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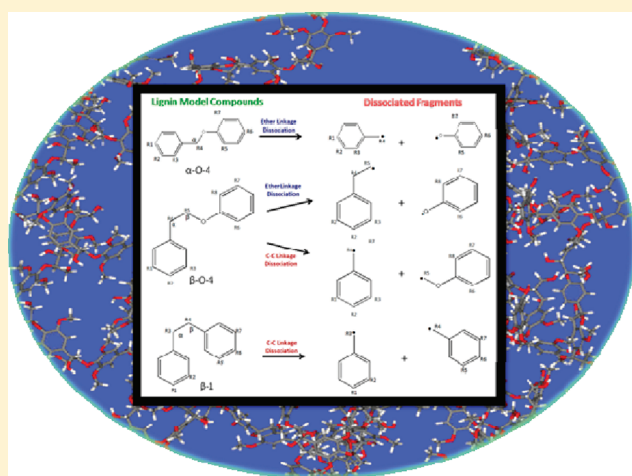
Theoretical Study of the Remarkably Diverse Linkages in Lignin

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Supporting Information

ABSTRACT: Lignin in plant cell walls is a potential renewable source of biofuels, chemicals, and value-added products. It consists of various aryl ethers, irregularly connected by a variety of linkages creating a complex structural network; hence, it is difficult to identify selective bond breaking events. In this study, we predict dissociation tendencies of a diverse set of lignin linkages encompassing 65 lignin model compounds using the density functional theoretical (DFT) approach. The chosen 65 lignin model compounds represent the most prevalent carbon–oxygen (ether) and carbon–carbon (C–C) bond linkages. Results from our systematic study identify the weakest and strongest linkages connecting arene rings in different classes of lignin model compounds. Also, the dissociating linkages can have different adjacent substituents, such as the methoxy group on the arene ring and hydrocarbon, methyl, and hydroxyl group substitutions on aliphatic carbon atoms. These substituents affect the ease of dissociation of lignin linkages and can be used to develop predictive models for delignification.

SECTION: Molecular Structure, Quantum Chemistry, General Theory



Plant cell walls consist of structural polysaccharides, cellulose, hemicellulose, and lignin, all of which provide shape, elasticity, and rigidity as well as protection to plants. Lignin is one of the most abundant naturally occurring aromatic biopolymers and acts as the essential glue that gives plants their structural integrity and fortification.^{1–3} It is a main constituent of lignocellulosic biomass (15–30% by weight, 40% in energy content), together with cellulose and hemicelluloses.⁴ Owing to its exceptional structure and varied chemical properties, a broad range of valuable bulk and fine chemicals, particularly aromatic compounds, as well as fuels, are potentially derivable from lignin.⁵ A recent perspective⁶ highlights that lignin is an attractive raw material for biofuels due to its relatively low oxygen to carbon ratio compared to cellulose and hemicellulose. The potential of lignin is yet to be fully realized and depends on developing selective transformations of the complicated lignin network.

Lignin results from the polymerization of three different cinnamyl alcohols: *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. These monolignols lead to 4-hydroxyphenyl (H), guaiacyl (4-hydroxy-3-methoxyphenyl, G), and syringyl (4-hydroxy-3,5-dimethoxyphenyl, S) units in lignin.⁷ The formation of lignin and the ratio of the three units change with the different types of cells and plants.¹ Lignin from grass is built up from H, G, and S units; softwood lignins essentially consist of G

units; hardwood lignin is from G and S units. Lignin compounds can be classified into two broad groups, namely, ether (C–O) linked lignins and carbon–carbon (C–C) bonded lignins, which contain β -O-4, 5-5, β -5, 4-O-5, β -1, dibenzodioxocin, and β - β linkages, of which the β -O-4 linkage is predominant.⁸ Interestingly, ether and C–C linkage patterns vary among plant species with different types of substitutions.⁹ A detailed summary of the identification and quantification of various structures and linkages in lignins can be found in the literature.^{1,3}

During the past three decades, several studies have been carried out on lignin degradation using mechanical, thermal, extractive, chemical, enzymatic, and microbial approaches.^{1,3,10–21} Here, we focus on lignin chemistry relevant to thermal delignification. Typically fast and slow pyrolysis protocols are considered in thermal delignification. Fast, high-temperature pyrolysis techniques such as flash vacuum pyrolysis (FVP) (500–600 °C, < 0.3 s residence time) involve primarily unimolecular decompositions such as bond breaking and intramolecular rearrangements.¹⁸ Slow pyrolysis occurs in the liquid phase at lower temperatures

