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CoMo sulfide-catalyzed hydrodeoxygenation of lignin model compounds: An extended reaction network for the conversion of monomeric and dimeric substrates

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ABSTRACT

In the present work, extensive hydrodeoxygenation (HDO) studies with a commercial sulfided $CoMo/Al_2O_3$ catalyst were performed on a library of lignin model compounds at 50 bar hydrogen pressure and 300 °C in dodecane, using a batch autoclave system. The catalyst was activated under hydrogen atmosphere prior to the reaction, and the spent catalyst was analyzed using thermogravimetric analysis. An extended reaction network is proposed, showing that HDO, demethylation, and hydrogenation reactions take place simultaneously. HDO of mono-oxygenated substrates proved to be difficult at the applied conditions. Starting from most positions in the network, phenol, and cresols are therefore the main final products, suggesting the possibility of convergence on a limited number of products from a mixture of substrates. HDO of dimeric model compounds mimicking typical lignin linkages revealed that coumaran alkyl ethers and β-O-4 bonds can be broken, but 5–5′ linkages not.

1. Introduction

With the depletion of fossil fuels, biomass becomes an important renewable feedstock for the production of fuels, chemicals, and energy. One particular component of lignocellulosic biomass that until recently has been somewhat overlooked as an important renewable resource is lignin [1]. This three-dimensional amorphous cross-linked biopolymer consists of phenyl-propane units, optionally substituted with methoxy and hydroxy groups [2]. It is a main constituent of lignocellulosic biomass and comprises 15–30% by weight and up to 40% by energy of biomass [3]. In plant cell walls, lignin can be found in the spaces between cellulose and hemicellulose, holding the lignocellulosic matrix together and adding rigidity to plant material [4].

Pretreatment of lignocellulosic biomass, for instance in a biorefinery operation, will give rise to large process streams of lignin, for which value-added applications will have to be found [5]. Catalytic conversion to bulk chemicals or fuel components is a possible scenario for future use of this lignin feedstock. To this extent, lignin or smaller fragments derived from this biopolymer (e.g. monomers or small oligomers) can be subjected to various chemical transformations. Several strategies can be followed, such as lignin bond hydrolysis [6,7] and catalytic oxidation reactions [8,9], in order to obtain value-added products. One approach that carries considerable potential is conversion by catalytic hydrodeoxygenation (HDO), as this allows removal of part of the extensive functionalities from the highly oxygenated structure resulting in the formation of bulk platform molecules, such as phenolics and BTX. Several studies on the catalytic hydrodeoxygenation of lignin or fragments derived from lignin have been reported [1,10,11].

The structural complexity and variability of lignin have prompted the use of several lignin model compounds to study lignin hydrodeoxygenation reactions. These model compounds, typically mono-aromatics, contain linkages and functional groups that resemble those found in the lignin polymer, and study of their reactivity provides insight into the reactivity of the lignin polymer itself. The models can thus be used to mimic the chemistry of typical lignin fragments and hold the additional benefit of greatly simplifying product analysis. In general, depolymerization feeds derived from lignin will likely consist of a mixture of aromatics, and the constituents of this mixture are mimicked in the library [12]. Moreover, reports on the hydrodeoxygenation of these lignin model compounds also bear relevance to the production and upgrading of bio-oils, as they can consist of up to 30–40% of oxygen-functionalized aromatics. Chemical processing of bio-oil, obtained for instance from a biomass pyrolysis process, is necessary to convert the bio-crude into useful transportation fuels. Stabilization of these bio-crudes can be achieved by removal of the oxygen functionalities via hydrodeoxygenation [11,13]. The traditional hydrotreating catalysts originally developed for the removal of sulfur and nitrogen from oil feeds could also be deployed for the removal of oxygen from biomass-derived product streams. Indeed, many of the studies on HDO of bio-oil or

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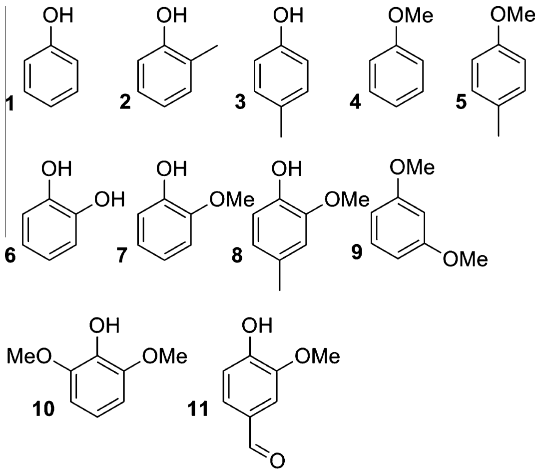
lignin-related components employ conventional cobalt- or nickel-promoted molybdenum catalysts [1,10]. An early study by Elliott, screening different commercial catalysts for their activity in phenol HDO, already showed that a sulfided CoMo catalyst gave the best results [14]. Because of their lower intrinsic hydrogenation activity, CoMo/Al_2O_3 catalyst is often preferred over the nickel analogs, as the aromaticity of the feeds should preferably be kept intact. This is in contrast to hydrodesulfurization or hydrodenitrogenation reactions where the heteroatom is commonly removed after ring saturation.

