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## 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 eucalyptus 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 utilization for energy. On the fuel procurement and waste management points of view, biomass sources are

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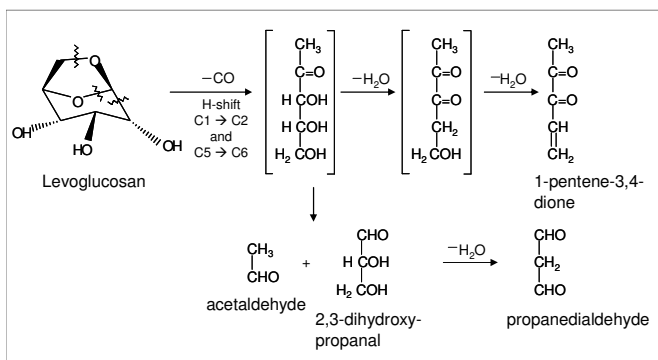
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relatively at zero cost<sup>2)</sup> and their carbon-neutral properties offset environmental impact since most of these are recovered from waste. In Japan, the potential energy equivalent of municipal wastes for 2005 and 2010 is statistically estimated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

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 al<sup>7)</sup>.

## 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.

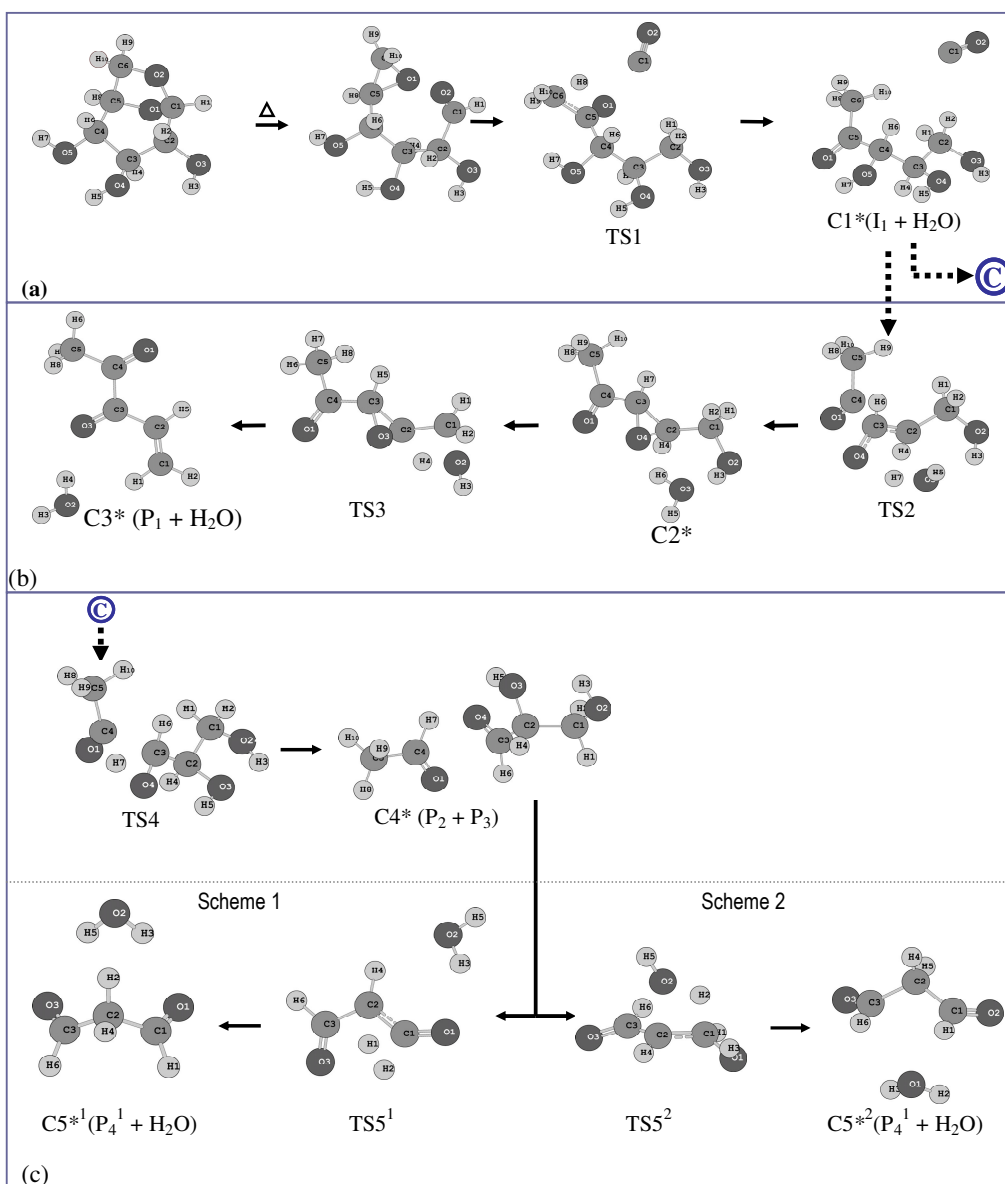
