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Modeling Study of Woody Biomass: Interactions of Cellulose, Hemicellulose, and Lignin

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ABSTRACT: Lignocellulosic biomass pretreatment and the subsequent thermal conversion processes to produce solid, liquid, and gas biofuels are attractive solutions for today's energy challenges. The structural study of the main components in biomass and their macromolecular complexes is an active and ongoing research topic worldwide. The interactions among the three main components, cellulose, hemicellulose, and lignin, are studied in this paper using electronic structure methods, and the study includes examining the hydrogen bond network of cellulose–hemicellulose systems and the covalent bond linkages of hemicellulose–lignin systems. Several methods (semiempirical, Hartree–Fock, and density functional theory) using different basis sets were evaluated. It was shown that theoretical calculations can be used to simulate small model structures representing wood components. By comparing calculation results with experimental data, it was concluded that B3LYP/6-31G is the most suitable basis set to describe the hydrogen bond system and B3LYP/6-31G(d,p) is the most suitable basis set to describe the covalent system of woody biomass. The choice of unit model has a much larger effect on hydrogen bonding within cellulose–hemicellulose system, whereas the model choice has a minimal effect on the covalent linkage in the hemicellulose–lignin system.

1. INTRODUCTION

Biomass, or bioenergy, is one of the most important alternatives energies because of environmental concerns and the future shortage of fossil energies. The utilization of biomass has the potential benefits of decreasing pollutant generation and being CO₂ neutral. Biomass is presently estimated to contribute about 14% of the world's energy supply.¹ Woody biomass represents the most abundant and available biomass source. Of the total sustainable worldwide biomass energy potential, which is about 100 EJ/a, the share of woody biomass is 41.6 EJ/a.¹ Biofuels from woody biomass, commonly called cellulosic or second generation fuels, are shown to have advantages over other fuels, including reducing greenhouse gas emissions and yielding a more favorable energy input–output ratio.² The thermal, biological, and mechanical conversion technologies for woody biomass have been studied extensively using experimental methods. As an important step for practical biomass conversion technologies, pretreatment is used extensively as a result of the potential for large improvements in efficiency and lowering costs through research and development. Biomass pretreatment is used to alter the macroscopic and microscopic chemical composition and structure of biomass so that the subsequent processing steps can be achieved more rapidly and with greater yields. Many experimental studies have already examined various pretreatment methods. However, modeling studies aimed at understanding the detailed mechanisms occurring in pretreatment process, especially on an atomic/molecular level, have remained elusive until recently.

Biomass structure simulations can be very important when studying the biomass pretreatment process and the subsequent conversion steps. The main components of woody biomass are cellulose, hemicellulose, and lignin. Cellulose is a natural linear polysaccharide in which D-glucopyranose rings are connected to one another with β -(1-4)-glycosidic links. Native cellulose is

composed of two phases, I α and I β .^{3,4} Cellulose from biomass contains the I α and I β crystalline allomorphs together with surface and disordered chains.^{5,6} Matthews et al.⁷ described the structure of cellulose using molecular mechanics simulations. It was concluded that different force field conformational preferences at the scale of a single cellobiose molecule lead to the radically different macroscopic properties of cellulose fibrils; however, the distribution of hydrogen bond angles and distances in these dramatically different structures is similar. Hemicelluloses^{8,9} are heterogeneous polymers made of pentoses (xylose, arabinose), hexoses (mannose, glucose, galactose), and sugar acids. Hemicelluloses in agricultural residues mainly consist of xylose and arabinose.⁹ Lignin from biomass is structurally variable with the plant species, but three major monolignols present in lignin polymers are coniferyl alcohol (G-units), paracoumaryl alcohol (H-units), and sinapyl alcohol (S-units).

Extensive studies were also carried out to investigate the interaction of the main components in biomass. Computer simulations of lignocellulosic biomass were provided by Petridis et al.,¹⁰ and they investigated the underlying molecular mechanisms governing the assembly of various cellulosomal modules. Hydrogen bonding is recognized as one important linkage between cellulose and hemicellulose as a result of the many suitable hydrogen bonding sites that exist in these polysaccharides.^{11–13} There are also intramolecular hydrogen bonds that exist in cellulose⁴ and xylan.¹⁴ For lignin, it was proposed that a pure lignin fraction is not present in wood because all of the lignin was found to exist chemically linked to polysaccharides.¹⁵ In spruce wood, a total of six lignin–carbohydrate complexes (LCCs) was obtained.

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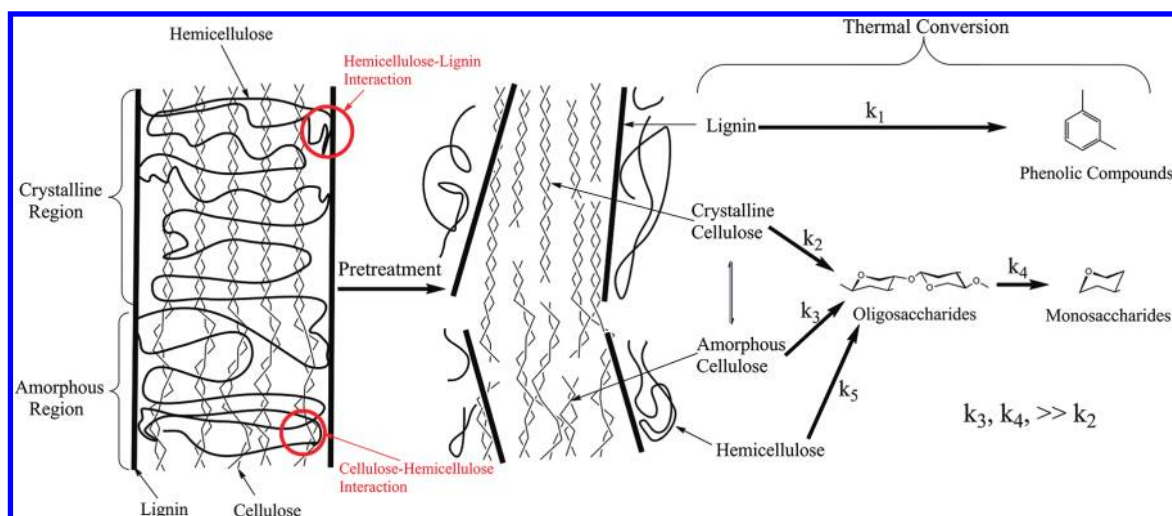


Figure 1. Schematic representation of the pretreatment of lignocellulosic biomass from literature studies.^{16,22,27–29}

