



# Pyrolysis mechanism of holocellulose-based monosaccharides: The formation of hydroxyacetaldehyde

Qiang Lu\*, Hui-yun Tian, Bin Hu, Xiao-yan Jiang, Chang-qing Dong, Yong-ping Yang

National Engineering Laboratory for Biomass Power Generation Equipment, North China Electric Power University, Beijing 102206, China

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## ABSTRACT

Fast pyrolysis of biomass will produce complex pyrolytic products. Hydroxyacetaldehyde (HAA) is one of the most important pyrolytic products, derived from fragmentation (ring scission) of holocellulose. In this study, density functional theory (DFT) calculations are employed to reveal the HAA formation mechanisms from fast pyrolysis of four holocellulose-based monosaccharides, i.e.,  $\beta$ -D-glucopyranose,  $\beta$ -D-mannopyranose,  $\beta$ -D-xylopyranose and *O*-acetyl- $\beta$ -D-xylopyranose. Moreover, the theoretical calculation results of the  $\beta$ -D-glucopyranose are confirmed by isotopic labeling fast pyrolysis experiments. The results indicate that during  $\beta$ -D-glucopyranose pyrolysis, the HAA is mainly derived from C1–C2, C5–C6 and C3–C4. The C2–C3 bond is easy to break via retro-aldol reaction to form 1,2-ethenediol (ED) which will tautomerize into the HAA from C1–C2 with high selectivity, accounting for the largest proportion of total HAA. The second largest origin of the HAA is the C5–C6 segment in multiple pathways with low energy barriers. However, these reactions to form the HAA from C5–C6 are thermodynamically unfavorable, and moreover, there are facile competing reactions to produce other products. Importantly, the HAA and levoglucosan (LG) are mainly formed via competing parallel pyrolytic pathways. Only a little HAA will be derived from the secondary cracking of LG. In addition, the HAA formation mechanisms from  $\beta$ -D-mannopyranose and  $\beta$ -D-xylopyranose are similar as those from  $\beta$ -D-glucopyranose. However, *O*-acetyl- $\beta$ -D-xylopyranose behaves differently from the other three monosaccharides due to the acetyl group at C2 position. The HAA will be mainly derived from C4–C5, accompanied with the formation of acetic acid (AA) from scission of the acetyl branch.

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## 1. Introduction

Fast pyrolysis of biomass is one of the most promising ways for the utilization of renewable biomass resources [1–4]. It can convert solid biomass mainly into a liquid product known as bio-oil which can be utilized after refining as a liquid fuel for thermal/power generation or a chemical source of valuable chemicals [3]. In order to selectively control the biomass pyrolysis process towards different target bio-oils, it is essential to understand the pyrolysis mechanism of biomass. During fast pyrolysis process, hundreds of parallel or successive pyrolytic pathways will take place, resulting in complex liquid products which consist of water, anhydrosugars, linear carbonyls, phenolics, furans, cyclopentanones, linear esters, linear alcohols, oligomers, and so on [5–7].

Among the biomass pyrolytic products, HAA is usually the most abundant linear carbonyl product [8–15], derived from both

cellulose and hemicellulose. It is regarded as the typical product of pyrolytic fragmentation (ring scission) of holocellulose. The formation of HAA from pyrolysis of cellulose has been widely investigated by experimental methods in previous studies. Early in 1986, Piskorz et al. [8] concluded that HAA was an important product of cellulose pyrolysis with a yield up to 12%. Based on the bond energy analysis, they pointed out that the glucose unit would decompose into the two-carbon (C1–C2) and four-carbon (C3–C6) fragments via the cleavage of the C1–O<sub>ring</sub> and C2–C3 bonds. They also proposed that the two-carbon fragment (C1–C2) would yield the HAA with a theoretical conversion ratio of 75%. Shen and Gu [16] and many other researchers [17,18] supported the above point that HAA was mainly derived from the C1–C2 segment of the glucose unit. Whereas Richards [9] proposed that the C5–C6 segment of the cellulose unit was the main origin of HAA through the retro-Diels-Alder reaction following the 1,2-dehydration between 3-OH and 2-H.

