# A Theoretical Study on Levoglucosan Pyrolysis Reactions Yielding Aldehydes and a Ketone in Biomass

by

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# Abstract

Cellulose composes most of domestic, industrial, and agricultural wastes, forest products and indigenous plant materials valued as biomass resources. The immensity of these materials should be a driving force to efficiently exhaust them as energy sources and, in effect, offset environmental impact of wastes. This study focuses on the pyrolysis reactions of cellulose as a main component in biomass through thermal degradation of levoglucosan – an intermediate crucial to the formation of char and other products. Theoretical calculations involving DFT and MP2 methods were employed to investigate molecular and activation energies as well as verify proposed reaction mechanisms in cellulose pyrolysis. The differences between the calculated proposed structures are illustrated.

**Keywords**: biomass, cellulose, levoglucosan, density functional theory (DFT), 2<sup>nd</sup> order Møller-Plesset (MP2) theory

# 1. Introduction

Cellulose, which is an abundant component in plants and wood, comes in various forms and a large fraction comes from domestic and industrial wastes. With the volume of wastes accumulating every day, these sources would best be recycled as biomass sources, which can be combusted to produce heat, fuel gases, and charcoal that may be stored as a reserve fuel, or converted to alcohols as an alternative fuel source to fossil fuels. At present, most countries are seriously considering biomass for energy. China, for example, is one of the major biomass consumers in the world exceeding 200% more than the quantities utilized by other countries in 2002. Brazil produces charcoal from eucalytus and ethanol from sugarcane and bagasse. The US uses forest products and residues for energy <sup>1</sup>. These are just a few of a myriad of examples of biomass sources are sources and waste management points of view, biomass sources are

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relatively at zero cost  $^{2)}$  and their carbon-neutral properties offset environmental impact since most of these are recovered from waste. In Japan, the potential energy equivalent of municipal wastes for 2005 and 2010 is statistically estimated to be 2~3% of its primary energy consumption  $^{3)}$ .

The main purpose of this paper is to show that effective biomass burning for alternative energy production boils down to efficient pyrolysis of cellulose. It is widely accepted that cellulose degradation through pyrolysis proceeds in two separate paths: (1) depolymerization, which is responsible for levoglucosan (1.4- $\beta$ -D-glucopyranose) production and (2) dehydration that accounts for char formation <sup>4)</sup>. Anhydrosugars constitute more than 40% <sup>5, 6)</sup> of the depolymerization products in path (1), which is mainly levoglucosan that further breaks down into other smaller and volatile substances <sup>7)</sup>. Polymerization of levoglucosan is deemed crucial not only in the formation of char in that its inhibition may preclude the production of the latter and limiting it eventually leads to the formation of the same <sup>8)</sup> but also other pyrolysis products that are essential chemicals. Identical pyrolysis products of both levoglucosan and cellulose were obtained; of these are formic acid, hydroxyacetaldehyde, 2, 3-butanedione, CO, CO<sub>2</sub>, acetaldehyde, and so on to name a few <sup>9,10)</sup>. A clear understanding of the reactions of levoglucosan degradation is therefore essential to elucidate the reaction mechanism of cellulose pyrolysis. Four reaction mechanisms of the thermal degradation of levoglucosan for the formation of smaller molecules that are mostly composed of aldehydes and a ketone were proposed by Pouwels et al <sup>11</sup>, and in this paper ab initio and quantum molecular calculations and were performed to confirm these reactions, however, only the first mechanism (see Fig.1) is discussed in this paper.



Fig. 1 One of the proposed mechanisms on the thermal decomposition of levoglucosan by Pouwels et  $a1^{7}$ .

## 2. Methods

Levoglucosan decomposition via dehydration, release of carbon monoxide, and ketone and aldehyde formation are theoretically verified according to the first mechanisms proposed by Pouwels et al.<sup>11)</sup> Theoretical chemical calculations are effective in numerically simulating chemical reactions and structures that are otherwise unobtainable through direct experimentations<sup>12)</sup>. The theoretical methods adhere to the fundamental physical laws that involve accurate orbital approximations of molecular structures consistent with actual experimental observations. Geometry optimizations and transition state (TS) structures calculations were carried out by employing the Becke-3-Lee, Yang, and Parr (B3LYP) level density functional theory <sup>13-15)</sup> and the second-order Møller-Plesset (MP2) perturbation theory with Dunning's correlation consistent, polarized valence, double zeta (cc-pVDZ) basis set <sup>16)</sup>. Harmonic vibrational frequencies were obtained at each level

of theory to characterize the stationary points at local minima or first-order saddle points, make zero-point vibration energy (ZPE) corrections, and generate force constant data needed in the intrinsic reaction coordinate (IRC) calculations <sup>17)</sup> for the reaction channels with a saddle point. The IRC method was used to track minimum energy paths from TS to the corresponding local minima. Basis set superposition errors (BSSE) were also corrected through counterpoise correction. All calculations were performed using the Gaussian 03 software package <sup>18)</sup>. For a thorough description of the above methods, refer to [19~21]. A brief introduction is discussed in our previous work <sup>22)</sup> with a focus merely onto the breakdown of levoglucosan into smaller components.