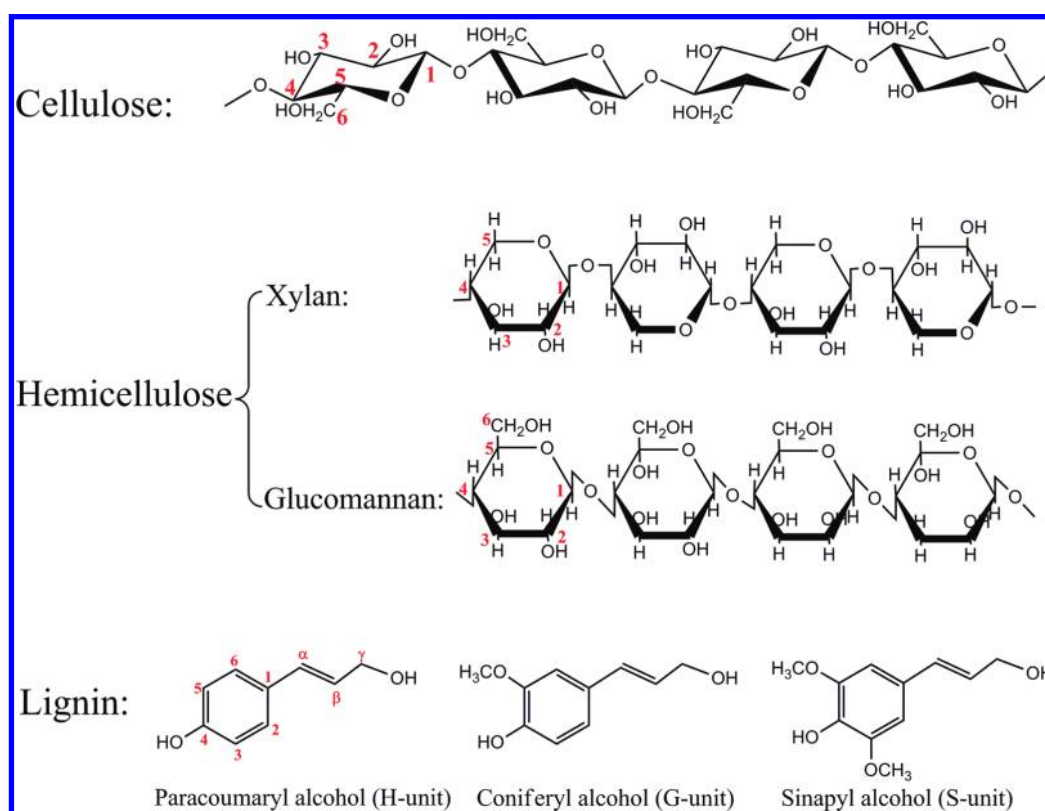


Figure 2. Structures of cellulose, hemicellulose, and lignin.

One of these was a glucomannan–lignin–xylan complex made predominantly of glucomannan over xylan, which contained 48% of the lignin present in the wood. Another complex, namely, xylan–lignin–glucomannan, which contained predominantly xylan over glucomannan, contained 40% of the lignin.^{15–17} Therefore, the study of complexes that contain glucomannan, lignin, and xylan is important when investigating the linkage of lignin and hemicellulose, and this type of complex contains 33.6% mannose, 12.5% glucose, and 41% lignin.¹⁵

Considerable experimental and simulation work has been carried out related to the structure of cellulosic biomass and its

main components. However, studies of the detailed interactions, which are aimed at finding out the mechanism of biomass pretreatment and further thermal conversion processes, are less prevalent. This work investigated the interactions between cellulose, hemicellulose, and lignin in the biomass cell wall to fill the gap in the engineering development and the fundamental understanding. The hydrogen bond network between cellulose and hemicellulose (mainly xylan and glucomannan) and the covalent linkage between lignin and hemicellulose were investigated in this paper using electronic structure methods. The linkages were investigated using different levels of electron structure methods,

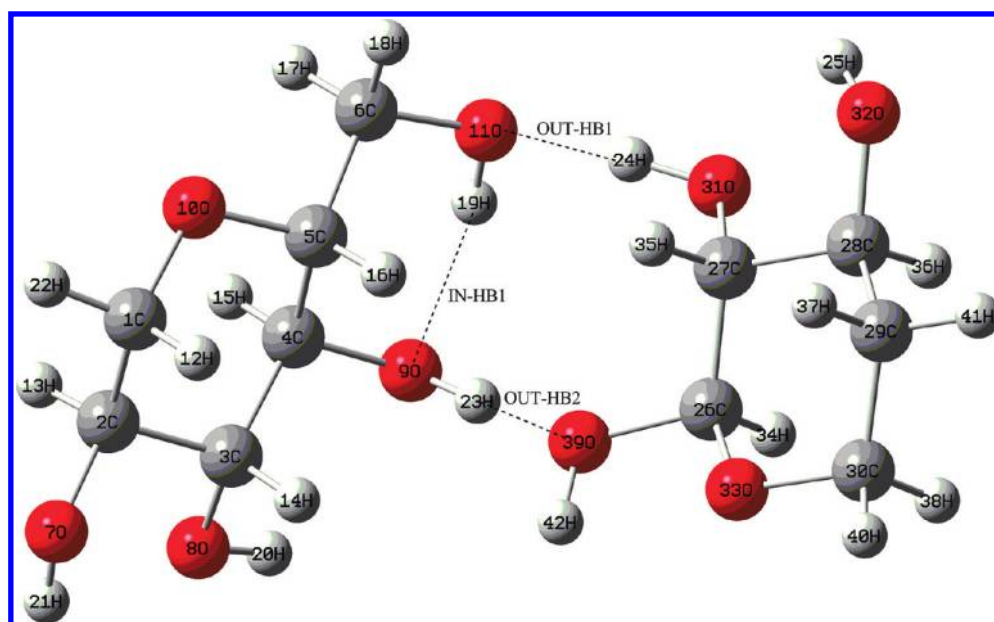


Figure 3. Hydrogen bond network between cellulose and xylan, one-unit system CX-1.

including the semiempirical Austin method 1 (AM1), Hartree–Fock (HF), and density functional theory (DFT). The results of these different methods are evaluated by comparing them with experimental data.

2. COMPUTATIONAL DETAILS

2.1. Computational Models. The concentration of the cellulose, hemicellulose, and lignin in biomass varies with the plant species and in different regions of the cell wall. Hardwood hemicelluloses contain mostly xylan, which is composed of heteropolysaccharides with homopolymeric backbone chains of 1,4-linked β -D-xylopyranose units. Softwood hemicelluloses contain mostly glucomannan,^{13,18,19} which is mainly a straight-chain polymer with a small amount of branching. The lignin in hardwood has both G-units and S-units, whereas softwood contains more than 95% G-units, and one important linkage of these different G-units in softwood is the β -O-4' linkage.²⁰ Different regions of the woody cell wall can also differ in their structure and chemical composition. The middle layer (including the middle lamella and primary wall) has the highest lignin concentration (40–60%), whereas the secondary wall is rich in cellulose (75–80%), with a lignin concentration of only amounts to 20–30%.²¹

It is difficult to give an exact structural description for woody biomass because of its complexity and diversity. However, studying a small part of the complicated biomass macrostructure is feasible. The system studied in this paper is spruce, a typical softwood, and several simplifications are used: (1) Because the degradation rate of amorphous cellulose is much higher than that of crystalline cellulose,²² only amorphous cellulose is considered in this work. (2) Because cellulose is a polymer of D-glucose ($C_6H_{12}O_6$) with β -1-4 linkages, the models for cellulose chosen here include one D-glucose unit and two D-glucose units. (3) On the basis of the research of Lawoko et al.,^{15–17} one complex containing glucomannan, lignin, and xylan contributes about 88% of the lignin in spruce; thus, both xylan and glucomannan are studied in this work. Xylan, similar to cellulose, was simulated using both a one xylose unit model and a two xylose units model. For glucomannan, we chose a model that includes β -(1-4)-linked D-mannose and D-glucose. This choice was based on work by Katsuraya,²³ which concluded that the component sugars for glucomannan are β -(1-4)-linked D-mannose and D-glucose in a ratio of

1.6:1, and the degree of branching is about 8% through β -(1-6)-glucosyl linkages. (4) More than 95% of the lignins in softwood components are G-units, and the most important linkage for different G-units is the β -O-4' linkage.²⁰ Thus, in this work, G-units linked in the β -O-4' manner are considered when studying the structural features of softwood lignin.