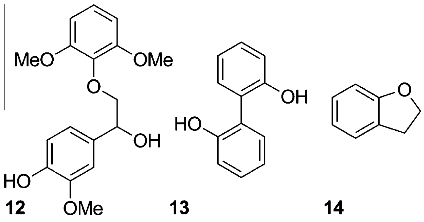
Several HDO studies using CoMo/Al_2O_3 catalysts were performed on simple aromatic model compounds, such as phenol, cresol, anisole and guaiacol, which mimic parts of the lignin structure and are important bio-oil constituents. Products originating from deoxygenation, (de)-methylation, and hydrogenation reactions were reported [15–18]. Hurff and Klein, for instance, observed the formation of catechol and phenol as main products for the conversion of guaiacol over a sulfided CoMo/Al_2O_3 catalyst. Formation of products in time confirmed that catechol is a primary product, which further reacts to phenol [19]. Several concise reaction schemes for the conversion of guaiacol and methylguaiacol were subsequently reported without information on selectivity [19,20]. Recently, Bui et al. reported on the promoting effect of cobalt on molybdenum sulfide catalysts and published a more comprehensive reaction scheme for guaiacol conversion also including the formation of heavy products [21]. The addition of cobalt was found to enhance the direct demethoxylation and direct deoxygenation pathways. Bredenberg et al. observed that the carbon–oxygen bond in phenol and cresols is more difficult to break than other carbon–oxygen bonds and that complete deoxygenation could therefore not be reached [16]. The role of the support material in HDO has also been investigated. The acid sites on alumina are thought to participate in the conversion of guaiacol, both in the formation of heavier products and steps that lead to ring methylated products [22–24]. The effect of support acidity on the performance of the catalyst has also been studied by addition of pyridine as selective poison [22]. Laurent and Delmon have studied the inhibition of CoMo/Al_2O_3 and NiMo/Al_2O_3 catalysts under HDO conditions with water, ammonia and H_2S, concluding that oxygen elimination reactions are poisoned by sulfur- and nitrogen-containing compounds [25–27]. Senol et al. reported the conversion of phenol in the presence of H_2S and also concluded that both the formation of benzene and cyclohexene are inhibited [28]. Recently, a renewed interest in HDO reactions has resulted in an increasing amount of literature available on the HDO conversion of lignin-derived streams. New approaches include co-feeding aromatic lignin model compounds like guaiacol with straight run gas oil for the direct addition of oxygenates to fuel streams [29,30] and mixed HDO of aromatic and aliphatic oxygenates.

Furthermore, when using depolymerized lignin streams, it is likely that in addition to monoaromatic compounds also various dimers and small oligomers are present in the reaction feed, necessitating the study of fragments that mimic specific structural linkages found in lignin under HDO conditions. Romero et al. [31] and Edelman et al. [32], for instance, showed that benzofuran could be hydrogenated to dihydrobenzofuran, which was further converted to ethylphenol. Petrocelli and Klein researched the reactivity of lignin structural linkages by using biphenolic model compounds in their HDO experiments, which were shown to be stable under HDO conditions [33].

Valuable insights were obtained from these studies, but direct comparison of the reported data is hampered by the varying experimental conditions under which they have been obtained. Indeed, a systematic study of the conversion of a library of lignin model compounds with one batch of catalyst under comparable reaction conditions and in the same reactor system is still lacking.



Scheme 1. Monomeric model compounds phenol (**1**), *o*-cresol (**2**) *p*-cresol (**3**), anisole (**4**), 4-methylanisole (**5**), catechol (**6**), guaiacol (**7**), 4-methylguaiacol (**8**), 1,3-dimethoxybenzene (**9**), syringol (**10**), and vanillin (**11**).



Scheme 2. Model compounds mimicking the β-O-4 (**12**), 5–5′ (**13**), and phenylcoumaran (**14**) linkages typically found in lignin.

Here, we report on the conversion of lignin model compounds with the aim of obtaining bulk aromatics with lower oxygen content. Several hydroxy- and methoxy-substituted monomeric aromatic model compounds (Scheme 1) were used to conduct catalytic studies with a sulfided CoMo/Al_2O_3 catalyst using a single set of reaction conditions. For the first time, mono-, di-, and tri-oxygenated compounds as well as both methylated and non-methylated substrates are used to provide more insight in the reaction pathways responsible for product formation. A reaction network is presented to show the major reaction pathways and reaction selectivities in more detail. In addition to conversion of mono-aromatic model compounds, the effect of the catalyst system on linkages typically present in the lignin polymer was also studied. The model compounds shown in Scheme 2 were chosen to represent both the β-O-4 (**12**) and phenylcoumaran (**14**) ether linkages, as well as the 5-5′ aryl–aryl linkage (**13**), which can be found in the lignin structure.

2. Materials and methods

2.1. Chemicals and catalyst

All model compounds, additives, and solvents were used as received: Phenol, *o*-cresol, *p*-cresol, anisole (Fluka, 99%), 4-methylanisole (Sigma–Aldrich, 99%), catechol (Acros, 99%), guaiacol (Sigma–Aldrich, 99%), 4-methylguaiacol (Sigma–Aldrich, 99%), 1,3-dimethylbenzene (Sigma–Aldrich, >98%), syringol (Sigma–Aldrich, 99%), vanillin (Sigma–Aldrich, 99%), coumaran (Sigma–Aldrich, 99%), 2,2′-biphenol (Sigma–Aldrich 99%), hexadecane (Sigma–Aldrich, 99%), pyridine (Acros, 99%), dodecane (Acros, 99%), diethylether (Biosolve, solvent grade), and methanol

(Biosolve, solvent grade). Gases (hydrogen, 99.999% and argon, 99.999%) were obtained from Hoekloos.

The β-O-4 lignin model compound **12**, i.e., 1-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)ethane, was synthesized according to a literature procedure [34]. The product was purified using a silica gel column with a hexanes and ethyl acetate mixture (1:3) as eluent, followed by repetitive crystallization. The purity of the compound was confirmed by ^1H NMR.

The $CoMo/Al_2O_3$ catalyst obtained from Albemarle Catalysts was presulfided. Prior to its use, the catalyst material was crushed and sieved to particles of size between 150 and 450 μm that were activated under 60 mL/min H_2 flow at 300 °C for 3 h. The activation method is similar to the industrially used activation procedure for this particular catalyst. Addition of H_2S or other sulfiding agents to the H_2 flow was not needed, as a sulfiding agent was already present in the sample. To ensure that sulfur-loss was limited under conditions of a catalytic run, elemental analysis of the fresh and spent catalyst was performed at the Mikroanalytisches Laboratorium Kolbe. No loss of sulfur was found, but the elemental analysis data rather showed a marginal increase in sulfur content of the catalyst after reaction in absolute amounts (13% increase relative to Al). NO adsorption experiments were also performed on the fresh and spent catalyst by IR spectroscopy, the results of which can be found in the Supporting information.