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(345–400 °C, several minutes reaction time) allowing additional bimolecular and radical chain processes.^{19,20}

Extensive experimental and theoretical studies have been conducted on phenethyl phenyl ether (PPE), a model for the lignin β -O-4 linkage.^{18–25} Britt et al. studied FVP of methoxy-substituted β -O-4 lignin model compounds in order to provide mechanistic insight into the relevant reaction pathways.^{18–20} Beste and co-workers have demonstrated the substitution effects on the homolysis of PPE.^{10,22–25} More recently, Elder reviewed the pyrolysis reactions on lignin model compounds and reported the homolytic cleavage reactions and chain propagating steps in thermal degradation of substituted β -O-4 linked dilignols using quantum chemical calculations.¹⁷ Under pyrolysis conditions, however, the rate and product distribution are substantially influenced by different substituents on the arene rings and linkages connecting the rings.

Even under FVP conditions, it is difficult to deduce how substitutions of different chemical groups in ring and linkage positions influence the initial homolysis event.^{12,14,18,22} As this initial event also determines the nature of product distribution from multiple reaction pathways, we have studied the initial homolytic cleavage of the carbon–oxygen bond and the carbon–carbon bond linkages. We have used quantum chemical approaches similar to those applied recently to characterize the catalytic conversion of lignin models to explore the initial homolytic cleavage reactions.¹¹ In the previous study, results from density functional theory (DFT) calculations on lignin model compounds were not only successful in predicting the bond dissociation energies (BDEs) and reactivity trends on experimentally observed product selectivities, but emphasized the roles of electron delocalization and methoxy group effects on radical cation formation.

Here, we calculate the BDEs of the ether and C–C bond linkages in 65 unique lignin model compounds with different substituents on the arene rings and aliphatic carbons connecting the rings for which no measured bond strengths exist. We examine this diverse set of lignin linkages³ to predict the relative ease of selected bond fragmentations and to quantify the molecular basis of delignification. Schemes 1 and 2 show the chosen lignin model compounds with ether and C–C linkages. Model compounds with these linkages involve dimeric arenes with varying methoxy and hydroxyl substituents on the arene rings, resembling dimers of *p*-coumaryl or coniferyl alcohols.

We have chosen 33 ether-linked lignin model compounds from β -O-4, α -O-4, and 4-O-5 subtypes (Scheme 1). The most abundant linkage in lignin is the β -O-4 linkage, which contains both ether and C_α - C_β linkages. The ether bond is readily cleaved; indeed, the fragmentation of these linkages tends to lead to the generation of water-soluble compounds containing phenolic hydroxyl groups.³ α -O-4 linked model compounds are present as part of the dibenzodioxocin or phenylcoumaran structural units, and the 4-O-5 aryl-aryl ether linkage is present in lignin mainly as the result of oligomer–oligomer couplings and leads to branching of the lignin polymer.³

To study representative C–C bonds (Scheme 2), we have selected 32 model compounds containing the subtypes of β -1, α -1, β -5, and 5-5 C–C linkages. The β -5 linkage is often found in a five-membered ring linking two aromatic structures. The C–C linkages in lignin constitute some of the most difficult bonds to break, but ether linkages are generally relatively weaker than C–C linkages. Of course, high-temperature processes are

not important for the biological role of lignin,¹ but the magnitude of the BDE of the various linkages can determine the product spectrum in thermal degradation (pyrolysis and combustion) processes.

The calculated bond distances of the C–C and ether linkages from the optimized geometries of lignin model compounds are reported in Table 1. Optimized structures for the lignin model compounds are presented in the Supporting Information. As mentioned above, the selected 65 model compounds can be classified into two broad categories depending on whether they contain ether or C–C bond linkages. Within the ether bond linkage types, 4-O-5 compounds contain the shorter linkages (shortest, L33 = 1.373 Å), and the β -O-4 and α -O-4 compounds tend to have longer ether bond lengths. The longest bond lengths are seen in β -O-4 (1.44 Å in L15) and α -O-4 (1.43 Å L29) compounds. In the C–C linkage category, the β -1 linkages, in L35, L42, and L45 compounds, generally comprise the larger C–C bond lengths (1.55 Å). The exceptions occur for the double bonded β -1 compounds (L43 and L44). The C–C bond lengths observed in the β -5 linkage subtypes are shorter, with a bond distance around 1.46 Å. In general, the linkages with ether bonds are comparatively shorter than those with C–C linkages except for those with C–C double bonds in the β -1 linkage subtype compounds.