2.2. Calculation Method. Electronic structure methods, which were used successfully in our previous studies related to the char gasification²⁴ and cellulose pyrolysis mechanisms,²⁵ were used for all molecular systems in this study. Several computational methods were examined, namely, AM1, HF, and DFT/B3LYP. The B3LYP functional method usually provides accurate geometrical parameters and bond energies, while less accurate methods (HF and AM1) were also included because of their lower computational cost, which is suitable to model larger woody biomass structures in the future work. For the HF and DFT, the evaluated basis sets include 6-31G, 6-31G(d,p), and 6-31G++(d,p). The unrestricted open-shell wave function was used in all open-shell cases. The calculations were carried out on the ground state. The stabilities of the optimized structures were certified by frequency analyses. The Gaussian 09 package²⁶ was used in this study, and all calculations were carried out on a high performance computer in the PDC of the Royal Institute of Technology (KTH), Sweden.

3. RESULTS AND DISCUSSION

A schematic representation of a fiber wall segment in woody biomass and the pretreatment and subsequent thermal conversion processes based on literature studies^{16,22,27–29} is shown in Figure 1, where cellulose is linear, hemicellulose is a two-dimensional polymer, and lignin is a three-dimensional macromolecule. The detailed structural characterization of cellulose, hemicellulose, and lignin are illustrated in Figure 2. Cellulose is the main structural component of plant cell walls, and different cellulose chains interact with each other by hydrogen bonding and van der Waals forces.⁴ Both Ia and Ib celluloses coexist in biomass,^{5,6} and it is thought that the interaction of cellulose microfibrils with hemicellulose may affect the ratio of type Ia and Ib cellulose.³⁰ Lignin is considered to be the cellular glue that provides the plant tissues and the individual fibers that yield compressive strength and stiffen the cell wall.

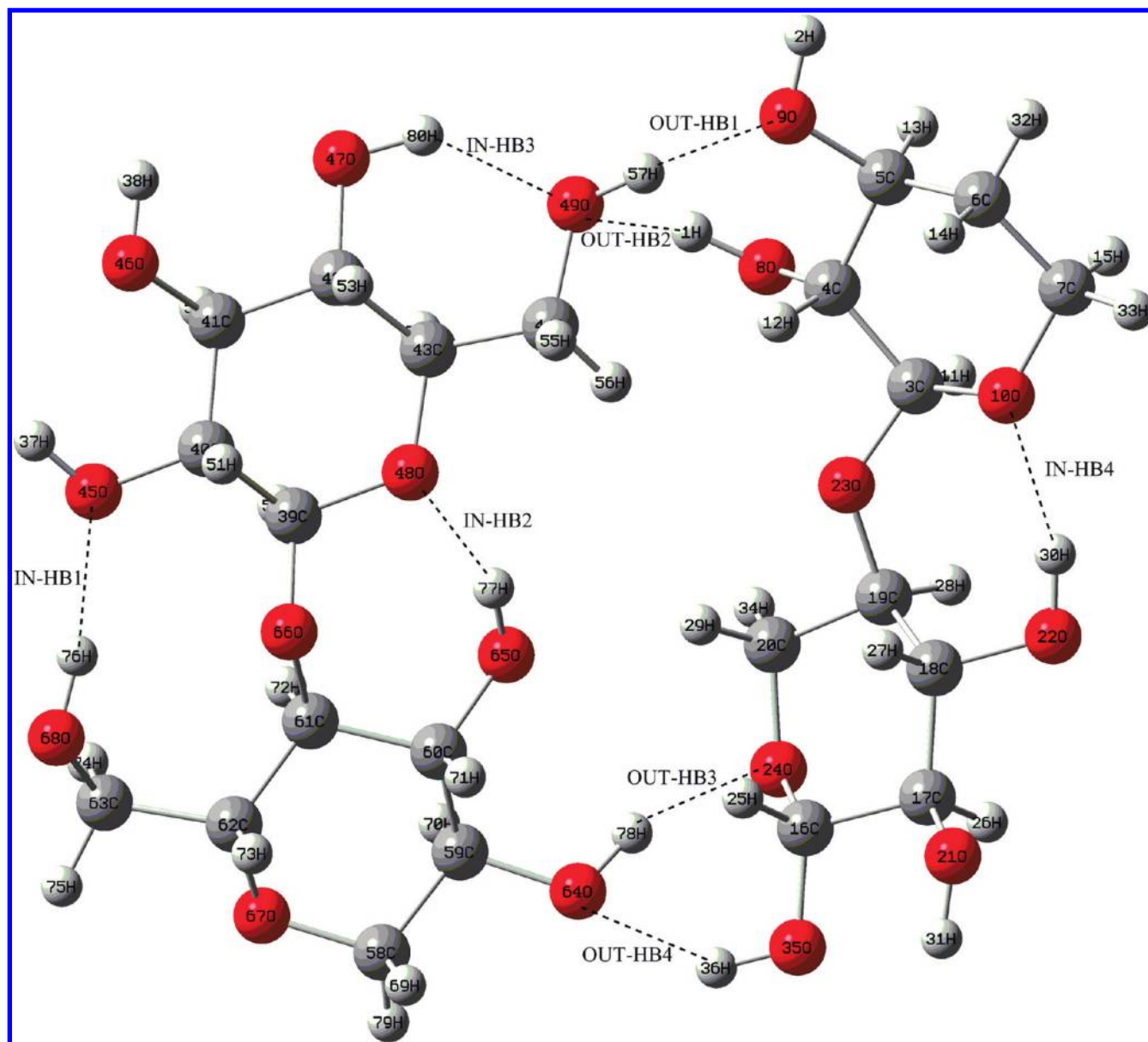


Figure 4. Hydrogen bond network between cellulose and xylan, two-unit system CX-2.

However, hemicellulose can link cellulose fibers into microfibrils and cross-link with lignin, creating a complex network of bonds that provide structural strength.^{31,32} To study the detailed cellulose–hemicellulose and hemicellulose–lignin interactions, a small part of the cellulose macrostructure, marked in red in Figure 1, is examined in this paper.

As shown in Figure 1, during the biomass pretreatment processes, the cellulose, hemicellulose, and lignin will be separated from each other. During the following thermal conversion processes, the polysaccharides (mainly cellulose and hemicellulose) will be degraded into oligosaccharides and then monosaccharides. The lignin will be converted into phenolic compounds. Cellulose from biomass contains the $I\alpha$ and $I\beta$ crystalline allomorphs, together with surface and disordered chains.^{5,6} The crystalline cellulose and amorphous cellulose can be converted to each other under different conditions, and both of them can be degraded into oligosaccharides during the biomass thermal conversion

processes, where the degradation rate of amorphous cellulose is much higher than that of crystalline cellulose.²²

3.1. Hydrogen Bonding between Cellulose and Hemicellulose. In woody biomass, there are intermolecular hydrogen bonds between cellulose and hemicellulose and between the different cellulose chains. There are also intramolecular hydrogen bonds within cellulose, xylan, or glucomannan. The hydrogen bond networks between cellulose and the two main hemicelluloses (xylan and glucomannan) were studied first and are called the cellulose–xylan and cellulose–glucomannan systems. Figure 3 presents a one-unit model for the cellulose–xylan system (denoted CX-1), where we chose one glucose unit for cellulose and one xylose unit for xylan. It can be seen that both intramolecular and intermolecular hydrogen bonds are present in the studied system. For the CX-1 system, one intramolecular hydrogen bond (IN-HB1) and two intermolecular hydrogen bonds (OUT-HB1 and OUT-HB2) are present. Figure 4 presents