#### 3.1 CO removal step

**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<sub>1</sub>-O<sub>7</sub> and O<sub>8</sub>-C<sub>6</sub> resulted to a C<sub>1</sub>-O<sub>8</sub> double bond formation and consequently, forming a cyclic C<sub>6</sub>-O<sub>7</sub>-C<sub>5</sub> bond. In MP2, this cyclic bond shifted to partial double bonds between C<sub>5</sub>-O<sub>7</sub> and C<sub>5</sub>-C<sub>6</sub>, with H19 breaking away from C<sub>5</sub> as it approaches C<sub>6</sub> during transition (TS1). In B3LYP, however, none of these partial double bonds were formed, but instead, a pseudo linear C<sub>1</sub>-O<sub>8</sub>=H<sub>12</sub> 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 ~100° 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</sup><sup>26)</sup> and some wood species whose activation energies are as high as ~109.9 kcal·mol<sup>-1</sup><sup>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<sub>8</sub>-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

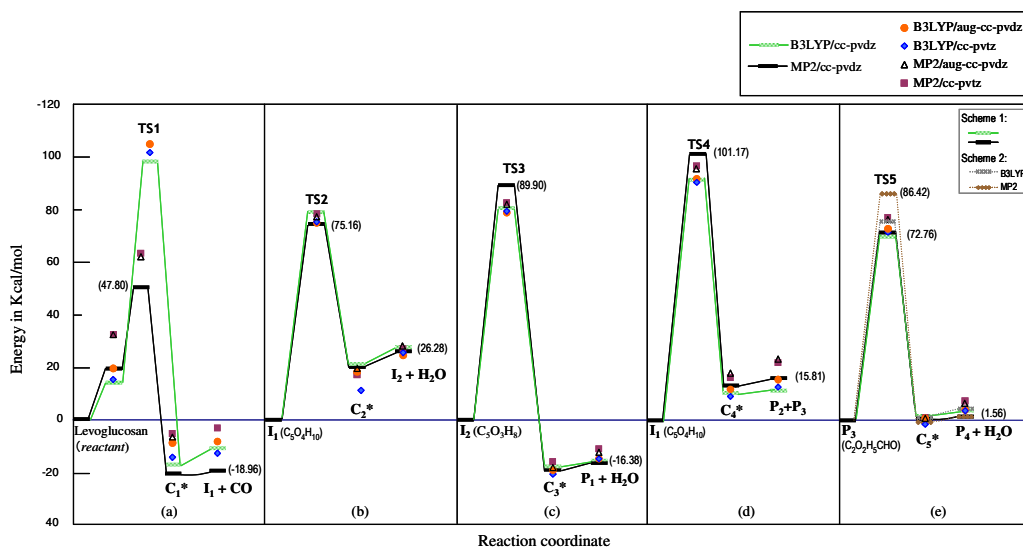


**Fig. 2** Optimized geometries and reaction mechanism of levoglucosan in the MP2 level. (a) CO elimination, (b) Dehydration, and (c) Aldehyde formation.