2.2. Catalytic reactions

The catalytic reactions were performed in a 100-mL stainless steel high-pressure Parr batch autoclave reactor. The temperature was monitored using a thermocouple, and stirring was performed using a magnetic driver equipped with an impellor at 750 rpm. In a typical reaction, the autoclave was loaded with 150 mg of the catalyst material, 1.5 g substrate (typically guaiacol), 0.5 g hexadecane as internal standard, and 30 g of the solvent dodecane. A fresh batch of catalyst was used in every run. The reactor was purged three times with argon, and the reaction mixture was heated to 300 °C, unless stated otherwise, then pressurized with H_2 to 50 bar, and the catalytic reaction was carried out for 4 h. After the reaction was stopped by cooling and release of pressure, the reaction mixture was diluted with an equal volume of diethyl ether in order to dissolve all of the products, the solid catalyst was removed by filtration and washed with diethyl ether.

2.3. Analysis

The reaction products were analyzed using a Shimadu GC-2010A gas chromatograph equipped with a WCOT fused silica CP-WAX 57-CB column and FID detector, and a Varian 430-GC gas chromatograph equipped with a VF-5 ms capillary column and a FID detector. Compounds were identified with gas chromatography coupled with a mass spectrometer using a Shimadzu QP2010 GCMS instrument equipped with a VF-5 ms capillary column and compared with retention times of pure standards. Response factors relative to hexadecane were determined experimentally when authentic samples were available. The β-O-4 lignin model compound was silylated with *N,O*-bis(trimethylsilyl)acetamide before GC analysis. Gas-phase products were analyzed on an Interscience compact GC equipped with a molsieve 5A column and a TCD detector. ^1H NMR analysis was performed on a Varian 300 Inova MHz spectrometer. Thermal gravimetric analysis (TGA) was performed with a Perkin–Elmer Pyris 1 apparatus. Typically, 15 mg of impregnated silica gel was heated with a ramp of $5\,°C\,min^{-1}$ to 600 °C in a $10\,mL\,min^{-1}$ flow of air. In parallel evolved gas, analysis was performed with a quadrupole Pfeiffer Omnistar mass spectrometer, which was connected to the outlet of the TGA apparatus. Ion currents were recorded for m/z values (m = molar mass of $Xz+$ ion, z = charge of the ion) of 28 and 32.

3. Results and discussion

3.1. Conversion of monomeric model compounds

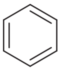
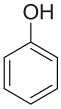
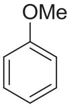
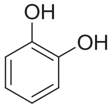
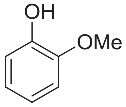
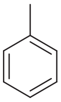
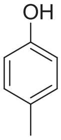
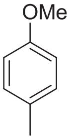
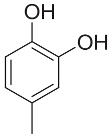
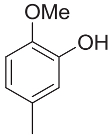
The conversion of the monomeric lignin model compounds **1**–**11** shown in Scheme 1 by a sulfided $CoMo/Al_2O_3$ catalyst was investigated under HDO conditions. General reaction conditions were 300 °C and 50 bar H_2 pressure. The catalytic results are reported in Table 1, and some general observations can be made based on the presented data. Conversions are found to differ widely after 4 h of reaction as only 20% of the substrate is converted for mono-oxygenated aromatics, whereas conversions of up to 90% are observed for some of the higher functionalized molecules, e.g., methylguaiacol and syringol, with mass balances that are closed from 56% for syringol to 96% for anisole. GC analysis of the liquid reaction product reveals complex reaction mixtures in which the main products vary depending on the reactant. High selectivities were obtained for benzene from phenol (**1**), phenol from anisole (**4**), and phenol and catechol from guaiacol (**7**). Methylated substrates, such as cresols (**2**,**3**) and methylguaiacol (**8**), give rise to methylated products. Furthermore, *o*- and *p*-cresol (**2**,**3**) were also found in reactions with non-ring-methylated substrates, e.g., selectivities up to 5% were obtained in the conversion of guaiacol. Unlike in the work of Gutierrez et al. where benzene was found to be the main product obtained from guaiacol, formation of completely deoxygenated products is not observed in large quantities [35].

In addition to *p*- and *o*-cresol, di- and trimethylated phenolics are also formed, as well as other methylated products, such as 4-methylguaiacol and toluene. Importantly, no quantifiable amounts of *m*-cresol were found, not even in the conversion of 4-methylguaiacol (**8**). For most reactions, mono-oxygenated products such as phenol make up the major part of the reaction mixture. In the case of syringol (**10**), however, also several di- and tri-oxygenated compounds are observed. The presence of small amounts of benzene and toluene in all reaction mixtures suggests that full deoxygenation does take place, albeit with low overall selectivity. The conversion of anisole and guaiacol, for instance, only yielded minor amounts of benzene, illustrating that it is not a major product in these reactions. The formation of mainly phenolics suggests that demethylation and deoxygenation are the main reaction pathways together with ring methylation (see Scheme 3 in which guaiacol is shown as a typical example).

Ring hydrogenation products, such as cyclohexanol, cyclohexene and methylcyclohexene, are only detected in low quantities with the total amount adding up to no more than 5 percent. In comparison, Hurff and Klein already found 10% cyclohexane after 4 h in the conversion of guaiacol with a sulfided $CoMo/Al_2O_3$ catalyst in the presence of sulfiding agent [19]. Bredenberg et al. also observed only small amounts of around 1% hydrogenation products in the conversion of guaiacol and anisole over a sulfided $NiMo/Al_2O_3$ catalyst in a continuous flow process [16]; nevertheless, over 5% ring hydrogenation was observed when a sulfiding agent was added to the feed [18]. Bui et al. reported around 4% hydrogenation products and found that the amount of hydrogenation products increases when a non-promoted MoS/Al_2O_3 catalyst is used [21].

For some reactions, not all products detected by GC could be unambiguously identified with either authentic samples or by GC–MS analysis. These products added together, however, do not represent more than a total selectivity of 4%. An overview of the most common reaction products is given in Table 1.

Table 1
HDO of different lignin model compounds over sulfided $CoMo/Al_2O_3$ catalyst at 300 °C and 50 bar H_2 pressure for 4 h.