The BDEs at 298 K (ZPE corrected) for the ether and the C–C linkages of the 65 lignin compounds are also shown in Table 1. Overall, except for the 4-O-5 type, the β -O-4 and α -O-4 ether linkages are found to be weaker than the C–C linkages. Ether bonds in 4-O-5 type linkages are the strongest and also exhibit the shortest bond lengths, as one would expect. Recently, nickel catalyzed hydrogenolysis has been shown to break these strong 4-O-5 ether linkages.²⁶ Calculations reveal that L27 from the α -O-4 subgroup (48.31 kcal/mol) and L39 (64.7 kcal/mol) from the β -1 subgroup are the weakest bonds in the ether and C–C bond categories, respectively. We find the weakest ether linkages among the α -O-4 types (48.31–51.32 kcal/mol), followed by β -O-4 types, one of the highly abundant linkages in nature, and followed by other linkages of the α -O-4 type. In the C_α - C_β linkage category, β -1 type bonds are the weakest (64.7–69.14 kcal/mol). They are followed by the β -O-4 linkage types, with C_α - C_β BDEs ranging between 72.05 and 80.07 kcal/mol. It is quite likely that the fragmentation in these β -O-4 linkage types is facilitated by the weaker ether linkages instead of the C_α - C_β cleavage; α -1 types show higher C–C BDEs compared to the β -O-4 and β -1 linkage types. Our calculations reveal that it will be difficult to cleave the β -5 and 5-5 C–C bonds as they exhibit BDEs of 110 kcal/mol or more. Therefore, fragmentation of these linkages probably requires catalysts or ring deformation reactions.^{1,3}

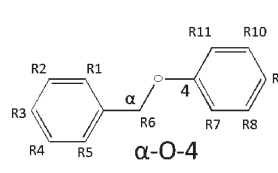
Next, we consider the effect of both ring and aliphatic carbon substitutions on BDEs. Previous studies have primarily considered ring substitutions with respect to the reactivity of lignins.¹⁰ Substitutions on the aliphatic carbons linking the arene rings significantly alter the BDEs of ether and C–C linkages and, hence, should influence homolysis selectivity.^{1,3,10} Figure 1 compares the ranges of the averaged BDEs at 298 K for lignin model compounds with ether and C–C linkages. To avoid confusion, C_α - C_β double bond linkages were grouped separately from the C_α - C_β bond linkage of β -1 model compounds. A complete ranking list of the BDEs is given in Figure S1 (see Supporting Information). The lowest BDEs are seen for α -O-4 linked lignin compounds in the ether linkage category where the arene

Scheme 1. Lignin Model Compounds (β -O-4, α -O-4, and 4-O-5 with Ether Linkages)^a

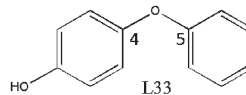
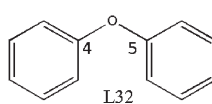
β -O-4