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

| Complexes, TS, and Products | Atom Numbers | Bond Lengths and Angles |          | Complexes, TS, and Products | Atom Numbers | Bond Lengths and Angles |                 | Complexes, TS, and Products | Atom Numbers | Bond Lengths and Angles |           |        |
|-----------------------------|--------------|-------------------------|----------|-----------------------------|--------------|-------------------------|-----------------|-----------------------------|--------------|-------------------------|-----------|--------|
|                             |              | B3LYP                   | MP2      |                             |              | B3LYP                   | MP2             |                             |              | B3LYP                   | MP2       |        |
| Levoglucosan                | C1-C2        | 1.5457                  | 1.5385   | Path 1:<br>C3*              | C1-C4        | 2.9268                  | 2.9335          | 1-pentene-3,4-dione         | C1=C2        | 1.3401                  | 1.3506    |        |
|                             | 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-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-O8        | 1.2110                  | 1.2221   | Path 2:<br>TS3              | C1-O4        | 1.2356                  | 1.219           |                             | C3=O7        | 1.2203                  | 1.2294    |        |
|                             | C6-O8        | 4.8921                  | 3.0902   |                             | 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  |        |
| TS1                         | C1-O8        | 1.1709                  | 1.1467   | Path 2:<br>C3*              | 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-O6                       | 1.2055       | 1.2188                  | acetaldehyde    | C1-C2                       | 1.5067       | 1.5097                  |           |        |
|                             | C5-C6        | 1.4720                  | 1.4293   | C1-C2-C3                    | 112.7904     | 108.4022                | C1=O3           | 1.2083                      | 1.2183       |                         |           |        |
|                             | C5-O7        | 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 | C3-O9                       | 1.2887       | 1.3035                  | C2-C1-O3-H4     | 180.0000                    | 180.0000     |                         |           |        |
| C1*                         | C1-O8        | 1.1338                  | 1.1460   | TS4                         | 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    |        |
| TS2                         | C1-C2        | 1.5223                  | 1.5194   |                             | C4*          | 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   | C1-O7                       |              | 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   | TS5                         | C3-O8        | 1.4314                  | 1.4307          |                             | C2-C3        | 1.5189                  | 1.5193    |        |
|                             | C2-C3        | 1.5097                  | 1.5144   |                             | C1-O7        | 1.7883                  | 1.7447          |                             | C1=O4        | 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   | C5*                         | C1-C2        | 1.3431                  | 1.3522          |                             | C1-H6        | 1.1224                  | 1.1209    |        |
|                             | C4-O6        | 1.2109                  | 1.2205   |                             | C2-C3        | 1.4780                  | 1.4853          | C2-O7                       | 1.0984       | 1.0998                  |           |        |
| C1-C2-C3                    | 111.5225     | 111.0711                | C3-O8    |                             | 1.2253       | 1.2319                  | C1-C2-C3        | 113.1136                    | 111.8547     |                         |           |        |
| Path 1:<br>TS3              | C1-O4        | 1.3970                  | 1.4042   |                             | C4-O6        | 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                       | O-H          | 0.9685                  | 0.9649    |        |
|                             | C3-O6        | 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 | O8-C3-C4-O6                 | 179.4583     | 179.7068                | Carbon monoxide | C-O                         | 1.1347       | 1.1472                  |           |        |

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 ( $P_1$ ) 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  $4177.693\text{kcal}\cdot\text{kg}^{-1}$  <sup>28</sup>) and  $\sim 4242\text{kcal}\cdot\text{Nm}^{-3}$  <sup>29</sup>) or approximately  $95\text{kcal}\cdot\text{mol}^{-1}$ . 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  $C_3$ - $C_4$  bond in the first intermediate (**Fig. 2c**). A simultaneous hydrogen transfer occurs from the larger to the smaller molecule, i.e., to  $C_4^*$ , 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  $15\text{kcal/mol}$  in MP2 and  $5\text{kcal/mol}$  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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