	Conversion	Balance						Methylated products[b]	Hydrogenated products[c]	X[a]
Phenol	27	86	37	x	–	–	–	–	4	6
Anisole	58	96	10	64	x	–	–	10	3	–
Catechol	80	56	1	36	–	x	–	<1	4	4
Guaiacol	84	76	<1	34	3	11	x	19	3	–
1,3-Dimethoxy benzene	78	60	<1	3	2	–	–	2	1	40
Syringol	83	57	<1	1	<1	3	5	6	1	26
										
o-Cresol	23	95	65	–	–	–	–	–	3	12
p-Cresol	22	91	60	<1	–	–	–	1	6	–
4-Methylanisole	85	85	13	47	x	–	–	13	2	2
4-Methylguaiacol	89	91	2	42	–	13[d]	x	23	–	4
Vanillin	53	75	–	3	–	9	23	–	–	17

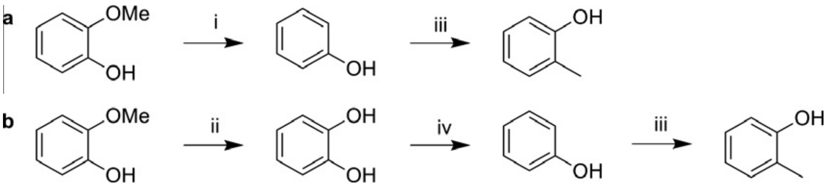
Selectivities are displayed as a percentage of the conversion in moles.

[a] X indicates the total sum of all other peaks in the chromatogram including dimethoxyphenol, methoxycatechol, resorcinol, dimethoxybenzene, methylmethoxyphenol, trimethoxybenzene, and 1,4-benzenediol.

[b] Methylated products include toluene, *p*- and *o*-cresol, di- and trimethylated phenols, 3- and 4-methylguaiacol, 4-methylcatechol and methylmethoxybenzene. For methylated substrates, only those products with more than one methyl functionality are included.

[c] Hydrogenated products include cyclohexene, cyclohexanol, methylcyclohexane, and methylcyclohexene.

[d] Both 4-methylguaiacol and 5-methylguaiacol are found in a 1:1 ratio.



Scheme 3. Reaction pathways in the conversion of guaiacol: (**a**) formation of phenol by HDO (i) followed by methylation to *o*-cresol (iii); (**b**) formation of catechol by demethylation (ii) followed by formation of phenol by HDO (iv) and methylation to *o*-cresol (iii).

3.2. Formation of heavy products

Intermolecular coupling between guaiacol or catechol-like molecules at higher temperatures can cause oligomerization, leading to higher molecular weight products [20,21]. When formed, these products cannot be detected by our GC analysis, resulting in mass balances that can be closed for 80–90% in most reactions. In general, we observe that substrates with more oxygen functional groups give a lower mass balance (e.g., syringol (**5**) 57% compared with guaiacol (**7**) 76%). Carbon balances of around 80% for di-oxygenated compounds such as guaiacol and around 90% for phenol and anisole, and 95% for methylated phenols are comparable to those previously reported for similar substrates [18–20,27]. The remainder being equal to the amount of heavy products observed by Bui et al. by GC–MS after gas-phase HDO of guaiacol [21,24]. In some cases, only the product distribution of the isolated products is published, leaving the not isolated products out of the mass balance [15,36]. Petrocelli and Klein found that the mass balance decreased with increasing reaction time [33] this is also indicative of an increase in formation of heavy products that could not be identified by GC methods. In our case, ESI-MS analysis of the reaction mixture indeed revealed some peaks of higher molecular weight in the product mixtures, but these products could not be identified. As blank reactions for guaiacol and anisole, run without catalyst, show a closed mass balance, it is clear that the side reactions that cause oligomerization of the substrate are also catalyzed by the sulfided $CoMo/Al_2O_3$ catalyst. Coke formation on the catalyst to such extent that it explains the observed weight loss, on the other hand, can be excluded. The catalyst sample shows no significant change in weight after reaction, whereas the missing weight should have increased the catalyst mass by 300%.

Thermogravimetric analysis of the spent catalyst was carried out to estimate the coke deposit after the reaction with guaiacol. The thermograms show a small increase in the formation of CO_2 with respect to the fresh catalyst and a total weight loss of 17%. Judging on the major weight loss at 440 °C, most of the coke formed on the catalyst is so-called hard coke, which consists of the more bulky and highly aromatic compounds [37].

3.3. Reaction network

The formation of several different products in each reaction suggests that HDO and O-demethylation reaction pathways, indicated

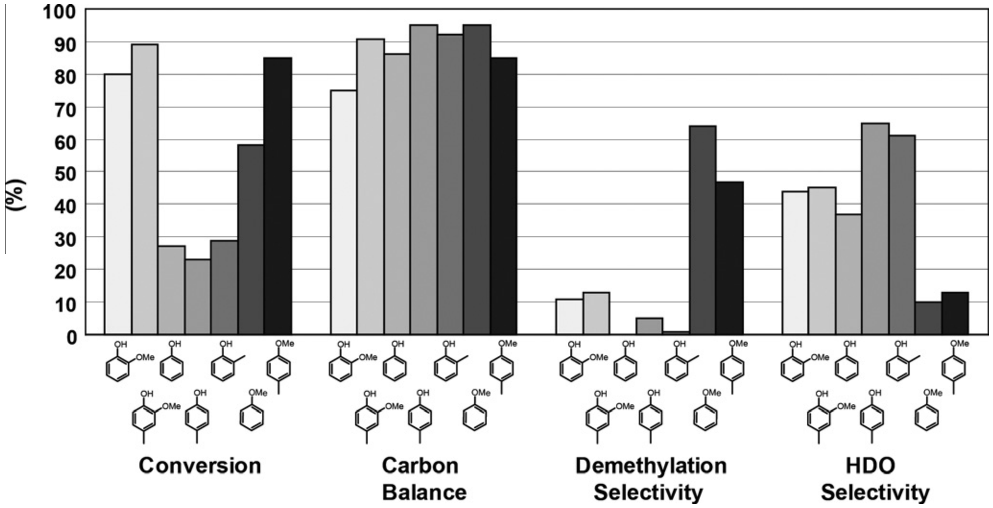


Fig. 1. Conversion, mass balance, demethylation, and HDO selectivity for ring methylated model compounds **2**, **3**, **5**, and **8** compared with non-methylated analogs **1**, **4**, and **7**.