Table 1. Optimized Bond Lengths at Different Methods and Levels for the Hydrogen Bond System between Cellulose and Xylan^a

model	param.	HF/6-31G	HF/6-31G(d,p)	HF/6-31++G(d,p)	B3LYP/6-31G	B3LYP/6-31G(d,p)	B3LYP/6-31++G(d,p)	AM1	ref
CX-1	IN-HB1	2.2991 ^b	2.1984 ^b	2.2300 ^b	1.8856 ^b	1.9795 ^b	2.0553 ^b	2.2177 ^b	1.9215 ⁴
		2.8718 ^c	2.8532 ^c	2.8624 ^c	2.6920 ^c	2.7911 ^c	2.8083 ^c	2.7240 ^c	2.8150 ⁴
	OUT-HB1	1.9793 ^b	2.1926 ^b	1.9829 ^b	1.6749 ^b	1.8473 ^b	1.8274 ^b	2.2431 ^b	
		2.8213 ^c	2.9202 ^c	2.9316 ^c	2.6648 ^c	2.7642 ^c	2.8074 ^c	2.6009 ^c	
	OUT-HB2	1.9193 ^b	2.0448 ^b	2.0612 ^b	1.7160 ^b	1.8392 ^b	1.9187 ^b	5.4749 ^b	
		2.8722 ^c	2.9048 ^c	2.9472 ^c	2.7099 ^c	2.8128 ^c	2.8384 ^c	4.8111 ^c	
	avg ^d	2.0659 ^b	2.1453 ^b	2.0913 ^b	1.7588 ^b	1.8887 ^b	1.9338 ^b	2.2304 ^b	
		2.8551 ^c	2.8927 ^c	2.9137 ^c	2.6889 ^c	2.7894 ^c	2.8180 ^c	2.6624 ^c	
	CX-2	1.9983 ^b	2.0814 ^b	2.1756 ^b	1.9260 ^b	1.9883 ^b	2.1731 ^b	2.1820 ^b	1.9215 ⁴
		2.9509 ^c	3.0212 ^c	3.1150 ^c	2.9046 ^c	2.9514 ^c	3.1316 ^c	2.9970 ^c	2.8150 ⁴
CX-2	IN-HB1	1.9541 ^b	2.0566 ^b	1.9030 ^b	1.8567 ^b	1.9483 ^b	1.7989 ^b	2.0815 ^b	1.8590 ⁴
		2.8261 ^c	2.8933 ^c	2.7776 ^c	2.7915 ^c	2.8518 ^c	2.7267 ^c	2.9046 ^c	2.7345 ⁴
	IN-HB2	1.9541 ^b	2.0566 ^b	1.9030 ^b	1.8567 ^b	1.9483 ^b	1.7989 ^b	2.0815 ^b	1.8590 ⁴
		2.8261 ^c	2.8933 ^c	2.7776 ^c	2.7915 ^c	2.8518 ^c	2.7267 ^c	2.9046 ^c	2.7345 ⁴
	IN-HB3	2.0701 ^b	2.0757 ^b	2.0902 ^b	1.9511 ^b	1.9553 ^b	2.0151 ^b	2.1718 ^b	
		2.7988 ^c	2.8148 ^c	2.8176 ^c	2.7784 ^c	2.7723 ^c	2.8047 ^c	2.8946 ^c	
	IN-HB4	2.0861 ^b	2.2663 ^b	2.1056 ^b	1.9415 ^b	3.1392 ^b	1.9314 ^b	2.2767 ^b	
		2.9153 ^c	3.0928 ^c	2.9378 ^c	2.8552 ^c	3.9512 ^c	2.8394 ^c	3.0328 ^c	2.9000 ¹⁴
	OUT-HB1	2.0529 ^b	2.3976 ^b	4.2499 ^b	1.8157 ^b	1.9975 ^b	4.0193 ^b	4.6004 ^b	
		2.9480 ^c	3.1763 ^c	5.1215 ^c	2.7683 ^c	2.9634 ^c	4.8769 ^c	4.4933 ^c	
	OUT-HB2	2.19733 ^b	2.2318 ^b	2.0374 ^b	1.9582 ^b	3.3393 ^b	1.8767 ^b	2.1858 ^b	
		3.0013 ^c	3.0338 ^c	2.9771 ^c	2.8378 ^c	3.7634 ^c	2.8498 ^c	2.6825 ^c	
	OUT-HB3	1.9328 ^b	2.0803 ^b	2.4808 ^b	1.8648 ^b	1.9286 ^b	2.1847 ^b	2.1182 ^b	
		2.7853 ^c	2.8891 ^c	3.1719 ^c	2.7362 ^c	2.7750 ^c	2.9765 ^c	2.8826 ^c	
	OUT-HB4	2.3217 ^b	2.3712 ^b	2.1103 ^b	1.9632 ^b	2.0160 ^b	1.9911 ^b	2.3387 ^b	
		3.0506 ^c	3.1260 ^c	2.9767 ^c	2.7715 ^c	2.8334 ^c	2.8556 ^c	3.0822 ^c	
	avg ^d	2.0767 ^b	2.1951 ^b	2.2603 ^b	1.9096 ^b	2.2891 ^b	2.1356 ^b	2.2378 ^b	
		2.9095 ^c	3.0059 ^c	2.9662 ^c	2.8054 ^c	3.1077 ^c	2.8835 ^c	2.9252 ^c	

^a The unit for bond length is Å. ^b The value here represents the H·····O distance in O—H·····O hydrogen bond. ^c The value here represents the O·····O distance in O—H·····O hydrogen bond, which shows the donor–acceptor distance. ^d The average value here does not count the hydrogen bond, whose length is longer than 4 Å.

a two-unit cellulose–xylan system (CX-2), where we used two glucose units as the cellulose chain and two xylose units as the xylan chain. From the two-unit model, the β -(1-4)-D-xylose linkage in xylan and β -(1-4)-D-glucose linkage in cellulose can be clearly seen. There are four intramolecular hydrogen bonds in the CX-2 model, three for cellulose (IN-HB1, IN-HB2, and IN-HB3) and one for xylan (IN-HB4), and there are four intermolecular hydrogen bonds (OUT-HB1, OUT-HB2, OUT-HB3, and OUT-HB4).

The typical parameters for the studied bonds in CX-1 and CX-2 are shown in Table 1. From the comparison of the different unit systems, it can be seen that the hydrogen bond length is longer in CX-2 than in CX-1. Moreover, in the two-unit system, we also can see the intramolecular hydrogen bond system of cellulose and xylan. The hydrogen bonds between cellulose and xylan make the whole system more complicated and closer to a real woody biomass system. It was also shown that the bond lengths calculated using the semiempirical method (AM1) are always longer than those calculated with the HF method. The DFT/B3LYP method always yields the tightest structure, and this phenomenon is because *ab initio* methods (HF and DFT) can better describe a macrostructure. However, for different *ab initio* methods, the HF method does not consider electron–electron correlation, and DFT considers too much of the electron–electron correlation interaction. By comparing them with the experimental data,^{4,14} it can be concluded that the B3LYP/6-31G method yields the best results for describing cellulose with respect to the

intramolecular hydrogen bonds. The hydrogen bond lengths calculated using B3LYP/6-31G are even closer to the reference values than those calculated with the higher level basis sets (B3LYP/6-31G(d,p) and B3LYP/6-31++G(d,p)). This phenomenon is due to the polarization and dispersion included in the higher level basis sets.