β -O-4	R1, R5, R6, R7, R9, R10 = H
L1	R2=H, R3=OH, R4=H, R6=OH, R7=CH2OH, R8=OCH3, R11=H, R12=H
L2	R2=H, R3=OH, R4=OCH3, R6=OH, R7=CH2OH, R8=OCH3, R11=H, R12=H
L3	R2=H, R3=OH, R4=OCH3, R6=OH, R7=CH2OH, R8=OCH3, R11=H, R12=OCH3
L4	R2=H, R3=OCH3, R4=OCH3, R6=OH, R7=CH2OH, R8=OCH3, R11=H, R12=H
L5	R2=H, R3=OCH2CH3, R4=OCH3, R6=OH, R7=CH2OH, R8=OCH3, R11=H, R12=H
L6	R2=H, R3=OH, R4=OCH3, R6=OH, R7=H, R8=OCH3, R11=COOH, R12=H
L7	R2=H, R3=OCH2CH3, R4=OCH3, R6=OH, R7=CH2OH, R8=OCH3, R11=H, R12=OCH3
L8	R2=H, R3=OCH2CH3, R4=OCH3, R6=O, R7=CH2OH, R8=OCH3, R11=H, R12=H
L9	R2=H, R3=OCH2CH3, R4=OCH3, R6=O, R7=H, R8=H, R11=H, R12=H
L10	R2=OCH3, R3=OH, R4=OCH3, R6=OH, R7=CH2OH, R8=H, R11=H, R12=H
L11	R2=OCH3, R3=OH, R4=OCH3, R6=OH, R7=H, R8=OCH3, R11=COOH, R12=H
L12	R2=H, R3=OH, R4=OCH3, R6=O, R7=H, R8=OCH3, R11=H, R12=H
L13	R2=H, R3=OCH3, R4=OCH3, R6=OH, R7=H, R8=OCH3, R11=H, R12=H
L14	R2=H, R3=OCH3, R4=OCH3, R6=O, R7=H, R8=OCH3, R11=H, R12=H
L15	R2=H, R3=OCH3, R4=OCH3, R6=O, R7=CH3, R8=OCH3, R11=H, R12=H
L16	R2=H, R3=H, R4=H, R6=CH2, R7=H, R8=H, R11=H, R12=H
L17	R2=H, R3=OCH3, R4=OCH3, R6=OH, R7=CH3, R8=H, R11=H, R12=H
L18	R2=H, R3=H, R4=H, R6=O, R7=H, R8=H, R11=H, R12=H
L19	R2=H, R3=H, R4=H, R6=CH2, R7=H, R8=H, R11=H, R12=OH
L20	R2=H, R3=H, R4=H, R6=CH2, R7=H, R8=OH, R11=H, R12=OH
L21	R2=H, R3=H, R4=H, R6=CH2, R7=H, R8=OCH3, R11=H, R12=OCH3

R6 – A HYDROGEN ATOM WAS NOT ADDED IF A KETO OXYGEN WAS PRESENT

 <p>α-O-4</p>	α -O-4	R1, R2, R8, R10 = H
L22	R3=H, R4=H, R5=H, R6=H ₂ , R7=OCH ₃ , R9=CH ₂ CH ₂ CH ₃ , R11=H	
L23	R3=H, R4=H, R5=H, R6=H ₂ , R7=H, R9=H, R11=H	
L24	R3=H, R4=H, R5=OCH ₃ , R6=H ₂ , R7=H, R9=H, R11=H	
L25	R3=OCH ₃ , R4=OCH ₃ , R5=H, R6=H ₂ , R7=H, R9=H, R11=H	
L26	R3=OCH ₃ , R4=OCH ₃ , R5=H, R6=H ₂ , R7=OCH ₃ , R9=H, R11=H	
L27	R3=OCH ₃ , R4=OCH ₃ , R5=H, R6=H ₂ , R7=OCH ₃ , R9=H, R11=OCH ₃	
L28	R3=OCH ₃ , R4=H, R5=H, R6=H ₂ , R7=H, R9=H, R11=H	
L29	R3=OCH ₃ , R4=H, R5=H, R6=H ₂ , R7=OCH ₃ , R9=H, R11=H	
L30	R3=OCH ₃ , R4=H, R5=H, R6=H ₂ , R7=OCH ₃ , R9=H, R11=OCH ₃	
L31	R3=H, R4=OCH ₃ , R5=H, R6=H ₂ , R7=OCH ₃ , R9=H, R11=OCH ₃	

4-O-5

^a β -O-4 contains both ether and carbon–carbon linkages.

rings are linked through single aliphatic carbon and oxygen atoms. Mulder's group has shown that under pyrolytic degradation α -O-4 ether bond is the weakest lignin linkage with high product yield.¹

Within the α -O-4 linkages category, methoxy group substitutions at the di-*ortho* position in the arene ring adjacent to the ether bond give rise to the lowest BDEs, single methoxy substitutions at *ortho* positions result in higher BDEs, and even higher BDEs are seen in α -O-4-linked compounds when there are no substitutions in the *ortho* position. The weakening of ether linkage can be attributed to steric hindrance induced

by the *ortho*-methoxy groups.¹ The incorporation of the methoxy substitutions into the arene ring adjacent to the ether bond significantly reduced C–O BDEs for the α -O-4 compounds (~ 6 and ~ 8 kcal/mol for one and two methoxy substituents, respectively). Similar substitution patterns studied by Beste and Buchanan¹⁰ for β -O-4 compounds also showed the same trends in bond strength of ether linkages akin to our work. They reported C–O (69.5 kcal/mol) and C–C (77.1 kcal/mol) linkage BDEs for a compound identical to the L16 model compound in this work, where our calculated bond strengths are 68.5 and 76.1 kcal/mol for C–O and C–C bonds,