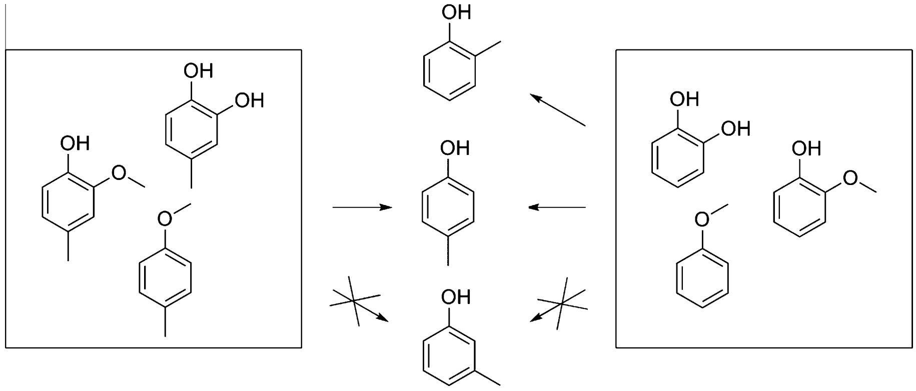
in Scheme 3, as well as the hydrogenation reaction pathway are taking place simultaneously. Depending on the substrate used, selectivity for one route may decline in favor of another. Nonetheless, the conversion of the different model compounds leads toward the formation of phenolic products via a combination of demethylation/dehydroxygenation steps. As previously observed, demethylation and methylation reactions are prone to take place on the alumina support [22–24].

Hydrogenation products are observed, but no oxygenated cyclohexanes are found. This implies that the demethylation and HDO reactions take place in an earlier stage of the reaction and that the reaction can be stopped at the point where HDO is completed before large amounts of hydrogenation products start to form.

Notable is the difference in reactivity of the compounds guaiacol (**7**), anisole (**4**), and phenol (**1**) compared with their ring-methylated derivates (**8**, **5**, **2** and **3**). As depicted in Fig. 1, conversion, mass balance, and selectivity toward deoxygenation products of the methylated substrates are slightly higher than for the non-methylated model compounds. The difference in HDO selectivity between phenol and both cresols is even more than 20%. Also, less ring methylation products are found for the methylated substrates. The presence of a methyl group on the ring, therefore, most likely makes addition of a second one sterically less favorable. The relative increase in HDO activity of the methylated compounds can also probably be attributed to steric factors, as a methyl group makes the aromatic ring more difficult to approach thus limiting alternative reactions, such as oligomerization and hydrogenation. It was previously noted that in order for hydrogenation to take place, the molecule must adsorb flat on the catalyst surface, whereas deoxygenation takes place by η_1 coordination of the oxygen on the edge of the MoS_2 phase [18,38]. Furthermore, in order for ring methylation reactions to take place, the aromatic ring must also approach the catalyst surface and forced non-planar coordination might hamper ring methylation reactions.

As most aromatic rings in the original lignin structure as well as in lignin-derived depolymerization feeds carry alkyl functionalities, the increased selectivity toward HDO observed for alkyl-substituted model compounds is useful when applied to lignin itself.

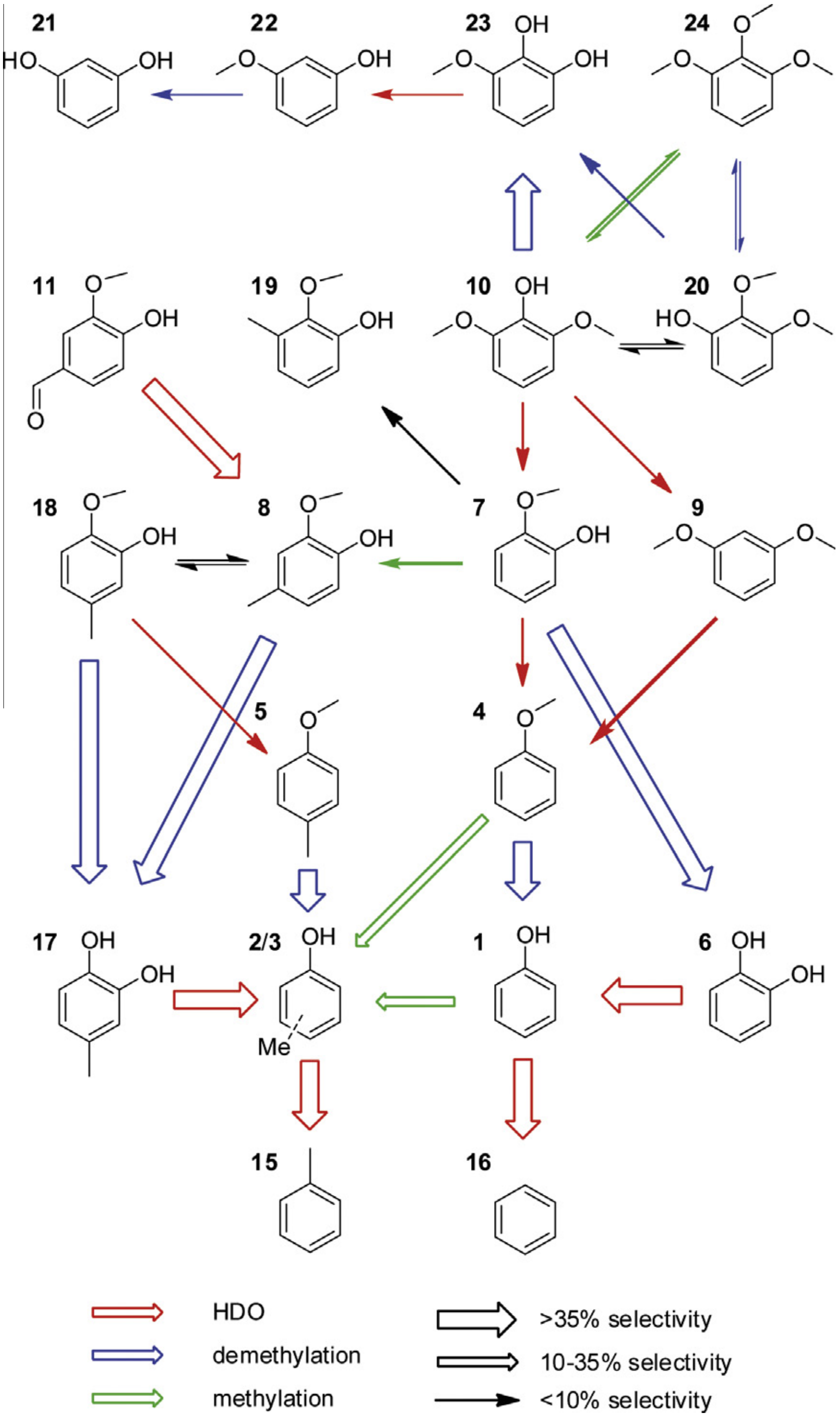
Several routes can be envisaged for the conversion of guaiacol to phenol and ultimately benzene. (i) The direct deoxygenation pathway (DDO) where phenol is formed via loss of the methoxy functionality; (ii) demethylation of the methoxy group followed by HDO. The phenol then further reacted toward benzene. Importantly, catechol (**6**) is observed as the main reaction intermediate in the conversion of guaiacol (vide infra), suggesting (ii) to be the dominant pathway. Experiments with catechol as the substrate also show that it readily reacts further via HDO to phenol (see Table 1). It is not clear, however, whether the reaction from guaiacol to phenol proceeds exclusively via catechol by means of consecutive demethylation and HDO (ii), or whether DDO (i) also takes place. Although minor amounts of methanol are clearly observed