In order to clearly elucidate the origin of HAA from cellulose, Ponder and Richards [17] performed pyrolysis experiments of <sup>13</sup>C-labeled glucans at 300 °C, and found that HAA was mainly from

\* Corresponding author.

E-mail address: [qiangu@mail.ustc.edu.cn](mailto:qiangu@mail.ustc.edu.cn) (Q. Lu).

C1–C2, and also from C5–C6. Paine et al. [18] also used the isotopic labeling method to analyze the HAA origin from D-glucose at the pyrolysis temperature of 1000 °C, and determined the order for HAA formation as C1–C2 > C5–C6 ≫ C3–C4 ≫ ≫ (C4–C5 and C2–C3). They proposed that the HAA from C1–C2 was produced via a retro-aldol reaction and an enol-keto tautomerization reaction. The HAA from C5–C6 was mainly formed in three ways, through the retro-aldol reaction of the erythrose or the 1,3-dehydration between 3-OH and 5-H(OH) of the D-glucose, or via the retro-ene reaction of the D-fructose which was generated by the isomerization (carbonyl transfer/hydride migration) of the D-glucose.

In addition, many researchers believed that HAA could be derived not only directly from the glucose unit of cellulose, but also be from the secondary cracking of LG [19–21]. LG is the predominant product from depolymerization of cellulose, and it was believed to undergo similar pyrolytic pathways as the glucose unit, to form HAA and other products. However, recent studies have confirmed that the formation pathways of HAA and LG occurred parallelly [13,22]. In other words, HAA was mainly produced directly from the glucose unit of cellulose, and only a little HAA would be formed from the secondary cracking of LG.

During hemicellulose fast pyrolysis process, HAA is also formed as the most abundant linear carbonyl product [14,15]. Compared with cellulose, hemicelluloses are complex amorphous polysaccharides. The primary hemicellulose components are galactoglucomannans (glucomannans) and arabinoglucuronoxylan (xylan), containing abundant O-acetyl and uronic acid units as side chains [23,24]. The HAA formation mechanism from hemicellulose has gained less investigation than that of cellulose. Branca et al. [15] detected HAA in the bio-oil of glucomannan fast pyrolysis but did not explain its formation mechanism. Shen et al. [14] postulated that the HAA from C1–C2 could be directly produced from 1,4-anhydro-D-xylopyranose which was formed from the homolytic cleavage and rearrangement of xylan. Moreover, they pointed out that HAA could also be derived from 4-O-methylglucuronic acid side chain of the 4-O-methylglucurono-xylan unit.

Recently, density functional theory (DFT) [25,26] has been confirmed to be a promising theoretical tool to reveal the pyrolysis mechanism of biomass and detailed formation pathways of different pyrolytic products [27–30], because this computational quantum chemical method can clearly indicate every elementary reaction at atomic/molecular level. Assary and Curtiss [27] proposed that the successive retro-aldol reactions were the important pathways for HAA formation. Zhang et al. [28] certified the importance of the retro-Diels-Alder reaction in theory. Besides the pathway proposed by Richards [9], they also studied the pathway in which the HAA from C1–C2 was formed via the retro-Diels-Alder reaction following the 1,2-dehydration reaction between 4-OH and 5-H of the β-D-glucopyranose. In addition, Zhang et al. [29] calculated the HAA formation from C5–C6 by the 2 + 2 + 2 mechanism proposed by Lomax et al. [31]. Based on this, they further proposed the 2' + 2' + 2' mechanism in which the C1–C2 bond, C3–C4 bond and C5–O bond of the β-D-glucopyranose were cracked to generate ED from C3–C4. They also proposed that the HAA from C5–C6 could be generated by successive ring-opening and retro-aldol reactions of the anhydroglucose intermediate containing the carbonyl group at C3 position. Similarly, for the xylose pyrolysis, Seshadri and Westmoreland [30] proposed that the xylose and its isomer xylulose could be derived from the 3-ketohexose (one of the isomers of D-glucose) via successive retro-aldol and tautomerization. Afterwards, they both could generate ED (or HAA) via the retro-aldol reaction.