Scheme 2. Lignin Model Compounds (β -1, α -1, β -5, and 5-5) with Carbon–Carbon Linkages

β -1

β -1	R1, R2, R5, R6, R7, R8, R12 = H
L34	R3=OCH3, R4=OCH3, R6=OH, R7=OH, R9=H, R10=H, R11=H
L35	R3=OH, R4=OH, R6=H, R7=H, R9=H, R10=OCH3, R11=OH
L36	R3=OCH3, R4=H, R6=OH, R7=CH2OH, R9=H, R10=OCH3, R11=H
L37	R3=OCH3, R4=H, R6=OH, R7=OH, R9=H, R10=OCH3, R11=H
L38	R3=OCH2CH3, R4=OCH3, R6=OH, R7=CH2OH, R9=H, R10=OCH3, R11=H
L39	R3=OCH3, R4=OCH3, R6=OH, R7=CH3, R9=H, R10=H, R11=H
L40	R3=OCH2CH3, R4=OCH3, R6=OH, R7=CH2OH, R9=H, R10=OCH2CH3, R11=OCH3
L41	R3=OCH3, R4=OCH3, R6=OH, R7=CH2OH, R9=H, R10=OCH3, R11=OCH3
L42	R3=H, R4=H, R6=H, R7=H, R9=H, R10=H, R11=H
L43	R3=H, R4=H, R6=R7, R9=H, R10=H, R11=H
L44	R3=H, R4=H, R6=R7, R9=OCH3, R10=OH, R11=OCH3
L45	R3=OH, R4=OCH3, R6=H, R7=H, R9=H, R10=OH, R11=OCH3
L46	R3=OH, R4=OCH3, R6=OH, R7=CH2OH, R9=H, R10=OH, R11=H

α -1

α -1	R1, R11= H
L47	R2=CH3, R3=H, R4=OH, R5=OCH3, R6=H2, R7=OCH3, R8=OH, R9=H, R10=CH3
L48	R2=CH2OH, R3=H, R4=CH3, R5=OH, R6=H2, R7=OH, R8=CH3, R9=H, R10=CH2OH
L49	R2=CH2O, R3=H, R4=OCH3, R5=OCH3, R6=H2, R7=OCH3, R8=OCH3, R9=H, R10=CH2O
L50	R2=OCH3, R3=OH, R4=OCH3, R5=H, R6=H2, R7=H, R8=OCH3, R9=OH, R10=OCH3
L51	R2=H, R3=H, R4=H, R5=H, R6=OH, R7=H, R8=H, R9=H, R10=H
L52	R2=CH3, R3=H, R4=OCH3, R5=OH, R6=H2, R7=OH, R8=OCH3, R9=H, R10=CH3
L53	R2=H, R3=H, R4=H, R5=H, R6=H2, R7=H, R8=H, R9=H, R10=H

β -5

β -5	R2, R4, R6, R9, R10 = H
L54	R1=OH, R3=CH2CH2CH3, R5=CH3, R7=OCH3, R8=OH
L55	R1=H, R3=CH2CH2COOCH3, R5=COOCH3, R7=H, R8=OH
L56	R1=OCH3, R3=CH2CH2COOCH3, R5=COOCH3, R7=OCH3, R8=OH
L57	R1=H, R3=CH2CH2CH3, R5=CH3, R7=OCH3, R8=OCH2CH3

5-5

5-5	R1, R3, R6 = H
L58	R2=CH3, R4=OCH3, R5=OH, R7=CH3, R8=H, R9=OCH3, R10=OH
L59	R2=CH2CH2CH3, R4=OCH3, R5=OH, R7=CH2CH2CH3, R8=H, R9=OCH3, R10=OH
L60	R2=CH3, R4=OH, R5=OH, R7=CH3, R8=H, R9=OH, R10=OH
L61	R2=CHO, R4=OCH3, R5=OCH2CH3, R7=CHO, R8=H, R9=OCH3, R10=OCH2CH3
L62	R2=H, R4=H, R5=OH, R7=H, R8=H, R9=H, R10=OH
L63	R2=H, R4=H, R5=H, R7=H, R8=H, R9=H, R10=OH
L64	R2=H, R4=H, R5=H, R7=H, R8=H, R9=H, R10=H
L65	R2=H, R4=H, R5=OH, R7=H, R8=OH, R9=H, R10=H