Scheme 4. Formation of *o*- and *p*-cresol in the sulfided $CoMo/Al_2O_3$-catalyzed conversion of ring-methylated and non-methylated monoaromatic model compounds. No *m*-cresol was observed for any of the substrates.

by GC for some of the reactions, it was not possible to reliably quantify the amount of methanol formed by demethoxylation. Overall, these results thus indicate that the demethylation pathway (ii) is the major pathway in the conversion of guaiacol, with demethoxylation (i) most likely being only a minor route. This might be expected as a result of the higher bond strength of the MeO–Ar compared with the ArO–Me bond. Indeed, the bond dissociation energy for RO–Ar bonds (422 kJ/mol) is higher than for RO–R bonds (339 kJ/mol) [10]. The absence of large quantities of anisole combined with the lower reactivity of anisole compared with catechol under HDO conditions further supports that the major reaction pathway from guaiacol to phenol goes via catechol. There is no evidence, however, to fully exclude demethoxylation (ii) as one of the many reaction routes that take place simultaneously. These results are in agreement with Laurent and Delmon [20] and Bredenberg et al. [18], who also concluded that demethylation to form catechol is the first step in guaiacol deoxygenation. In contrast, in a general reaction network proposed by Petrocelli and Klein [33], it was concluded that demethylation was only a minor pathway.

Similarly, it is difficult to distinguish between the two possible routes for catechol formation from guaiacol, as both demethylation



Scheme 5. Reaction pathways in HDO of lignin model compounds. Hydrogenation is very limited, and these pathways are not included; arrow size contains no information on conversion.

as well as hydrogenolysis of the O–Me bond can be envisaged. The observation of various ring methylated structures in addition to some activity observed for the support itself (vide infra) points to the former route. Nonetheless, gas-phase analysis of a guaiacol conversion reaction shows some formation of methane, showing that hydrogenolysis also takes place, a least to a minor extent.

Interestingly, conversion of 4-methylguaiacol (**8**) gives methylated catechol (**17**) and *p*-cresol (**3**) as the main reaction products. As *p*-cresol is formed selectively and no *m*-cresol is observed, the HDO step must be selective for the oxygen in the 2 position. Reactions with *m*-cresol show no formation of *p*-cresol, so fast isomerization of this product can be excluded and *p*-cresol is the only cresol formed via HDO of methylated aromatics (Scheme 4). This is not in line with the results obtained by Bui et al. who reported the formation of *m*-cresol in the conversion of guaiacol over pure γ-alumina [24]. Huuska and Rintala [22] have previously reported a preference for ring methylation at the *o*-position in the conversion of anisole over a $NiMoS/Al_2O_3$ catalyst in a continuous flow system, claiming this as evidence for a non-planar orientation of the phenoxide ion. However, in the conversion of non-methylated substrates, we observe a slight excess in *p*-cresol over *o*-cresol, again no *m*-cresol is found (Scheme 4).

No evidence was found for ring demethylation reactions at equal or comparable rates to O-demethylation reactions. Catalytic tests on methylated model compounds, 4-methylguaiacol, 4-methylanisole and the cresols, show no formation of ring demethylated products. Small amounts of phenol that are found in cresol reaction mixtures can be attributed to impurities in the starting material. Reactions with 4-methylguaiacol, however, show evidence for reversible O-methylation, as equal amounts of 4-methylguaiacol and 5-methylguaiacol are found.

The use of both methylated and non-methylated substrates provided more insight in the mechanisms responsible for the formation of the observed products. Scheme 5 shows a reaction network for the reductive conversion of methoxy- and hydroxy-functionalized mono-aromatics over sulfided $CoMo/Al_2O_3$. The reaction pathways presented in this network are based on the experiments discussed above and those listed in Table 1. For the sake of simplicity, not all minor direct demethoxylation routes are shown in the proposed reaction network. However, when the demethylated intermediate was not identified, only direct demethoxylation routes are included, for example, in going from syringol (**10**) to guaiacol (**7**).

In summary, distinction is made in the reaction network between three types of reactions that occur simultaneously. The arrow size indicates reaction selectivity for this path, but does not contain information on conversion. All tested mono-aromatic model compounds follow the same three pathways that eventually lead to the formation of phenol and benzene or cresols and toluene.

