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Unravelling Some of the Key Transformations in the Hydrothermal Liquefaction of Lignin

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Abstract: Using both experimental and computational methods, focusing on intermediates and model compounds, we elucidate some of the main features of the reaction mechanisms that operate during the hydrothermal processing of lignin. We propose key reaction pathways and their connection to different structural features of lignin. Under neutral conditions, subcritical water was demonstrated to act as a bifunctional acid/base catalyst for the dissection of lignin structures. In a complex web of mutually dependent interactions, guaiacyl units within lignin were shown to significantly affect overall lignin reactivity.

Hydrothermal liquefaction (HTL) is becoming an important process to convert biomass into fuel and chemicals.^[1] This process involves the heating of biomass feedstock in water at moderate to high temperature (250–500 °C) and pressure (5–25 MPa).^[2] A base catalyst is often added to improve the performance of the conversion process. HTL is superior to many other biomass conversion processes in terms of the relatively low oxygen content of the resulting liquids. Thus, e.g. bio-oils, produced from the HTL process are of significantly higher energy density than pyrolysis oils. It is particularly attractive for the conversion of wet biomass since, unlike gasification or pyrolysis treatments, pre-drying of feedstock is unnecessary. Besides the liquid bio-oils, gaseous products (mostly CO₂ and minor amounts of, e.g. CH₄ and H₂) are also formed as a result of HTL.^[3]

Lignin constitutes 25–35% of the organic matrix of lignocellulosic biomass, adding strength and rigidity to cell walls.^[4] The complex structure of lignin contains aromatic units connected by linkages such as β -O-4, α -O-4, 4-O-5, 5-5, β -5 and β - β cross-links. Of these, the β -O-4 linkage predominates, accounting for over 50% of the cross-links.^[5] Functional groups such as benzylic alcohols^[6] as well as methoxy-groups^[7] are also present on the aryl rings. Additionally, lignin is the most readily available source of renewable aromatics and is a major by-product of the paper and pulp industries.^[8]

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conditions when linkages such as β -O-4 and α -O-4 are broken down through free radical chemistry and react further in pericyclic reactions.^[10]

The hydrothermal conversion of benzyl phenyl ether, a simple model compound reminiscent of α -O-4 linkages, has been studied by Siskin/Katritzky^[11] and Lercher^[12]. They demonstrated that the ether hydrolyzed to benzyl alcohol and phenol. Furthermore, it was proposed that the stable benzyl cation intermediate, arising from benzyl alcohol, abstracted a hydride to give toluene or alkylated the phenol fragment.^[11] In another study, Barbier and co-workers examined the hydrothermal conversion of 4-(benzyloxy)phenol as a model for the α -O-4 linkage at 370–390 °C.^[13] The conversion of 4-(benzyloxy)phenol was similar to that of benzyl phenyl ether: The ether compound was hydrolyzed to generate hydroquinone and benzyl alcohol, hydroquinone then underwent ring benzylation.

Vanillin (benzaldehyde) structural units (Figure 1) have been found in lignin samples^[14] as end-groups^[15] and vanillin is recovered in large amounts following the basic extraction and hydrothermal conversion of lignin.^[16,17] Vanillin is therefore proposed to be a key intermediate. Besides vanillin units, coniferaldehyde (cinnamaldehyde) units (Figure 1) are also commonly found as end-groups in lignin.^[15] A NMR study by Capanema *et al.* showed that spruce milled wood lignin contains 4 units/100 Ar of coniferaldehyde and 5 units/100 Ar of vanillin subunits respectively.^[18]



Figure 1. Coniferaldehyde (left) and vanillin (right) end-groups in lignin.

To understand the conversion of coniferaldehyde units under hydrothermal conditions, cinnamaldehyde 1 and 3,4dimethoxycinnamaldehyde 2 (Scheme 1), which act as model compounds of coniferaldehyde units, were heated to 350 °C with water or aqueous NaOH (0.1 M) solution under N₂ for 10 min, in a 316 stainless steel reactor using rapid heat transfer via a fluidized sand bath followed by a fast quench. The 3,4dimethoxy groups of 2 represent the guaiacyl subunits found in coniferaldehyde. Under neutral conditions, benzaldehyde (70%) was the major product obtained from the conversion of 1. The conversion of 2 was quantitative, giving 90% yield of veratraldehyde. Cinnamaldehyde is known to hydrolyze to benzaldehyde and acetaldehyde in the presence of base catalysts such as NaOH^[19] and Al-Mg hydrotalcite,^[20] and it has been suggested that these products are formed through retroaldol condensation. DFT calculations at the B-PW91/6-31+G(d) level show that the hydrations of 1 and 2 are both associated with reasonable barriers of ca 120 kJ mol⁻¹, indicating viable conversion to alcohols 3 and 4 (Scheme 1). Under subcritical COMMUNICATION

greater concentrations of OH^- and H^+ , both of which are likely to be involved in the catalysis of the hydrolysis process. In our proposed mechanism, Michael addition of OH^- to **1** and **2**, with carbonyl group activation by H^+ , followed by keto-enol tautomerization gives the hydration products **3** and **4**. These species then undergo retro-aldol reactions generating the benzaldehyde derivatives (**5** and **6**) and acetaldehyde.