Figure 5 presents the cellulose–glucomannan two-unit system (CG), where cellulose includes two D-glucose units, and glucomannan includes a D-mannose unit and a D-glucose unit that are β -(1-4)-linked to each other. There are nine hydrogen bonds in CG: four are the intramolecular hydrogen bonds of cellulose (IN-HB1, IN-HB2, IN-HB3, and IN-HB4); three are the intramolecular hydrogen bonds of glucomannan (IN-HB5, IN-HB6, and IN-HB7); and the final two bonds are the intermolecular bonds (OUT-HB1 and OUT-HB2) between the cellulose and xylan chains. Table 2 gives the typical bond lengths for the CG model, and the same as with the cellulose–xylan system, it can be concluded that the DFT/B3LYP/6-31G method provides the best description for the cellulose–glucomannan system. The average bond length of the cellulose–xylan hydrogen bond network is always longer than that of the cellulose–glucomannan network, which indicates that the bond strength between cellulose and xylan is smaller than that between cellulose and glucomannan. This is in agreement with the data from a dynamic FT-IR spectroscopy study carried out previously by other researchers.^{12,13}

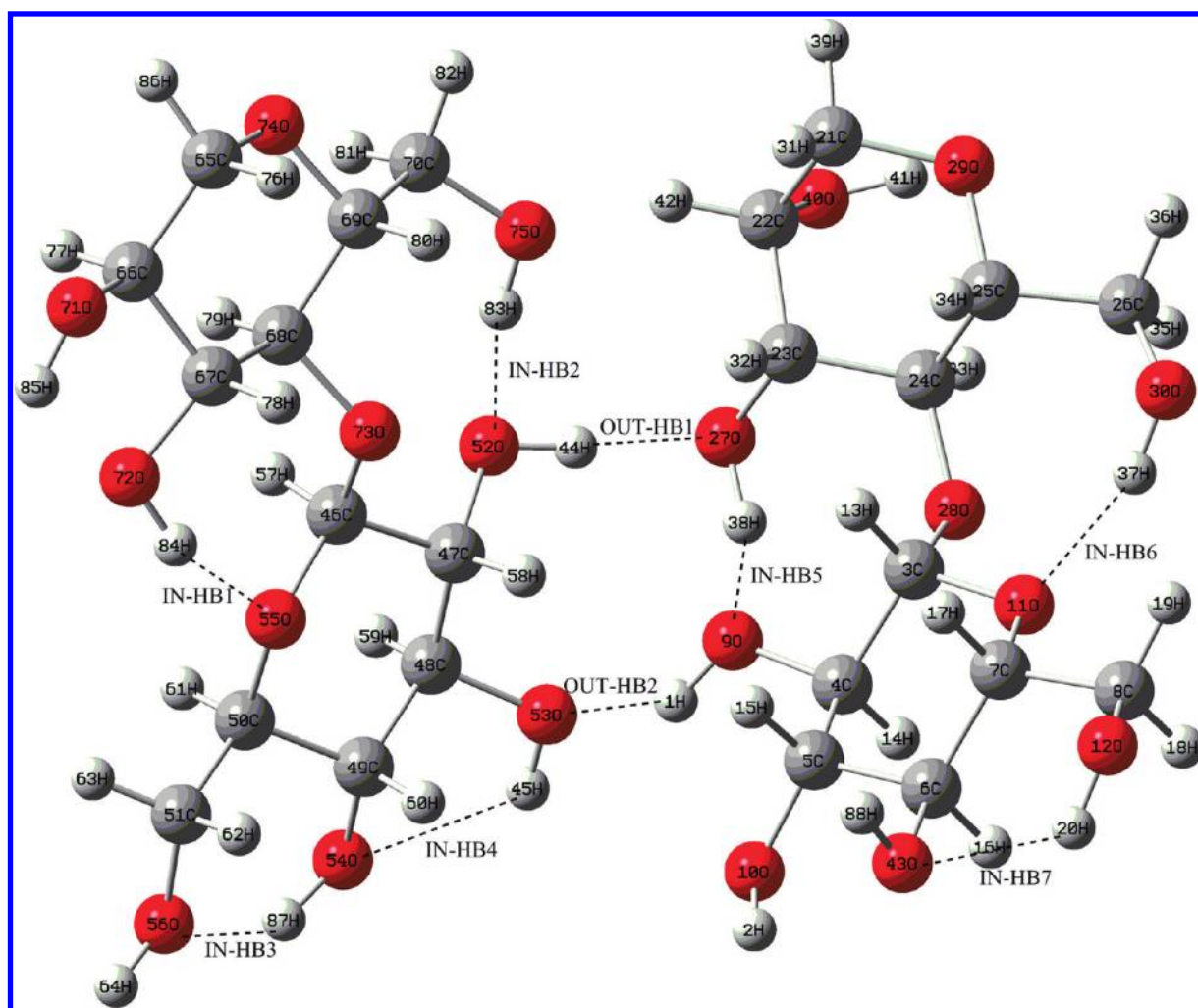


Figure 5. Hydrogen bond network for the cellulose–glucomannan system CG.

3.2. Covalent Bonding between Hemicellulose and Lignin. Covalent linkages between lignin and carbohydrates (LC bonds) have been proposed to exist in wood.^{15,33} The most frequently proposed lignin-carbohydrate linkages are α -ether, α -ester, and phenyl glycosidic linkages.¹⁵ Two xylan–lignin models are studied in this paper, as shown in Figures 6 and 7, which are named the one-unit system (XL-1) and two-unit system (XL-2), respectively. In XL-1, the left part is a xylose unit, and it is linked with a G-unit, which represents lignin. In XL-2, two xylose units are used to represent xylan, which are linked with two G-units. The two G-units in lignin are linked together by a β -O-4' linkage, and it can be seen that there is a phenyl glycosidic linkage between xylan and lignin. The related bond lengths and bond angles are shown in Table 3. For the bond parameters, there is a minimal difference between the one-unit system and two-units systems. Similar to case of the hydrogen bond system, the semiempirical method resulted in a looser structure than the *ab initio* methods. There are few parameter data published in the literature, so the bond lengths and bond angles calculated for these covalent systems cannot be compared with experimental data.

The two models used to study the linkage between lignin and glucomannan are shown in Figures 8 and 9. The LG-1 and LG-2 systems consist of G-units to simulate the lignin and use one glucose unit and one mannose unit to simulate glucomannan.