- O-demethylation is the fastest pathway; the removal of methyl groups from methoxy functionalities is more favorable than direct demethoxylation. In the conversion of anisole, for instance, phenol is observed as the main product, whereas only small amounts of benzene were formed. O-demethylation goes hand in hand with methylation of the aromatic ring. Indeed, aromatic alkylations are observed in most reaction mixtures for which the *p*- and *o*-positions are strongly favored over the *m*-position. It is likely that also transfer of the methyl groups between hydroxy functional groups occurs, as is indicated by the isomerization of 4-methylguaiacol to 5-methylguaiacol. Methylation and demethylation activity are often attributed to support acidity [23,24].
- Hydrodeoxygenation is occurring at a slower rate than O-demethylation. Both methoxy and hydroxy groups can be removed via HDO although demethoxylation is much slower. Conversion of catechol has a selectivity of 36% to mono-oxygenated products, whereas dimethoxybenzene produces single oxygen products with a selectivity of around only 5% (note that these can also be formed by subsequent demethylation and deoxygenation). Substrates containing only one oxygen atom such as phenol and cresols (conversion ~20%) appear to be much more stable than higher functionalized aromatics such as catechol and guaiacol (conversion ~80%).
- Hydrogenation activity has been commonly observed with HDO catalysts. Only very small amounts of hydrogenation products are observed after 4 h, however, under our present conditions (<5%). Hydrogenated products mainly consist of cyclohexene and cyclohexanol, but in some cases also small amounts of methylated hydrogenation products are found. The low amounts of these products in the reaction mixture indicate that hydrogenation is the least favorable pathway for this system.

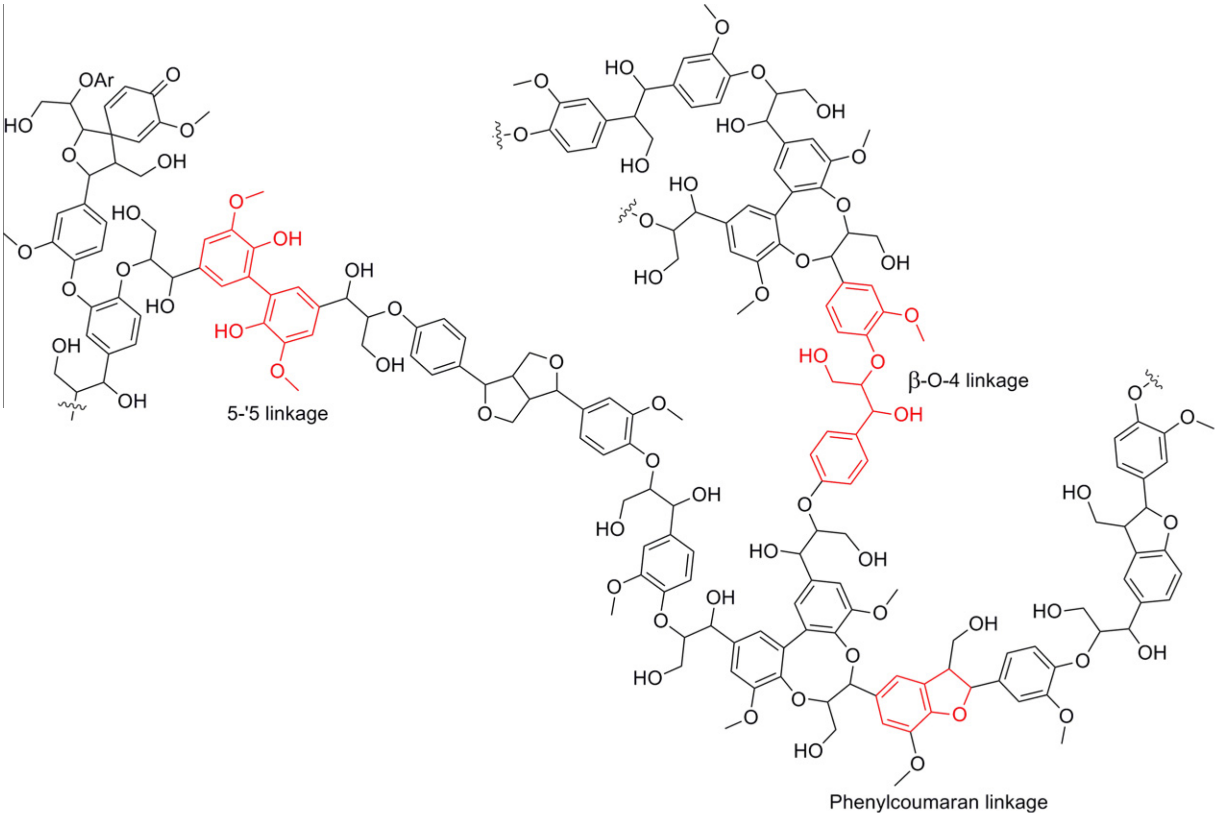
Although reactions starting from phenol and cresol show a high selectivity toward HDO products benzene and toluene, activity is rather low, as total phenol and cresol conversions are under 30%. This indicates that phenol itself is quite stable under the applied reaction conditions. From a lignin valorization point of view, phenol and cresols constitute attractive targets for this type of conversions. It is therefore important to note that starting from every position in the reaction network, phenol and cresols can indeed be obtained as the main reaction products under these process conditions.

3.4. Conversion of dimeric model compounds

During plant growth, the lignin polymer is generally believed to be formed via radical polymerization of three phenylpropane monomeric units, i.e., p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol [1]. As a result of the radical nature of lignin synthesis, many different linkages can be found in the resulting biopolymer. The most common of these linkages are the so-called β-O-4, 5–5′ and β-5 ones, which are present in different quantities in native lignin depending on the plant species and in processed lignin depending on the pretreatment method. Scheme 6 shows a typical softwood lignin fragment with some examples of different linkages highlighted. The β-O-4 linkage is by far the most abundant, and model compound **12** (Scheme 2) was synthesized to investigate the reactivity of this linkage under HDO conditions. The compounds 2,2′-biphenol (**13**) and coumaran (**14**) represent some key features of the 5–5′ and the phenylcoumaran-type linkages encountered in lignin and are commercially available.

The results of the HDO reaction of the β-O-4 lignin model compound **12** are shown in Table 2 and Scheme 7. ^1H NMR analysis of the reaction mixture showed complete conversion of the substrate **12**. Only mono-aromatic products could be identified by GC analysis with a total amount of 33% of aromatics recovered after 4 h of reaction; the presence of these monoaromatic compounds confirms cleavage of the β-O-4 bond under HDO conditions. Phenol, guaiacol, and syringol-like products are mainly obtained. No ethylbenzene derivatives could, however, be identified which indicates that all observed products likely originate from the syringol part of **12**.

