processes. Not only is use of these compounds important for better understanding of the lignin chemistry, but reactions with substrates with similar functional groups allow for proper catalysis comparisons in terms of activity and selectivity.

Several of the catalysts used for lignin valorization are based on catalyst technology developed specifically for petroleum refining. The biorefinery presents unique chal-

lenges, however, that originate from the wide range of feedstocks and pretreatment methods. In particular, the nature of biomass feedstocks (C<sub>n</sub>H<sub>m</sub>O<sub>o</sub>), which contain a high oxygen content and various ether linkages that make them more hydrophilic, differs significantly from hydrophobic petroleum feedstocks (C<sub>n</sub>H<sub>m</sub>). These differences have ramifications for the development of suitable catalysts. On the other hand, with the new feedstocks come new opportunities as well. For instance, the presence of numerous methoxy-groups in lignin presents opportunities to produce simple C<sub>1</sub> compounds, such as methanol, which is a valuable chemical not as easily obtained from petroleum streams, in addition to aromatics with the development of appropriate catalytic technology. This C<sub>1</sub> product stream can then subsequently be converted into other products with conventional technology, such as the methanol-to-olefins process. Therefore, intensified efforts should involve the development of new catalyst materials specifically designed to meet these challenges rather than simply applying the “old” catalyst technology, developed for petroleum refining, to new substrates. In any case, short- to medium-term biorefinery development will likely incorporate existing petroleum refinery infrastructure to circumvent high capital costs,<sup>35</sup> which may otherwise be prohibitively expensive. In this respect, considerable effort is still required to address the separation challenges associated with the product streams derived from biomass, because conventional separation techniques used in petroleum refineries (such as distillation) are not necessarily best applied to the potentially highly functionalized, nonvolatile biorefinery product streams.

There are potential analogies between the 20th century petroleum refinery and the 21st century biorefinery. In the beginning, the petroleum refinery made few products and incorporated little chemical and energy integration. Development of the petroleum refinery took considerable effort, spanning decades, to become the highly efficient, integrated system that exists today, and many of the breakthroughs that allowed this remarkable transformation involved catalytic developments. In a similar course, current biorefineries, which are still in their infancy, produce relatively few chemicals (primarily ethanol or bio-oils) with little chemical and energy integration. In analogy to the history of the petroleum refinery, with the development of catalytic technology, the biorefinery can become an efficient, highly integrated system to meet the chemical and fuel requirements of the 21st century. In order to realize this system, the lignin fraction of biomass should be transformed from a low-quality, low-price waste product into a high-quality, high-value feedstock for bulk and specialty chemicals by the development of the appropriate catalytic technology. This transformation is critical because lignin represents the only viable source to produce the renewable aromatic compounds on which society currently depends.

## 8. Abbreviations

Ad	adsorbed
AFEX	ammonium fiber explosion
AMIM	1-allyl-3-methylimidazolium
BMIM	1-butyl-3-methylimidazolium
BM <sub>2</sub> IM	1-butyl-2,3-dimethylimidazolium
B,T,X	benzene, toluene, xylene
BzMIM	1-benzyl-3-methylimidazolium
Bz-ome-MIM	1-methoxybenzyl-3-methylimidazolium
BenzylMIMDca	1-benzyl-3-methylimidazolium dicyanamide



BMPy	1-butyl-3-methylpyridinium
DMSO	dimethylsulfoxide
DSA	dimensionally stable anode
DTNE	1,2-bis-(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)-ethane
ECOENG	1,3-dimethylimidazolium-dimethylphosphate
EMIM	1-ethyl-3-methylimidazolium
IPS	3-(1-imidazolyl)propylcarbamoyl-3'-aminopropyl-silica
HDN	hydrodenitrogenation
HDO	hydrodeoxygenation
HDS	hydrodesulfurization
HMIM	1-hexyl-3-methylimidazolium
HRI	Hydrocarbon Research Institute
MMIM	1-methyl-3-methylimidazolium
Mtoe	million tons of oil equivalent
NMI	N-methylimidazole
ns	not specified
PcTS	phthalocyaninetetra(sodium sulfonate)
rt	room temperature
salen	N,N'-bis(salicylidene)ethane-1,2-diaminato
TACN	1,4,7-trimethyl-1,4,7-triazacyclononane
TAML	tetraamido macrocyclic ligand
TBAF	tetrabutylammonium fluoride
TPPS	meso-tetrakis(p-sulfonatophenyl)porphyrin
TPPDS	P(C <sub>6</sub> H <sub>5</sub> )(C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> <sup>-</sup> ) <sub>2</sub>
TPPS <sub>4</sub>	5,10,15,20-tetrakis(2',6'-dichloro-3'-sulfonatophenyl)porphyrin
XS	xylenesulfonate

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