



# A theoretical study on the mechanism of xylobiose during pyrolysis process



Zeyu Li<sup>a</sup>, Chao Liu<sup>a,\*</sup>, Xiaoxiao Xu<sup>a</sup>, Qibin Li<sup>b</sup>

<sup>a</sup> Key Laboratory of Low-grade Energy Utilization Technologies and Systems, Ministry of Education, College of Power Engineering, Chongqing University, Chongqing 400044, China  
<sup>b</sup> College of Aerospace Engineering, Chongqing University, Chongqing 400044, China

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## ABSTRACT

In order to better understand the pyrolysis behavior of hemicellulose and unveil pyrolytic products distribution at molecular level, xylobiose was selected as a model compound of hemicellulose and relevant degradation processes were theoretically investigated by employing density functional theory (DFT) method. Several important reaction routes including directly bond breaking, Retro-Aldol reaction and Retro-Diels-Alder mechanism were analyzed, and the influence from adjacent xylose on the pyrolytic mechanism of xylobiose was interpreted systematically. The results indicate that the ring-opening of xylose unit dominates in the initial stage, followed by the cleavage of  $\beta$ -1,4-glycosides bond. Retro-Aldol reaction is kinetically favored and therefore leads to the formation of glycolaldehyde. Furfural, on the other hand, is generated via the cleavage of C1–O bond and subsequent ring forming between C2 and C5, which has a lower reaction energy barrier than that of 1-hydroxy-2-propanone. Aldehyde prefers to generate via Retro-Aldol reaction and decarbonylation. Although dehydration reaction is hard to occur in the initial pyrolysis process, it is still the major reaction channel to obtain formaldehyde and 1-hydroxy-2-propanone.

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## 1. Introduction

With the excessive combustion of fossil fuels and the associated concerns of environmental pollution, biomass resource as a replacement of traditional energy has drawn the continuous attention. As the unique renewable carbonaceous resource, biomass is widely available in nature [1] and has the potential to provide fuels and valued-added chemicals with zero carbon foot print [2,3]. Biomass can be converted into fuels and chemicals through several thermochemical conversion methods. For instance, pyrolysis, one of the most efficient thermal decomposition way, can convert tremendous biomass feedstock into the high-quality chemicals in the absence of oxygen [4,5]. Therefore it is regarded as a promising method that plays a pivotal role in biodegradation [6,7]. It is well known that the biomass is mainly composed of cellulose, lignin and hemicelluloses which cover in general 20–40, 40–60, and 10–25%, respectively [8]. Compared with cellulose and lignin, there is little study on the hemicellulose pyrolysis because hemicelluloses have more complicated composition [9]. Although some efforts have been paid to achieve the extraction and purification

procedures of hemicelluloses, the pure hemicellulose cannot be obtained completely from raw biomass without degradation due to the complex structure and its cross-linking with other biomass components, and thus blocks the route of uncovering pyrolytic mechanism of hemicellulose [10,11]. Therefore, systematical experimental and theoretical studies on fast pyrolysis of hemicellulose are in high demand for filling the knowledge gap.

Currently, various experimental studies, which primarily focus on the extracted/isolated methods and the distribution of pyrolytic products, have been reported in literatures on the pyrolysis of hemicelluloses. Many isolation methods have been presented including hot alkali, organic solvent, acid hydrolysis, microwave heat fractionation and so on. Unfortunately, the extraction methods, which are able to extract all hemicellulose polysaccharide from biomass [12], have not been reported. Hence, Monosaccharides or xylan were used as the model compounds to investigate pyrolytic behavior of hemicelluloses and the formation of the gaseous products together with the typical compounds in bio-oil [9,13]. Whereas, these model compounds possess less characters of hemicellulose because real hemicellulose has a matrix of different polysaccharides and its structure is diverse in nature [14], which have been proved to play a vital role in the yields and composition of bio-oil and bio-gas [15]. In order to fully describe these

\* Corresponding author.

E-mail address: [liuchao@cqu.edu.cn](mailto:liuchao@cqu.edu.cn) (C. Liu).

effects, two minimally damaged hemicelluloses were successfully isolated by using a neutral solvent, DMSO. The results showed that the O-acetyl groups and high degrees of polymerization branching in hemicelluloses were well preserved. As a result, the major component of hemicelluloses, L-arabino-4-O-methyl-D-glucurono-D-xylan was obtained and the evolution of some characteristic volatiles such as acetic acid and carbon monoxide from pyrolysis of extracted hemicellulose were analyzed by TG-FTIR and Py-GC/MS [16].

In order to explain aforementioned experimental results, the potential reaction pathways and the evolution of main products have been suggested by theoretical studies. For instance, Huang et al. [17] used xylose as the monomer model compound and found the main products of xylose pyrolysis were glycolaldehyde, acetaldehyde, furfural, acetone and CO. In addition to the conventional pyrolysis technology, thermal plasma was also introduced to thermal conversion of hemicellulose. It was found that active H<sup>+</sup> will highly accelerate dehydrogenation reactions during pyrolysis of hemicelluloses and the major products of hemicellulose pyrolysis were CO, H<sub>2</sub>, CO<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> [17]. The formation pathways of some platform chemical compounds also attracted researchers' interest. Wang et al. [18] studied the evolutionary processes from xylose to furfural by using DFT theory, and indicated that the xylulose was a significant intermediate in the formation of furfural.