#### 3. Results and Discussion

The optimized geometries of all stationary points are shown in **Fig.2** according to their order of formation and decomposition in the proposed reaction mechanism. The bond angles and bond lengths of optimized product species and some of the important reaction sites are listed in **Table 1**. The relative energies and corrected barrier heights integrated with ZPE corrections of all species at MP2 and B3LYP levels are shown in **Fig. 3**. The maximum activation energy achieved for both levels without the introduction of ZPE corrections is about 7% higher than the ones introduced with ZPE corrections. Single point calculations were also performed to evaluate effects on the results as the quality of basis sets is improved; augmented cc-pvdz and cc-pvtz were used. A uniform decrease in the molecular energies of each species was observed, however, nothing conclusive can be made on the activation and complex energies. Formation of the first intermediate and the ketone are exothermic while the rest are endothermic, and these are discussed in each of the reaction steps in the succeeding sections.

## 3.1 CO removal step

Figures 2a and 3a show the molecular structures and energetics of the CO removal step. Opening of the pyranose ring in levoglucosan due to the cleavage of  $C_1$ - $O_7$  and  $O_8$ - $C_6$  resulted to a  $C_1$ - $O_8$  double bond formation and consequently, forming a cyclic  $C_6$ - $O_7$ - $C_5$  bond. In MP2, this cyclic bond shifted to partial double bonds between C5-O7 and C5-C6, with H19 breaking away from  $C_5$  as it approaches  $C_6$  during transition (TS1). In B3LYP, however, none of these partial double bonds were formed, but instead, a pseudo linear  $C_1-O_8=H_{12}$  bond was found at TS. Culmination of the carbon monoxide release reduced the molecule to the first intermediate— a five-member carbon chain, 3,4,5-trihydroxy-2- pentanone (I<sub>1</sub>) with O<sub>7</sub> rotating right-handedly at  $\sim 100^{\circ}$  from the its original orientation. The barrier height in B3LYP is 3 times greater than in MP2. This over-approximation may be attributed to the long-range interaction energy obtained by the dynamical correlation which is not thoroughly considered in the DFT method <sup>19</sup>, hence, only the optimized structures in MP2 are illustrated. In ref. [22] and [23] as cited in [24], cellulose and levoglucosan are known to have similar enthalpies of formation, which suggests that the dissociation of both to other substances will occur in a relatively similar fashion, and can be supported by the presence of similar condensation products <sup>25)</sup> from separate thermal decomposition processes of both substances. Thus, the reaction should proceed easily at an activation energy of 26.96 kcal-mol<sup>-1</sup> (in MP2) since this is small compared to that of microcrystalline cellulose calculated at ~45 kcal mol<sup>-1 26</sup> and some wood species whose activation energies are as high as ~109.9 kcal-mol<sup>-1 27</sup>).

#### 3.2 Dehydration step and Ketone Formation

Breakdown of the aforementioned intermediate led to simultaneous bond cleavages in C<sub>3</sub>-C<sub>4</sub>,

 $O_8$ -H<sub>14</sub> from C<sub>2</sub>, and deprotonation of O<sub>9</sub> in favor of the leaving OH to produce water resulted to a partial double bond formation between O<sub>9</sub>-C<sub>3</sub> and C<sub>3</sub>-C<sub>2</sub> during TS2; see **Fig.2b**. The main molecule divides into two separate structures during the transitory separation between C<sub>3</sub> and C<sub>4</sub>. From the B3LYP calculation, C<sub>3</sub>-C<sub>4</sub> bond does not break during TS nor a partial double bond formed between C<sub>3</sub>-C<sub>2</sub>, however, O<sub>9</sub>=C<sub>3</sub> weakens after being transformed to a partial double bond. Water was released after H<sub>16</sub> bonded with O<sub>8</sub>-H<sub>14</sub> thus forming the second intermediate where a C<sub>3</sub>-O<sub>9</sub>-C<sub>2</sub> cyclic bond was formed. This differs from the proposed structure where O<sub>9</sub> is doubly bonded to C<sub>3</sub>. Further dehydration took place prior to the formation of the final product. Cleaving



**Fig. 2** Optimized geometries and reaction mechanism of levoglucosan in the MP2 level. (a) CO elimination, (b) Dehydration, and (c) Aldehyde formation.