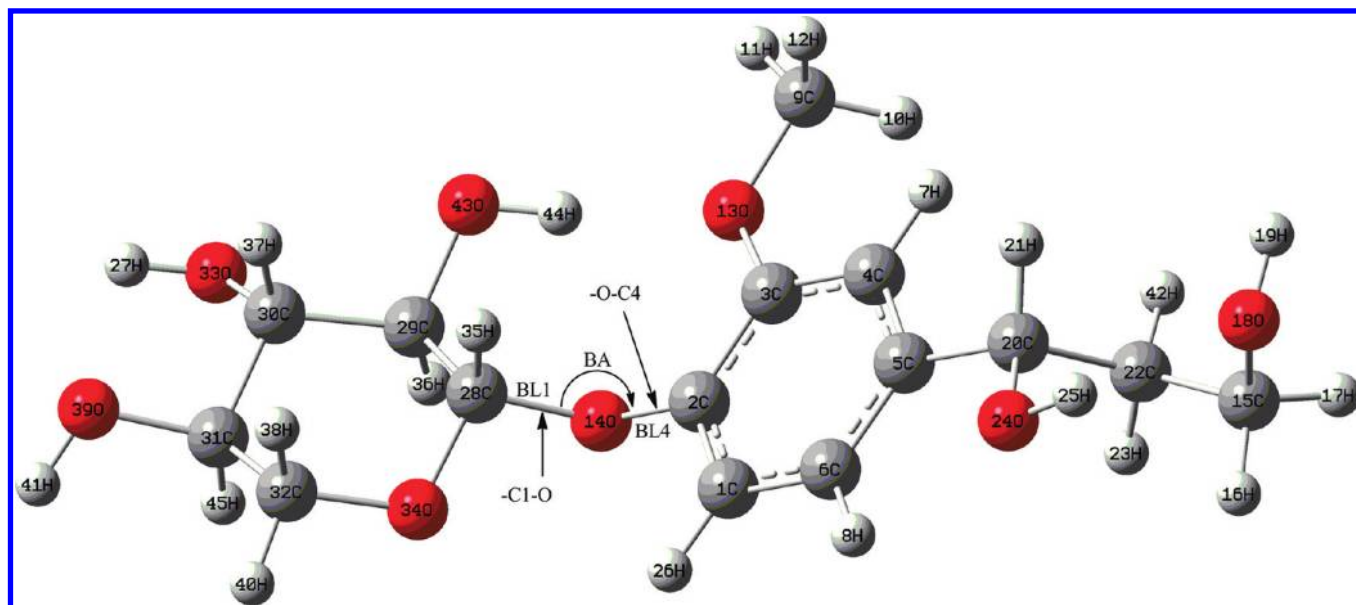
For LG-1 in Figure 8, the left part is a G-unit, and the right part is one D-mannose and one D-glucose. For LG-2 in Figure 9, β -O-4'-linked G-units are used to simulate lignin, and the linkage for glucomannan is an α -ether bond. The related bond parameters are given in Table 4. There is an ether linkage between lignin and glucomannan. It can also be seen that there is a minimal difference between the parameters of the one-unit and the two-units systems. This conclusion is similar to that made for the lignin–xylan system.

3.3. Energetic features. For the covalent systems, there are always two C–O bonds in the linkage, named the –C1–O bond and the –O–C4 bond for xylan–lignin systems and the – β -O bond and the –O–C4 bond for lignin–glucomannan systems. These bonds are also shown in Figures 6–9. To compare the bond strength of all linkage systems, the bond dissociation energies for these C–O bond types were calculated using different electronic structure methods. As shown in Figure 10, the numbers 1 and 2 present one-unit and two-unit systems, and 1, 4, and β , represent the –C1–O bond, –O–C4 bond, and – β -O bond, respectively. CX, CG, XL, LG represent the cellulose–xylan, cellulose–glucomannan, xylan–lignin, and lignin–glucomannan systems, respectively. The bond dissociation energies (BDEs) were calculated as the standard enthalpy change before and after cleavage at 0 K (absolute zero).

Table 2. Optimized Bond Lengths at Different Methods and Levels for the Hydrogen Bond System between Cellulose and Glucomannan^a

model	param.	HF/6-31G	HF/6-31G(d,p)	HF/6-31++G(d,p)	B3LYP/6-31G	B3LYP/6-31G(d,p)	B3LYP/6-31++G(d,p)	AM1	ref
CG	IN-HB1	1.9406 ^b	2.0035 ^b	2.0011 ^b	1.8739 ^b	1.9351 ^b	1.9248 ^b	2.1416 ^b	1.9215 ⁴
		2.8203 ^c	2.8589 ^c	2.8623 ^c	2.8051 ^c	2.8418 ^c	2.8423 ^c	2.9063 ^c	2.8150 ⁴
	IN-HB2	1.9132 ^b	1.9899 ^b	2.0040 ^b	1.8281 ^b	1.9075 ^b	1.9031 ^b	2.2141 ^b	1.8590 ⁴
		2.8645 ^c	2.9292 ^c	2.9386 ^c	2.8052 ^c	2.8704 ^c	2.8678 ^c	3.0615 ^c	2.7345 ⁴
	IN-HB3	2.0108 ^b	2.0443 ^b	2.0751 ^b	1.8748 ^b	1.9501 ^b	1.9878 ^b	2.1587 ^b	
		2.7300 ^c	2.7729 ^c	2.7908 ^c	2.6829 ^c	2.7418 ^c	2.7666 ^c	2.9219 ^c	
	IN-HB4	2.4711 ^b	2.4449 ^b	2.5262 ^b	2.2845 ^b	2.2919 ^b	2.3926 ^b	2.3691 ^b	2.1975 ⁴
		2.7787 ^c	2.7881 ^c	2.8244 ^c	2.7457 ^c	2.7656 ^c	2.7991 ^c	2.8217 ^c	2.8415 ⁴
	IN-HB5	1.8388 ^b	1.9606 ^b	2.0578 ^b	1.6973 ^b	1.8373 ^b	1.8434 ^b	2.1829 ^b	
		2.7124 ^c	2.8148 ^c	2.9651 ^c	2.6251 ^c	2.7311 ^c	2.7545 ^c	2.7572 ^c	
	IN-HB6	1.9875 ^b	2.1065 ^b	2.1068 ^b	1.9059 ^b	1.9557 ^b	1.9526 ^b	2.1375 ^b	
		2.8431 ^c	2.8885 ^c	2.9484 ^c	2.8129 ^c	2.8358 ^c	2.8669 ^c	2.8973 ^c	
	IN-HB7	2.0189 ^b	2.3144 ^b	2.3219 ^b	2.1794 ^b	2.1546 ^b	2.2221 ^b	2.1950 ^b	
		2.7415 ^c	2.8841 ^c	2.9143 ^c	2.8340 ^c	2.8521 ^c	2.8921 ^c	2.7770 ^c	
	OUT-HB1	1.8418 ^b	1.9801 ^b	2.0398 ^b	1.6646 ^b	1.7843 ^b	1.7836 ^b	2.1578 ^b	
		2.7737 ^c	2.8963 ^c	2.9008 ^c	2.6610 ^c	2.7615 ^c	2.7648 ^c	3.0736 ^c	
	OUT-HB2	2.0183 ^b	2.3174 ^b	5.0782 ^b	1.7159 ^b	1.8908 ^b	2.0047 ^b	2.1552 ^b	
		2.7662 ^c	2.9164 ^c	4.0134 ^c	2.5863 ^c	2.6921 ^c	2.7726 ^c	2.9568 ^c	
	average ^d	2.0045 ^b	2.1291 ^b	2.4679 ^b	1.8916 ^b	1.9675 ^b	2.0016 ^b	2.1902 ^b	
		2.7812 ^c	2.8610 ^c	2.8931 ^c	2.7287 ^c	2.7880 ^c	2.8141 ^c	2.9081 ^c	

^a The unit for bond length is Å. ^b The value here represents the H...O distance in O—H...O hydrogen bond. ^c The value here represents the O...O distance in O—H...O hydrogen bond, which shows the donor–acceptor distance. ^d The average value here does not count the hydrogen bond, whose length is longer than 4 Å.

**Figure 6.** Covalent bond between xylan and lignin, one-unit system, XL-1. BL1, BL4, and BA represent the bond length for the —C1—O bond, the bond length for the —O—C4 bond, and the bond angle, respectively.