Although previous studies have made great contributions to reveal the HAA formation mechanism, there is still lack of systematic study to obtain acknowledged mechanism for HAA formation from holocellulose. This is because during holocellulose

pyrolysis, more than one hundred potential pathways might take place to form HAA, including various different possible reactions. Currently, no one has thoroughly considered all possible pyrolytic reactions and investigated these pathways to find out the most favorable ones. Hence, in this study, four basic monomers of holocellulose, i.e., β-D-glucopyranose, β-D-mannopyranose, β-D-xylopyranose and O-acetyl-β-D-xylopyranose are selected as the model compounds of holocellulose. These monomers are widely employed as model compounds of holocellulose for mechanism study [14,27,32,33]. Theoretical DFT calculations are employed to investigate the possible HAA formation pathways including many reactions that have not been considered in previous studies, and thus, to reveal the formation mechanism of HAA from them. The calculation results from the β-D-glucopyranose are confirmed by isotopic labeling fast pyrolysis experiments. To clearly discuss the DFT calculations, the possible HAA formation mechanisms from the β-D-glucopyranose, β-D-mannopyranose and β-D-xylopyranose are classified into three categories based on the first-step reaction, i.e., C–O bond scission-first mechanism, C–C bond scission-first mechanism, dehydration-first mechanism. Differently, the pyrolysis mechanism of the O-acetyl-β-D-xylopyranose is classified based on the sequence of the ring-opening reaction and branch scission reaction. Finally, the similarities and differences of the HAA formation from the four monosaccharides are compared and elucidated.

## 2. Experiment and calculation

### 2.1. Isotopic labeling fast pyrolysis experiments

#### 2.1.1. Materials

The materials employed for fast pyrolysis experiments included an unlabeled glucose and six <sup>13</sup>C-labeled glucoses labeling at C1, C2, C3, C4, C5 and C6 positions, respectively. The unlabeled glucose was purchased from Aladdin company, the 6-<sup>13</sup>C-glucose was purchased from Sigma company, and the other five labeled glucoses were purchased from the CIL company. The purity of the 1-<sup>13</sup>C-glucose and 5-<sup>13</sup>C-glucose samples is 98%–99%, while the purity of the other samples is 99%.

#### 2.1.2. Analytical Py-GC/MS experiments

Fast pyrolysis of the glucose samples were performed using the CDS Pyroprobe 5200HP pyrolyzer (Chemical Data Systems) connected with the Perkin Elmer GC/MS (Clarus 560). The details of analytical Py-GC/MS experiments can be found in our previous study [34]. The glucose quantity was strict to be 0.20 mg in each test. Fast pyrolysis was performed at six typical temperatures (300 °C, 350 °C, 400 °C, 450 °C, 500 °C and 800 °C) for 20 s with the heating rate of 20 °C/ms. The pyrolysis vapors were on-line analyzed by the GC/MS using an Elite-35MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The GC oven was heated from 40 °C (holding for 2 min) to 280 °C (holding for another 2 min) at a heating rate of 15 °C/min. The mass spectrometer was operated in electron ionization (EI) mode at 70 eV. The mass spectra were obtained from *m/z* 20–400. The pyrolytic products were identified according to the NIST MS library, Wiley library, and the literature data.

#### 2.1.3. Calculation of HAA origin from different carbon atoms

Identification of the HAA origin was achieved by the *m/z* peak of 60 or 61 from the mass spectra of HAA. The molecular weight (MW) is 60 for unlabeled HAA, and 61 for <sup>13</sup>C-labeled HAA. The mass spectrum of the HAA from unlabeled glucose only contains the *m/z*=60 peak, without the *m/z*=61 peak. While both *m/z*=60 and 61 peaks will appear in the mass spectra of the HAA derived from <sup>13</sup>C-labeled glucoses. Therefore, for either <sup>13</sup>C-labeled glucose, the

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