Complexes, TS,	Atom	Bond Lengths and		Complexes, TS,	Atom	Bond Lengths and		Complexes, TS,	Atom	Bond Lengths and	
and Products	Numbers	nbers Angles		and Products	Numbers	Angles		and Products	Numbers	Angles	
		B3LYP	MP2			<b>B3LYP</b>	MP2			<b>B3LYP</b>	MP2
	C1-C2	1.5457	1.5385	Path 1:	C1-C4	2.9268	2.9335	1-pentene-3,4-dione	C1=C2	1.3401	1.3506
Levoglucosan	C1-O8	1.4315	1.4346		C1-O5	1.2077	1.2175		C2-C3	1.4845	1.4900
	C1-O8-C6	106.8681	106.5015	C3*	C3-O6	1.2077	1.2175		C3-C4	1.5487	1.5428
	C3-C4-C5	109.2310	109.0597		C1-C2-C3	113.7650	113.1129		C4-C5	1.5067	1.5094
C6-O8 cleavage	C1-08	1.2110	1.2221	Path 2:	C1-04	1.2356	1.219		C3=07	1.2203	1.2294
	C6-O8	4.8921	3.0902	TS3	C2-O5	3.1537	3.2342		C4=O6	1.2153	1.2256
	C6-O7	1.4326	1.4432		C3-O6	1.2230	1.2296		C1-C2-C3	120.6989	120.0001
	C5-O7-C6	61.9493	61.5662		C1-C2-C3	119.0760	118.449		C3-C4-C5	116.1143	115.8130
	C1-O8	1.1709	1.1467	Path 2:	C1-O4	1.2111	1.2188		C1-C2-C3-C4	180.0000	-179.9963
	C1-H12	1.0930	-		C2-O5	3.3477	3.4527		6-C2-C3-O7	-179.9788	-179.9940
	C2-H12	1.7625	1.0989	C3*	C3-O6	1.2055	1.2188	acetaldehyde	C1-C2	1.5067	1.5097
TS1 C1* TS2	C5-C6	1.4720	1.4293		C1-C2-C3	112.7904	108.4022		C1=O3	1.2083	1.2183
	C5-07	1.4405	1.2936		C2-C3	1.4673	1.4342		C1-H4	1.1239	1.2145
	C6-O7	1.4376	-		C3-C4	1.6132	1.7970		O3-C1-C2	124.8189	124.5996
	O7-C5-C6	59.1331	109.2190	TS4	C3-O9	1.2887	1.3035		C2-C1-O3-H4	180.0000	180.0000
	C1-O8	1.1338	1.1460		C4-O6	1.1985	1.2046	2,3-dihydroxypropanal	C1-C2	1.5417	1.5349
	C5-O7	1.2202	1.2279		C3-H15	1.1665	1.1164		C2-C3	1.5104	1.5131
	C1-C2	1.5223	1.5194		C2-C3	1.4850	1.4849		C3=O6	1.2133	1.2228
	C2-C3	1.5323	1.5312		C2-O9	1.4366	1.4394		C1-O4	1.4088	1.4110
	C3-O9	1.3544	1.3558		C3-O9	1.4337	1.4377		C2-O5	1.4108	1.4136
	C4-C5	1.5067	1.5098	C4*	C1-07	1.4070	1.4094		C1-C2-C3	111.5478	110.8859
	C4-O6	1.1955	1.2056		C3-H15	1.0975	1.0983		C1-C2-C3-O6	-116.6375	-114.3603
	C1-C2-C3	114.8078	115.5404		C2-O9-C3	62.3112	62.1419	propanedialdehyde	C1-C2	1.5189	1.5193
C2*	C1-C2	1.5416	1.5348		C3-O8	1.4314	1.4307		C2-C3	1.5189	1.5193
	C2-C3	1.5097	1.5144	TS5	C1-07	1.7883	1.7447		C1-=04	1.2060	1.2169
	C3-O9	1.2165	1.2233		C2-O8-C3	61.9825	61.6987		C3=O5	1.2060	1.2169
	C4-C5	1.5045	1.5077		C1-C2	1 3431	1 3522		C1-H6	1 1224	1 1 2 0 9
	C4-06	1 2109	1 2205		C2-C3	1 4780	1 4853		C2-07	1 0984	1 0998
	C1-C2-C3	111 5225	111 0711	C5*	C3-08	1 2253	1 2319		$C_{1}-C_{2}-C_{3}$	113 1136	111 8547
Path 1.	C1-04	1 3970	1 4042	0.5	C4-06	1 2148	1 2253		C1-C2-C3-O4	-130 2777	-126 7239
	C2-O5	1.9986	1.9187		C1-C2-C3	121.9504	120.9830	water	0-Н	0.9685	0.9649
TS3	C3-06	1.2129	1.2227		C2-C3-C4-C5	179.5063	179.7284		H-O=H	102.7508	101.8938
	C1-C2-C3	121.4828	120.1297		08-C3-C4-O6	179.4583	179.7068	Carbon monoxide	C-0	1.1347	1.1472