From Figure 10, it can be clearly seen that the hydrogen linkages for the cellulose–xylan systems (CX-1 and CX-2) and the cellulose–glucomannan system (CG) have bond dissociation energies lower than 100 kJ/mol, which is in the hydrogen bonding range. The bond dissociation energies of the xylan–lignin systems (XL-1-C1, XL-1-C4, XL-2-C1, and XL-2-C4) and the

lignin–glucomannan systems (LG-1-β, LG-1-C4, LG-2-β, and LG-2-C4) are always higher than those of the hydrogen bonding systems. It also can be seen that B3LYP always yields a higher dissociation energy because DFT overestimates electron–electron correlation. However, we can see that, for hydrogen bonding systems, the B3LYP/6-31G method gives better results than

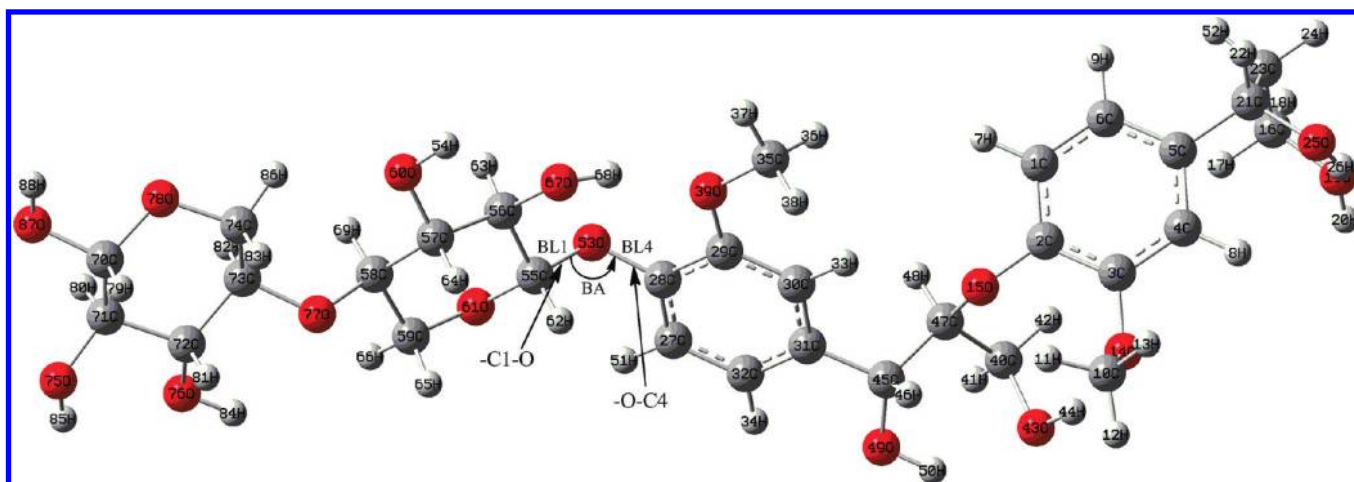


Figure 7. Covalent bond between xylan and lignin, two-unit system, XL-2. BL1, BL4, and BA represent the bond length for the —C1—O bond, the bond length for the —O—C4 bond, and the bond angle, respectively.

Table 3. Optimized Bond Lengths and Angles at Different Methods and Levels for the Covalent Bond System between Xylan and Lignin^a

model	param.	HF/6-31G	HF/6-31G(d,p)	HF/6-31++G(d,p)	B3LYP/6-31G	B3LYP/6-31G(d,p)	B3LYP/6-31++G(d,p)	AM1
XL-1	BL1	1.4077	1.3853	1.3854	1.4346	1.4070	1.4070	1.4247
	BL4	1.3836	1.3660	1.3657	1.4039	1.3812	1.3824	1.3879
	BA	120.86	117.86	118.25	118.68	117.36	117.84	114.66
XL-2	BL1	1.4060	1.3837	1.3841	1.4344	1.4061	1.4068	1.4236
	BL4	1.3847	1.3668	1.3664	1.4052	1.3819	1.3830	1.3883
	BA	121.03	118.01	118.36	118.77	117.46	117.96	114.60

^a The unit for bond length is Å, and the unit for bond angle is deg.

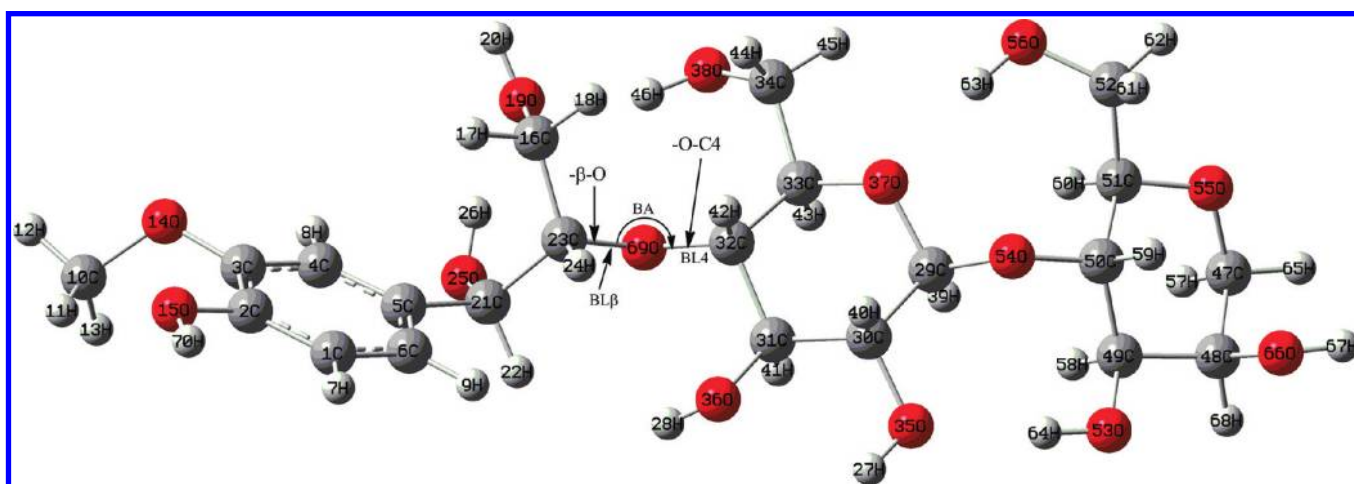


Figure 8. Covalent bond between lignin and glucomannan, one-unit system, LG-1. BL β , BL4, and BA represent the bond length for the $\text{—}\beta\text{—O}$ bond, the bond length for the —O—C4 bond, and the bond angle, respectively.

other basis sets; this is in agreement with the phenomenon that the bond parameters calculated with B3LYP/6-31G are the closest to the experimental data. However, for covalent systems, B3LYP/6-31G(d,p) always gives the strongest bond dissociation energy. Thus, it can be concluded that B3LYP/6-31G is a suitable method for hydrogen bonding systems in woody biomass and that B3LYP/6-31G(d,p) is a suitable basis set for describing the covalent linkages in woody biomass.