respectively. Lower BDEs for the β -O-4 linkage types are seen for compounds with a carbonyl group at the C_α position and an aliphatic carbon at the C_β position with methoxy substitution at the *ortho* position in the arene ring adjacent to an ether linkage. Note that our calculations suggest that the presence of *ortho*-methoxy substitutions tends to lower the BDEs of ether linkages in both α -O-4 and β -O-4 model compounds. These observed trends are consistent with a FVP experiment that showed methoxy groups at *ortho* and *di-ortho* positions enhance the homolysis of the β -O-4 ether linkage.^{17,20}

In the C-C linkage category, the lowest BDEs are seen in the β -1 C_α - C_β bond types. An interesting observation is that in β -1 model compounds, substitution of a hydroxymethyl group (CH_2OH) at the C_β position results in higher BDEs, whereas substitution at the C_α position with a hydroxyl group or substitution at the C_β position with methyl, hydrocarbon, and hydroxyl groups lowers the C_α - C_β bond strength. Unsurprisingly, β -1-type linkages with C_α - C_β double bonds exhibit the highest BDEs among all model compounds containing C-C bond linkages. In the β -O-4 linkage category, substitutions at C_β with methyl or CH_2OH groups lower the C_α - C_β bond

Table 1. Computed Bond Distances and Respective BDEs of the C–C and Ether Bond Linkages of Different Classes of Lignin Model Compounds

β -O-4	bond distances (Å)		BDE - ZPE corrected (kcal/mol)		β -1	bond distances (Å)		BDE - ZPE corrected (kcal/mol)	
	C–C bond	ether bond	C–C bond	ether bond		C–C bond	C–C bond		
L1	1.531	1.431	75	66.38	L34	1.541		65.29	
L2	1.531	1.429	75.46	67.33	L35	1.546		67.54	
L3	1.53	1.427	75.71	64.61	L36	1.541		68.83	
L4	1.531	1.429	75.48	67.04	L37	1.541		66.62	
L5	1.53	1.429	75.58	67.1	L38	1.54		68.59	
L6	1.523	1.424	76.4	68.35	L39	1.543		64.7	
L7	1.53	1.427	75.74	64.3	L40	1.542		69.14	
L8	1.536	1.432	79.09	56.54	L41	1.541		68.87	
L9	1.526	1.412	77.75	59.88	L42	1.546		68.54	
L10	1.54	1.423	76.99	72.3	L43	1.338		165.8	
L11	1.524	1.426	76.25	68.71	L44	1.339		162.1	
L12	1.524	1.425	80.07	55.96	L45	1.546		67.83	
L13	1.523	1.423	76.11	65.91	L46	1.541		68.53	
L14	1.525	1.425	79.75	55.75	α -1	C–C		C–C	
L15	1.537	1.438	78.8	53.94	L47	1.518		91.59	
L16	1.523	1.416	76.09	68.45	L48	1.516		92.56	
L17	1.533	1.422	72.05	69.35	L49	1.517		93.33	
L18	1.525	1.41	78.13	59.64	L50	1.518		90.94	
L19	1.523	1.428	77.08	64.39	L51	1.518		86.27	
L20	1.522	1.429	77.73	62.24	L52	1.516		92.74	
L21	1.523	1.428	78.45	61.37	L53	1.518		90.26	
α -O-4		O–C		O–C	β -5	C–C		C–C	
L22		1.428		50.24	L54	1.461		125.5	
L23		1.421		56.43	L55	1.462		127.1	
L24		1.412		57.28	L56	1.462		127.6	
L25		1.422		56.24	L57	1.461		125.2	
L26		1.43		51.32	5-5	C–C		C–C	
L27		1.428		48.31	L58	1.484		117.3	
L28		1.421		56.34	L59	1.485		117.3	
L29		1.432		50.62	L60	1.484		117	
L30		1.429		48.45	L61	1.488		118.4	
L31		1.427		48.89	L62	1.485		117.5	
4-O-5	C–O	O–C	C–O	O–C	L63	1.485		114.9	
L32		1.375		82.54	L64	1.484		115.4	
L33	1.373	1.382	82.28	77.74	L65	1.483		116.5	

strengths. These compounds with low C_α – C_β bond strengths tend to contain hydroxyl substitutions at the C_α position. Unlike the case in ether bond linkages where the presence of a methoxy group, particularly in the *ortho* positions, lowers the ether bond strength, methoxy substitution has only a negligible effect on the C–C BDEs. In the α -1 linkage category, hydroxyl substitutions on the linkage aliphatic carbon lower the bond strength. Overall, arene ring substitutions have a negligible effect on C–C BDEs in model compounds in the C–C linkage category.