2,2′-Biphenol (**13**) was used as a simple analog of the 5–5′lignin carbon–carbon bond. The results are shown in Table 3 and Scheme 8. 2,2′-Biphenol is not soluble in the reaction mixture at room temperature, leading to some losses of the remaining starting material during workup. This can in part account for the relatively low mass balance found in this reaction. Nonetheless, all detected products still contain the aryl–aryl linkage. The recalcitrance of the 5–5′ bond and its insensitivity toward chemical reactions is not unexpected, as previous research on treatments for lignin-derived



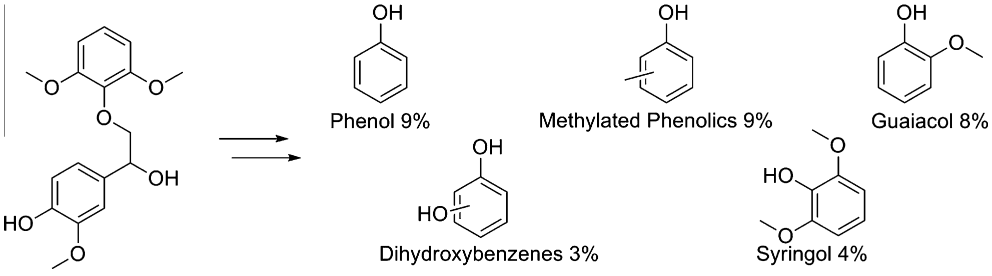
Scheme 6. Schematic representation of a softwood lignin structure, highlighting examples of the β-O-4, phenylcoumaran, and 5–5′ linkages.

Table 2
HDO conversion and selectivities in mol% of β-O-4 lignin model compound **12** over sulfided $CoMo/Al_2O_3$ catalyst at 300 °C and 50 bar H_2 pressure for 4 h.

Conversion (%)	100
Mass balance (%)	33
Phenol (%)	9
o-Oresol (%)	2
p-Cresol (%)	2
Dimethylphenol (%)	5
Catechol (%)	1
Resorcinol (%)	2
Guaiacol (%)	6
Methoxyphenol (%)	2
Syringol (%)	4

molecules always report the 5–5′ link to remain intact [33]. In line with the observations made for catechol and other bis-oxygen-functionalized substrates, only one hydroxy group is removed by HDO activity leading to a mono-oxygenated product. Possibly, at least one oxygen atom is needed for positioning of the molecule to the catalyst surface so that the other can react. Interestingly, large amounts of dibenzofuran are found in the reaction mixture. Dibenzofuran can be formed via an acid-catalyzed dehydration reaction of the 2,2′-biphenol in which the ring closing step is an intramolecular nucleophilic attack of one of the hydroxy groups [39,40]. This indicates that dibenzofuran and 2-hydroxybiphenyl are formed from 2,2′-biphenol via separate pathways and that dibenzofuran formation competes with HDO.

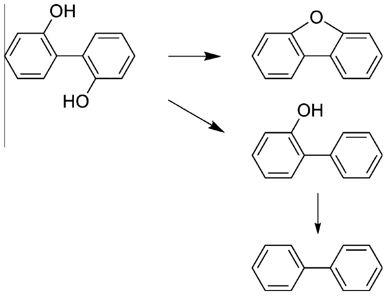
Dihydrobenzofuran or coumaran (**14**) is a common probe molecule for HDO reactions [31] and can serve as a model compound that resembles phenylcoumaran linkages in lignin. After reacting over a sulfided $CoMo/Al_2O_3$ catalyst for 4 h at 300 °C and 50 bar hydrogen pressure, 18% of the substrate was converted. As can be seen in Table 4 and Scheme 9, high selectivity toward 2-ethylphenol is obtained. This is in line with the results obtained by Romero et al. [31], who found 2-ethylphenol to be the main product and ethylbenzene the main deoxygenated product after HDO over a $NiMoP/Al_2O_3$ catalyst using a fixed-bed reactor. They contributed the low conversions to an inhibitive effect of coumaran itself on the HDO activity of the catalyst. The obtained results do



Scheme 7. Conversion of β-O-4 dimer **12**.

Table 3
HDO conversion and selectivities in mol% of 2,2′-biphenol (**13**) over sulfided $CoMo/Al_2O_3$ catalyst at 300 °C and 50 bar H_2 pressure for 4 h.

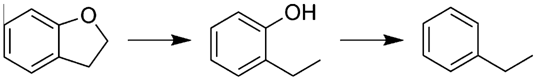
Conversion (%)	55
Mass balance (%)	79
Biphenyl (%)	2
2-Hydroxybiphenyl (%)	22
Dibenzofuran (%)	34
Tetrahydrodibenzofuran (%)	4



Scheme 8. Conversion of 2,2-biphenol (**13**) to dibenzofurane, 2-hydroxybiphenyl and biphenyl.

Table 4
HDO conversion and selectivities in mol% of coumaran (**14**) over sulfided $CoMo/Al_2O_3$ catalyst at 300 °C and 50 bar H_2 pressure for 4 h.

Conversion (%)	18
Mass balance (%)	97
Ethylbenzene (%)	3
Phenol (%)	6
2-Ethylphenol (%)	65



Scheme 9. Conversion of coumaran.

indicate that, albeit at low conversion, it is possible to cleave the alkyl–oxygen bond in phenylcoumaran linkages with a sulfided $CoMo/Al_2O_3$ catalyst. Cleavage of this ether bond is a promising result leading to weakening of the lignin structure, also with respect to other ether linkages present in lignin, such as β–β or dibenzodioxocin linkages.

4. Conclusions

The hydrodeoxygenation of mono-aromatic lignin model compounds on a sulfided $CoMo/Al_2O_3$ catalyst at 300 °C and 50 bar H_2 pressure gives products with lowered oxygen content as well as demethylated and ring methylated products. An extended reaction network shows that the reactions take place via demethylation of methoxy groups followed by deoxygenation. Mono-oxygenated compounds like phenol are very stable under the applied conditions, and almost no full deoxygenation products are observed. Together with a minor hydrogenation route, they lead to the formation of phenol and cresols in high selectivities for most starting materials. Conversion of dimeric model compounds that mimic lignin linkages shows that both the β-O-4 and β-5 ether linkages can be broken under HDO conditions. The rigidity of the 5–5′ linkage prevents cleavage of the 5–5′ model compound 2,2′-biphenol.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2011.10.006.

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