For the xylan–lignin systems, it can be seen that the BDE of the —C1—O bond is always weaker than that of the —O—C4 bond, and for lignin–glucomannan systems, the BDE of the $\text{—}\beta\text{—O}$ bond is always weaker than that of the —O—C4 bond. Therefore, the —C1—O bond in xylan–lignin systems and the $\text{—}\beta\text{—O}$ bond in lignin–glucomannan systems will probably be broken first during biomass pretreatment processes. Additionally, the covalent bond in xylan–linked lignin is less stable than

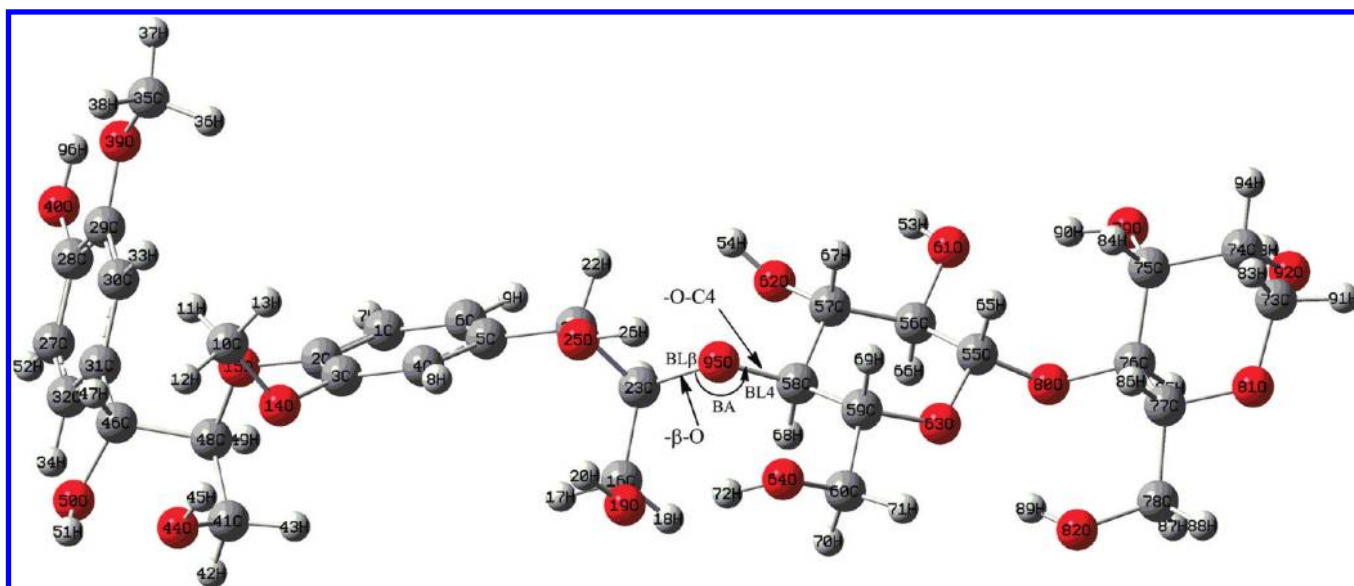


Figure 9. Covalent bond between lignin and glucomannan, two-unit system, LG-2. BL β , BL4, and BA represent the bond length for the $-\beta-O$ bond, the bond length for the $-O-C4$ bond, and the bond angle, respectively.

Table 4. Optimized Bond Lengths and Angles at Different Methods and Levels for the Covalent Bond System between Lignin and Glucomannan^a

model	param.	HF/6-31G	HF/6-31G(d,p)	HF/6-31++G(d,p)	B3LYP/6-31G	B3LYP/6-31G(d,p)	B3LYP/6-31++G(d,p)	AM1
LG-1	BL β	1.4432	1.4104	1.4108	1.4667	1.4262	1.4338	1.4294
	BL4	1.4295	1.4024	1.4027	1.4576	1.4319	1.4275	1.4262
	BA	121.11	118.12	118.49	116.94	116.24	116.96	114.15
LG-2	BL β	1.4418	1.4095	1.4097	1.4655	1.4314	1.4326	1.4345
	BL4	1.4301	1.4031	1.4040	1.4588	1.4269	1.4285	1.4251
	BA	121.32	118.06	118.36	116.83	116.08	117.04	113.95

^a The unit for bond length is Å, and the unit for bond angle is deg.

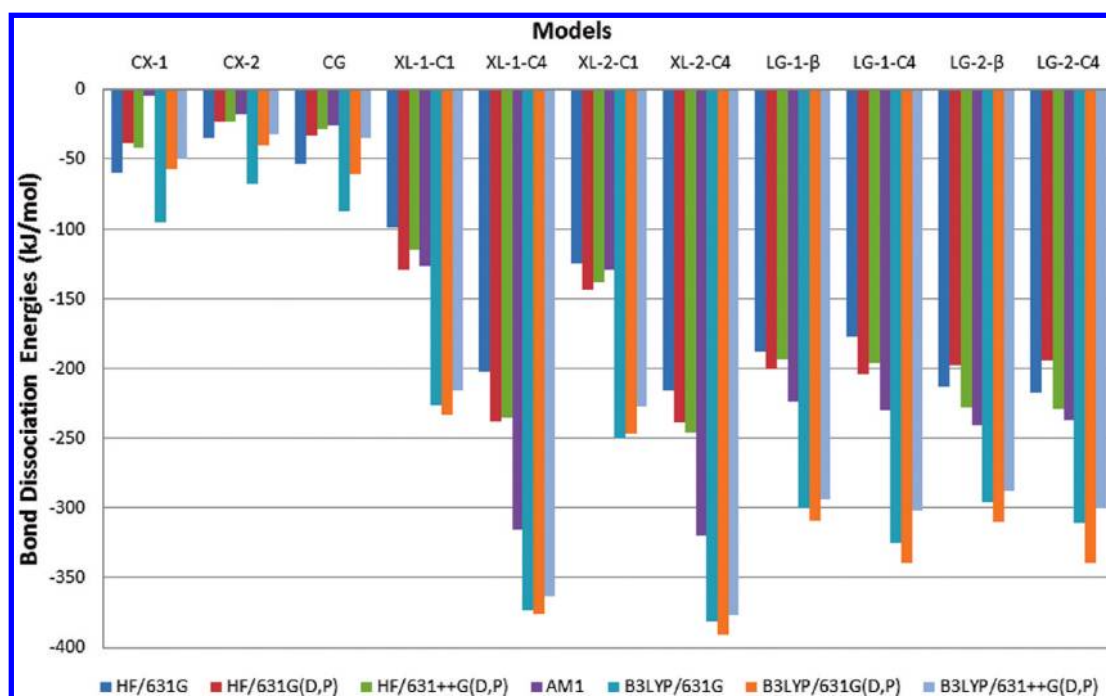


Figure 10. Bond dissociation energies of the linkage bonds between three components at different levels of theory.

that in glucomannan–linked lignin, and the hydrogen bond energies between cellulose and xylan are slightly less than those between cellulose and glucomannan, which is in agreement with the experimental results.¹²

4. CONCLUSIONS

The accurate simulation of biomass pretreatment processes and subsequent thermal conversion processes presents significant challenges. An important first step is the study of the interactions between the three main biomass components. Both the intramolecular and intermolecular hydrogen bonds between cellulose and hemicellulose and the covalent bonds between hemicellulose and lignin are included in this study. It is concluded that theoretical calculations provide a feasible method to study the interactions between simple models of woody biomass components.

The choice of model system has a much larger effect on the hydrogen bonding system between cellulose and hemicellulose, but the choice has a minimal effect on the covalent linkages between hemicellulose and lignin. B3LYP/6-31G is a reasonably accurate method to describe the hydrogen bond network in woody biomass. To study the covalent linkages in woody biomass systems, B3LYP/6-31G(d,p) provides a better description. The –C1–O bond in xylan–lignin systems and the – β –O bond in lignin–glucomannan systems will probably be broken first during biomass pretreatment processes; the interaction between xylan and lignin is less stable than that between glucomannan and lignin.

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