Scheme 1. Conversion of coniferaldehyde units under neutral hydrothermal conditions.

Benzaldehyde is found to be the major product from **1** in both neutral *and* basic media (from hydration and subsequent retro-aldol reaction). Under basic conditions, benzyl alcohol and benzoic acid were also observed in addition to the major product. Previously, Strauss and co-workers reported that benzaldehyde decomposes in 0.1 M NaOH at 290 °C in 60 min, undergoing a Cannizzaro reaction to give benzoic acid and benzyl alcohol.^[21] When **2** was converted under similarly basic conditions, the major products were vanillin, guaiacol and catechol. Vanillin was likely to be formed by methyl group hydrolysis of veratraldehyde **6**, which itself was produced by the retro-aldol process, described above, being detected in trace amounts by GC-MS.

To better understand how catechol and guaiacol were formed, the hydrothermal conversions of 3,4-disubstituted benzaldehydes (veratraldehyde and vanillin) were then examined under neutral and basic conditions (350 °C, 160-170 bar, 10 min). When veratraldehyde (6) was reacted under neutral conditions, the methoxy groups on the aromatic ring were hydrolyzed affording vanillin and isovanillin (Figure S1 in Supporting Information). A trace amount of veratrole was generated in the process. Conversely, when 6 was heated with aqueous sodium hydroxide solution, a significantly greater amount of veratrole as well as guaiacol, veratryl alcohol and veratric acid were formed. It was evident that the base played an important role in removing the carbonyl group from veratraldehyde (6). In addition, the presence of veratryl alcohol and 4-methylveratrole, formed by reduction of the starting material, is consistent with a transfer hydrogenation process occurring in-situ.

A set of reactions that unify all of these processes is shown in Scheme 2. The theoretical viability of this mechanism was examined using quantum chemical computations at the B-PW91/6-31+G(d) level. The corresponding reaction profile is shown in Figure 2: for the uncatalyzed decarbonylation, there is a high barrier of 375 kJ mol⁻¹. The carbon monoxide could then undergo an (uncatalyzed) water-gas shift reaction to generate hydrogen and carbon dioxide. In comparison, the addition of a hydroxide to veratraldehyde has a barrier of 31 kJ mol⁻¹, which is followed by dehydrogenation of the carboxylate with a barrier of 122 kJ mol⁻¹. The water-assisted decarboxylation is associated with a barrier of 173 kJ mol⁻¹, and this completes the overall reaction. Thus, hydroxide does appear to provide a significantly lower-energy pathway for the generation of veratrole

with overall reaction barriers of 407 kJ mol⁻¹ for the uncatalyzed process and 108 kJ mol⁻¹ for the catalytic one.



Scheme 2. Conversion of coniferaldehyde and vanillin units under basic hydrothermal conditions.

Sawama and Sajiki^[22] demonstrated previously that aliphatic and aromatic aldehydes can be converted to the corresponding carboxylic acid in the presence of NaOH and noble metal catalysts. In particular, benzyl alcohols were converted to benzoic acids with Pd/C and Rh/C catalysts at low temperatures (80-100 °C). It was proposed that the hydroxide ion of NaOH facilitated the formation of a geminal diol. The benzoic acids were then generated as a result of the dehydrogenation of geminal diols. Our calculations support such a proposal, i.e. that veratrole is generated from the hydration of giving veratric acid, which veratraldehvde. thermally decarboxylates. It is noteworthy that benzoic acid, which lacks any alkoxy groups, does not readily decarboxylate under these conditions. In addition, the proposed mechanism is also consistent with our independent results showing thermal decarboxylation of veratric acid at 350 °C to veratrole, which then undergoes rapid hydrolysis of one methoxy group affording quaiacol.





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The hydrogen generated in the dehydrogenation of geminal diols could be utilized for the reduction of veratraldehyde. In parallel a classical Cannizzaro reaction might take place, as in the report of Strauss and co-workers.^[21] The presence of 4-methylveratrole however, suggested that hydrogenolysis of veratryl alcohol occurred. In separate HTL experiments, some veratryl alcohol dehydrogenated to veratraldehyde, liberating reductive equivalents which were able to hydrogenolyse a portion of the remaining veratryl alcohol to 4-methylveratrole (and water). In these processes the stainless steel reactor wall potentially acted as a catalyst for the (de)hydrogenations and hydrogenolyses.^[23]

Similarly, when vanillin was heated under neutral conditions only a trace of guaiacol was generated. But heating under basic conditions generated a variety of products, including guaiacol, catechol and 4-methylguaiacol. The formation of these products is consistent with the mechanism describing the conversion of veratraldehyde (Scheme 2). In addition, "scrambling" of methoxy groups was also observed as veratraldehyde, veratrole and 4-methylveratrole were formed. Under basic conditions, methanol generated by hydrolytic demethylation may methylate phenoxide groups. Alternatively, direct methyl group transfer, e.g. from veratraldehyde to guaiacolate, may also occur.