Considering the limitations of computing power, most of researchers used simple monosaccharides as model compounds of hemicellulose to investigate its mechanism of pyrolysis. However, hemicellulose has a high degree of polymerization and rich in branches [19]. Therefore, xylose could not present sufficient features of entire hemicelluloses because it does not contain the glycosides bond, which is an important bond during depolymerization. Previous theoretical studies merely considered the ring-opening reaction rather than taking the cleavage of glycosides bond into account. It is reported that the rupture of glycosidic bond will lead to the formation of various vital intermediate units, and then these intermediates will induce subsequent different reaction mechanism and reaction pathways [12]. Besides, the energy barriers of pyrolysis of hemicellulose were also affected by adjacent carbohydrate units. Zhang et al. [20] used cellotriose as the model compound of cellulose and found that the adjacent glucose units will affect the opening of pyran ring. Adjacent carbohydrate also plays the role of proton donor in pyrolysis of hemicellulose and subsequently affects the distribution of products. Lu et al. [21] used cellobiose as the model compounds in order to clarify the mechanism for LGO formation from cellulose.

Above simulation studies of hemicellulose pyrolysis have not wholly revealed thermal decomposition mechanism, and therefore selecting an appropriate model compound is of practical importance for better representing hemicellulose to study its behavior during pyrolysis processes.

## 2. Model and method

### 2.1. Computation model

Hemicellulose is a group of structurally diverse polysaccharides with amorphous structure. Commercially available xylan, verified as the most common saccharide for the backbone of hemicellulose in different biomass [22], is mainly composed of xylose units linked by  $\beta$ -1,4-glycosides bond. Xylobiose is the cycle unit of xylan, and contains most of the chemical characters appear in xylan-based hemicellulose, such as the presence of glycosidic bond and adjacent xylose unit. Therefore, it is feasible to employ xylobiose as the model compound because the energy barriers of different initial reactions can be compared and the reaction pathways of pyrolysis process can be designed more comprehensively.

### 2.2. Computational details

Quantum calculations were performed using Gaussian 09 program [23], and the results were used to obtain energies of reactants and transition states and products. The equilibrium geometries of all reactants, intermediates, transition states and products involved in each chemical reaction were fully optimized by using the M06-2X level [24,25] and the 6-31+G(d,p) basis set [26,27], which performs well for description of medium range correlation such as hydrogen bonding [28]. Several studies have substantiated the feasibility of density functional theory (DFT) method [29–33]. The energies of structures were obtained after zero-point energy (ZPE) corrections. The transition states were found using QST3 methods, which were ascertained by inspecting the imaginary frequencies with the same basis set. The validity of all optimized structures were confirmed via frequency analysis, where the transition states had only one imaginary frequency and reactants and products had no imaginary frequency. Further intrinsic reaction coordinate (IRC) calculations [34,35] were also performed to confirm whether the transition state connected corresponding reactant and product. In addition, activation energies, which is defined as the energy difference between the reactants and transition states, were obtained.

## 3. Results and discussions

### 3.1. Parameters of the optimized geometries

The optimized geometries of all transition states involved in each reaction are shown in [Supplementary Materials](#). Each transition state is marked with the serial numbers, which is consistent with the numbers mentioned in this paper. The distance of atoms, participating in the reaction, has also been labeled.

### 3.2. Initial reaction

First, the initial reaction pathways are shown in [Fig. 1](#). The concerted decomposition steps of xylobiose might occur via three kinds of possible mechanisms, including glycoside bond cleavage, ring-opening and dehydration. From Path-A, it can be seen that the activation energy of the ring-opening reaction is 204.3 kJ mol<sup>-1</sup>, which makes xylobiose convert into acyclic carbonyl isomer IM1 via transition state TS-A. The reaction is endothermic reaction, and the value of heat absorption is 60.6 kJ mol<sup>-1</sup>. In this process, hydrogen atom transfers to the oxygen atom from the hydroxy of C(1') to O(6'), at the same time hemiacetal linkage C(1')–O(6') bond breaks and C(1')–O(7') bond shortens, and then the carbonyl and hydroxy functional groups will be generated. Huang et al. [36] indicated that the carbonyl functional groups can be formed through the breakage of hemiacetal C–O bond. Compared with the other five pathways, it will be easily found that the ring-opening reaction is the most kinetically favorable pathway. Wang et al. [18] investigated the conversion of xylose to furfural and concluded that the energy barrier of ring-opening reaction is much lower, 176.3 kJ mol<sup>-1</sup>. Huang et al. [17] also indicated that xylose is firstly converted to its isomer via ring-opening reaction with a low energy barrier of 170.4 kJ mol<sup>-1</sup>. By the comparison of the activation energy of these three kinds of initial ring-opening reactions, the energy barrier of the ring-opening reaction of xylobiose is a little bit higher than that of xylose, 28.0 kJ mol<sup>-1</sup> and 33.9 kJ mol<sup>-1</sup>, respectively.

Path-B to Path-E reflect the cleavage of  $\beta$ -1,4-glycosides bond. The calculation results show that the energy barriers of these reactions are higher than that of Path-A and the activation energy of Path-D is the highest one among the six initial reactions. Due to

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