Finally, we evaluate the level of correlation between the calculated bond lengths and the corresponding BDEs at 298 K of the linkages in the 65 lignin model compounds treated here. As shown in Figure 2, a linear regression analysis was performed. We find a strong ($R = 0.94$) linear relationship between C–C bond distances and BDEs where the stronger bonds are shorter and weaker bonds are longer. However, ether bonds do not

exhibit such a strong correlation ($R = 0.58$). Thus, one cannot reliably predict bond strengths from the ether bond linkage distances. This also indicates that, unlike the case with C–C bond linkages, substitutions on the linkage carbon and on the arene ring adjacent to the ether linkage impact the ether linkage in a more complicated manner. One of the key factors that influences the ether linkage is *ortho*-methoxy substitution induced steric strains. Overall, the bond distance can serve as a good indicator of bond strength for C–C bond linkages, whereas substitution patterns serve as a good indicator of bond strengths for ether bond linkages.

We have calculated the BDEs of ether and C–C linkages in 65 lignin model compounds, to capture the salient features of the dominant linkages found in the lignin polymer. The model compounds were selected with different linkages containing key substitutions on the arene rings and on the linkage aliphatic

carbons that might significantly change the ether and C–C linkage BDEs and, hence, the homolysis selectivity. The magnitudes of the ether and C–C linkage bond strengths are influenced by the nature and location of these substitutions. In general, it is easier to fragment the ether bond than the C–C bond. The ether bond in the α -O-4 linkage type is found to be the weakest linkage among the different ether lignin linkages studied in this investigation. The C_α – C_β bond of β -1 linkages has the lowest BDE among the lignin model compounds with C–C bond linkages.

The ether linkage is substantially weakened when substituted by electron donating methoxy groups on the adjacent arene ring in the *di-ortho* positions. On the other hand, the C–C linkage BDE is influenced by hydrocarbon, methyl, and hydroxyl group substitutions at the aliphatic carbon positions in the linkage. In the case of C–C bond linkages, the effect of the substitution can be inferred from a strong correlation between the bond distances and strengths. However, in the case of ether bond linkages, such a strong correlation is not seen, and the effect of

substitutions cannot be predicted so easily. The reported results for the lignin model compounds provide valuable information regarding the chemistry of lignin degradation and possible transformations to value-added products. It also offers details that could be useful in the selection and genetic design of plants having types of lignin structures that lead to optimal efficiencies for feedstock or biofuel production.

COMPUTATIONAL DETAILS

The geometry optimizations of 65 model lignin compounds reported in this article (Schemes 1 and 2) were performed using DFT with the M06-2X hybrid exchange-correlation functional²⁷ and the 6-311++G(d,p) basis set in the gas phase using the Gaussian 09 suite of programs.²⁸ This meta-hybrid density functional chosen in this study has been shown to provide excellent performance for main-group thermochemistry and kinetics.²⁷ The M06-2X functional was tested in recent studies for reaction energies involving radicals including the BDE of methyl benzyl ether ($\text{CH}_3\text{O}-\text{CH}_2\text{Ph}$) and proved to be in good agreement with the G3(MP2)-RAD method.²⁹ Beste et al. and Elder verified the reliability of this method in predicting properties of β -O-4 linked lignin compounds and showed reasonable agreements with measurements for anisole and *ortho*-substituted phenethyl phenyl ether (PPE-*o*-CH₃).^{10,17} It is worth noting that our calculated BDE (66.04 kcal/mol, ZPE corrected) value for the anisole ($\text{C}_6\text{H}_5\text{O}-\text{CH}_3$; methoxybenzene) ether bond is in very good agreement with the experimental BDE of 65.3 kcal/mol.¹ The BDE predicted in our calculation is better than those of the G3MP2 (66.7 kcal/mol) and CBS-4 m (67 kcal/mol) methods for this molecule.¹⁷ BDEs were obtained as the difference of the sum of the energies of the dissociated product fragments and the energy of the molecule.