Table 1 Selected bond lengths (in angstroms) and angles (in degrees) of active sites in the transition, complex, and optimized product structures.

off of the hydroxyl bond from  $C_1$  did not have any effect on the cyclic bond; at TS3 in MP2, the hydrogen approached  $O_7$  of this hydroxyl group. Water was formed exothermically unlike the endothermic requirement of the first dehydration step. A full left-handed rotation of  $C_3$ - $C_4$ - $C_5$  produced the stable trans-isomer of a planar 1-pentene-3, 4-dione (P<sub>1</sub>) molecule. There was no mention of whether the molecule existed as a *cis*- or *trans*-isomer in the proposed mechanism. B3LYP results showed no double bond in  $C_1$ - $C_2$  during TS. Dry  $\alpha$ -cellulose has a heating value of 4177.693kcal-kg<sup>-1</sup><sup>28</sup>) and ~4242kcal-Nm<sup>-3</sup><sup>29</sup>) or approximately 95kcal-mol<sup>-1</sup>. Comparing the barrier heights in **Fig. 3b** and **3c**, TS2 has a much lower energy requirement and may proceed



Fig. 3 Potential energy diagram of the thermal decomposition of levoglucosan where  $C_i^*$ ,  $I_i$ , and  $P_i$  are the product complexes, intermediates, and products in the reactions. All values are BSSE and ZPE corrected.

spontaneously after heat treatment, TS3 however, is close to the above limits and may proceed slowly and forms products in rather small quantities. This is consistent to the mass spectrometry (MS) data given by Pouwels et al.

## 3.3 Aldehyde Formation

Acetaldehyde and 2,3-dihydroxypropanal are also formed after cleavage of the C<sub>3</sub>-C<sub>4</sub> bond in the first intermediate (**Fig. 2c**). A simultaneous hydrogen transfer occurs from the larger to the smaller molecule, i.e., to C4\*, during TS4, which is highest (**Fig. 3d**) among all reactions in this proposed path. 2,3-Dihydroxypropanal is dehydrated to form propanedialdehyde and there are two possible ways by which this is achieved. The first mechanism is the cleavage of the hydroxyl group of the  $\alpha$ -carbon and simultaneous deprotonation of the hydroxyl group in the  $\beta$ -carbon to bond with the leaving OH due to steric effects. The second mechanism differs in that the one leaving is the hydroxyl group of the  $\beta$ -carbon followed by migration of the one bonded to the  $\alpha$ -carbon to replace it. One of the two remaining H atoms on the terminal carbon delocalizes to bond with the  $\beta$ -carbon. However, with a relatively consistently large difference of 15kcal/mol in MP2 and 5kcal/mol in B3LYP for the TS energy (**Fig. 3e**), only the first condition is likely to occur. Though the activation energy, TS5, for the dehydration of 2,3-dihydroxypropanal to produce propanedialdehyde is quite low, the preceding reaction, although just mildly endothermic, requires too high an energy that propounds less probability for such reaction to occur in this particular step.

Basing on the calculation results, the transition energies are too high for the reactions to proceed and since such are slightly endothermic this particular path may not be ideal for heat production.

#### 4. Conclusion

The present results corroborate the proposed reaction mechanisms. In addition to these, we found some notable differences from our results: (1) dehydration of 2,3-dihydroxypropanal to form propanedialdehyde formation is only possible via  $\alpha$ -carbon release, however, due to a very high activation energy of acetaldehyde and 2,3-dihydroxypropanal formation, such reaction might not be the appropriate pathway for production of these aldehydes; (2) the first dehydrated intermediate, I<sub>1</sub>, possesses a cyclic C-C-O bond; and (3) 1-pentene-3, 4-dione exists as a more stable *trans*-isomer, which is not considered in the proposed mechanism. However, the high activation energies suggest that the reactions in this present mechanism are unlikely to occur, and that the species obtained from the experimental observations of our reference paper must have undergone through another separate mechanism. Moreover, since the overall reaction in the mechanism presented here is slightly endothermic, this path is not suitable on the viewpoint of biomass as a heat source. A complete and thorough evaluation of the rest of the proposed mechanisms will be presented in a separate paper with an aim to find pathways of lower energy requirements and thus can be deemed ideal for energy production and evolution of other valuable chemicals; further calculations are in progress.

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