To understand how the β -O-4 linkage reacts under hydrothermal conditions, model compound 7, which has been used in other conversion studies,^[24] was subjected to hydrothermal treatment under both neutral and basic conditions. Only trace products were generated when 7 was heated with water at 350 °C for 10 min. Conversely, 7 was fully converted to give acetophenone and phenol under basic conditions (0.1 M NaOH). Rather than hydrolysis to give styrene glycol and phenol, the linkage was broken down by hydroxide-mediated elimination in which the phenoxide acted as the eventual leaving group, with the resultant enol tautomerizing to acetophenone. Indeed, our DFT calculations indicate that the conversion to acetophenone is thermodynamically favorable, with both steps shown in Scheme 3 being exothermic (by 68 and 77 kJ mol⁻¹ for the first and second step, respectively). The first step involving proton abstraction by hydroxide, has a low calculated reaction barrier of 20 kJ mol⁻¹.



Scheme 3. Conversion of $\beta\mbox{-}O\mbox{-}4$ model compound 7 under basic hydrothermal conditions.

To strengthen our conclusions we investigated the conversion of a β -O-4 compound (8) with guaiacyl instead of phenyl subunits^[23b], which much more closely resembles a typical lignin linkage. Under neutral HTL conditions, various products were formed. Besides trace amount of the "base-catalyzed" product 3,4-dimethoxyacetophenone, enol ether compounds (compound 9 as *E*/*Z* isomers), 3,4-

dimethoxyphenylacetaldehyde and phenol were detected as major products by GC. A possible reaction pathway is shown in Scheme 4, consistent with the enol ether compounds having been generated as a result of dehydration of the model compound **8** by means of acid-catalyzed elimination. To verify that the enol ether compounds are the intermediates that generate phenol and (3,4-dimethoxyphenyl)acetaldehyde, compound **9** (predominantly *Z*) was subjected to the same hydrothermal treatment. As predicted, phenol and 3,4dimethoxyphenylacetaldehyde were formed. Proton transfer to **9** was facilitated by the increase in self-ionization of water at 350°C by more than 2 orders of magnitude and the resulting intermediate was hydrolyzed to form the monomeric products.



Scheme 4. Conversion of β-O-4 model compound **8** under neutral hydrothermal conditions.



To underpin these mechanistic interpretations, we have performed DFT computations for these acid-catalyzed pathways (for both **7** and **8**, Figure 3). Together with the modeling for the base-catalyzed reactions for **7**, the calculations enable us to elucidate the features that lead to the different reaction outcomes. Whereas the steps involved in the base-catalyzed reaction of **7** are all exothermic, the first step of the acid-catalyzed reaction, namely protonation of **7**, is endothermic (by 69 kJ mol⁻¹). Thus, under neutral (equilibrium) conditions in which protonation is thermodynamically fairly unfavorable, the acid-catalyzed reaction does not proceed.

The electron-donating alkoxy substituents on **8** facilitate the formation of the carbocation intermediate, with the first step being endothermic by only 35 kJ mol⁻¹. This intermediate then further undergoes a series of near-thermoneutral or exothermic transformations to form the (3,4-dimethoxyphenyl)acetaldehyde and phenol products. Overall, the difference in the reactivities of **7** and **8** can be attributed to the difference in the thermodynamics of the initial protonation. We note that a similar mechanism was indeed suggested for the acidic hydrolysis of model compound **7**.^[25] Such a proposal is also consistent with our calculated energetics. Thus, under acidic conditions where the endothermic protonation of **7** is facilitated, subsequent steps with more favorable thermodynamics then occur.

Once again, subcritical water acted as a bifunctional catalyst in the HTL of β -O-4 linkage, even though the acid catalysis route is the dominant pathway.

Thus, lignin HTL is dominated by ionic, rather than radical chemistry. Under neutral conditions, water is a bifunctional catalyst, promoting base-catalyzed hydrations/retro-aldol reactions and acid-catalyzed E1-eliminations/hydrolyses. Basic conditions facilitate a reaction cascade, coupled with transfer hydrogenation/hydrogenolysis likely promoted by the reactor wall. In the context of lignin HTL, the energy-density of the biooil product is increased by oxygen atom removal as H₂O through elimination and hydrogenolysis and as CO_2 from thermal decarboxylation: with the decarboxylation and hydrogenolysis steps coupled by hydrogen transfer processes.

Only when appropriate model compounds, containing substituents which mimic key (stereo)electronic effects of the lignin backbone are studied, can the intricacies of lignin behavior under HTL be unravelled. The combined approach of experimentation and computational evaluation, provides a coherent, unifying account of the otherwise seemingly disparate reaction pathways which operate simultaneously during the HTL processing of lignin.

Experimental Section

Experimental Details are provided in the accompanying Supporting Information.

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Keywords: Biomass • Lignin • Hydrothermal Liquefaction • Density Functional Theory • Mechanism

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

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Water, water everywhere and all the bonds did shrink: A tandem experimental/computational approach to understand complex processes that proceed during the hydrothermal liquefaction of lignin is presented. The choice of the right model compounds to represent key linkage-motifs and end-group functionalities is paramount for achieving realistic insight into these reaction cascades.



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