$$\text{BDE} = (E_{\text{Frag1}} + E_{\text{Frag2}}) - E_{\text{Mol}} \quad (1)$$

where E_{Mol} is the total energy of the molecule, E_{Frag1} and E_{Frag2} are energies of the dissociated products through the selected linkage (either the ether or C–C linkage). All dissociated fragments were fully optimized. Low-energy conformations were studied in all cases and were confirmed to be minima by means of frequency calculations. In addition, the energies of these model

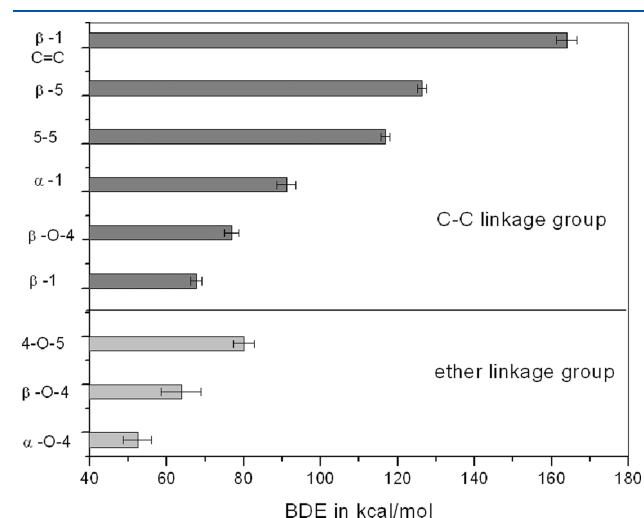


Figure 1. Comparison of averaged BDEs for the lignin model compounds with ether and C–C linkage groups. Standard deviations are also shown in the figure.

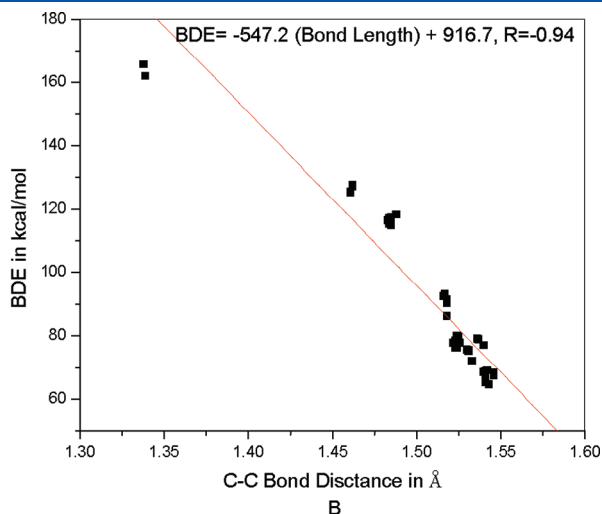
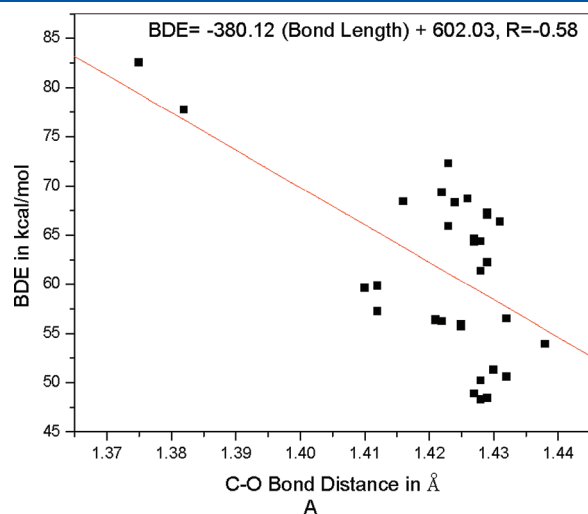


Figure 2. Correlation plots of the BDEs versus the corresponding computed bond lengths for different lignin compounds. (A) Ether linkage BDEs versus their bond lengths. (B) C–C linkage BDEs versus bond lengths.

compounds and their fragments were corrected by including the zero-point energies (ZPEs), and the thermal contributions at 298.15 K were also added. Although pyrolysis reactions occur at much higher temperatures, 298 K is defined as the standard state for enthalpy calculations.^{10,17}

■ ASSOCIATED CONTENT

S Supporting Information. A schematic representation of lignin and the most dominant linkages studied in this work. Optimized structures for the 65 lignin model compounds are also provided as well as complete reference 28. This material is available free of charge via the Internet at <http://pubs.acs.org>

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