



# Degradation mechanism of monosaccharides and xylan under pyrolytic conditions with theoretic modeling on the energy profiles



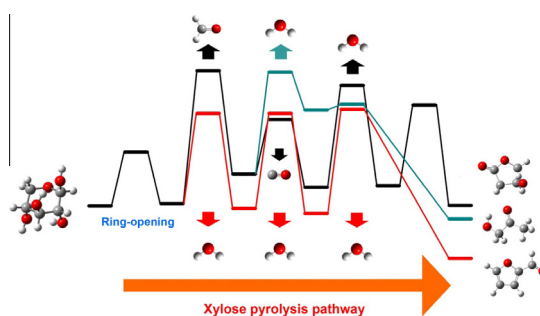
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## HIGHLIGHTS

- Xylan, mannose, galactose, and arabinose were used to represent hemicellulose.
- The evolution of typical pyrolysis products were illustrated by TG-FTIR.
- Three possible routes for xylose pyrolysis were discussed via DFT calculation.
- Insights were obtained into the formation pathways of furans and acetic acid.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Xylan and three monosaccharides (mannose, galactose, and arabinose) were selected as model compounds to investigate the mechanism of hemicellulose pyrolysis. The evolution of several typical pyrolysis products were observed by thermogravimetric analysis coupled to Fourier transform infrared spectroscopy. Monosaccharides underwent similar pyrolysis routes involving ring opening and secondary decomposition. Breakage of the *O*-acetyl groups and 4-*O*-methylglucuronic acid units in xylan branches resulted in its different pyrolysis behavior for the formation of acetic acid, CO<sub>2</sub>, and CO. The detailed reaction pathways of the monosaccharides were studied using density functional theory calculations. Furfural formation was more favorable than the formation of 1-hydroxy-2-propanone and 4-hydroxydihydrofuran-2(3H)-one during xylose degradation. However, in the pyrolysis of mannose and galactose, formation of 5-hydroxymethyl-2-furaldehyde was preferred because of the high energy barrier of the dissociation of the hydroxymethyl group. Meanwhile, the breakage of *O*-acetyl groups leading to acetic acid formation easily occurred because of its lower energy barrier.

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## 1. Introduction

As a promising thermochemical conversion route for biomass utilization, pyrolytic technology has been used for producing high-quality fuels. However, the widespread utilization of biofuels from pyrolysis is restricted by their complexity and instability (Maschio et al., 1992; Guo et al., 2010; Wang et al., 2012a).

Consequently, the mechanism of biomass pyrolysis should be studied to find an efficient solution to this problem.

It is well known that biomass consists of three major components, namely, cellulose, hemicellulose, and lignin. As cellulose (or glucose) is a common and abundant component, its pyrolytic behavior has been considerably studied (Luo et al., 2004; Lin et al., 2009; Shen and Gu, 2009). However, less attention has been paid to the pyrolysis of hemicellulose because of its complex composition and branched structure. Hemicellulose is a complex polymer mainly composed of pentoses (xylose and arabinose) and hexoses (mannose, galactose, and glucose). Hemicellulose is present in biomass at a typical proportion of 20–40%, and has

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significant influence on the pyrolytic behaviors of cellulose and lignin (Wang et al., 2008; Wang et al., 2011). The abundant branches linked to the main chain of hemicellulose easily decompose into small molecular products (CO, CO<sub>2</sub>, acetic acid, etc.) at low temperature (Yang et al., 2007). Another challenge in hemicellulose pyrolysis research is the acquisition of real hemicellulose samples. Hemicellulose almost cannot be completely extracted from biomass, and its chemical properties change with the isolation technique (Zeitoun et al., 2010). Xylan is the most commonly used model compound for hemicellulose in previous mechanistic studies, as it is the basic building block of hemicellulose. Xylan mainly consists of xylose, arabinose, and galactose, whose amounts depend on the biomass species. Birch-wood xylan contains 89.3% xylose and 1% arabinose (Kormelink and Voragen, 1993). Corn-fiber xylan contains 48–54% xylose, 33–35% arabinose, and 5–11% galactose (Saha and Bothast, 1999). Yang et al. (2007) studied the pyrolysis behavior of birch-wood xylan using thermogravimetric analysis, and found that xylan mainly decomposed in the temperature range of 220–315 °C. The lower initial decomposition temperature of hemicellulose compared with that of lignin might be ascribed to its lower degree of polymerization (Patwardhan et al., 2011). The main decomposition products of xylan are acetic acid, furfural, 1-hydroxy-2-propanone, CO<sub>2</sub>, CO, H<sub>2</sub>O, and so forth. Among them, acetic acid and furfural are considered as the main products that have significant influence on the biofuel quality (Patwardhan et al., 2011; Nowakowski et al., 2008).

Besides xylan, there are other polysaccharides in hemicellulose. Glucomannan, which is abundant in softwood hemicellulose, is mainly composed of D-mannose and D-glucose (Nowakowski et al., 2008). Di Blasi et al. (2010) pointed out that for softwood hemicellulose pyrolysis, 5-hydroxymethyl-2-furaldehyde (HMF) is the main product, which is different from that of hardwood. Räisänen et al. (2003) investigated the pyrolytic behaviors of xylose, mannose, and arabinose. They found that the pyrolytic products of xylose are almost the same as those of arabinose. However, they found HMF only in the products of mannose pyrolysis. Therefore, hexoses and pentoses in hemicellulose have different pyrolytic behaviors. In the present study, four typical model compounds (xylan, mannose, galactose, and arabinose) were chosen to represent hemicellulose for the corresponding research on hemicellulose pyrolysis behavior.

Recently, density functional theory (DFT), a quantum-mechanical modeling method used to describe the electronic structure of many-body systems, has been introduced to study the biomass pyrolysis mechanism. Wang et al., 2012b pointed out that HMF formation is more favorable than levoglucosan formation for the decomposition of the D-glucopyranose unit. Zhang et al. (2010) studied the dehydration behavior of cellulose, and found that the location of the hydroxyl group has a significant influence on this process. However, few studies have focused on the details of hemicellulose decomposition. Huang et al., 2012 proposed five possible pyrolytic pathways of xylose and indicated that furfural could be easily formed because of its lower energy barriers. However, these results have very limited explanation of the complex process of hemicellulose pyrolysis since they are only based on purely theoretical calculations. In the present study, TG-FTIR was first carried out to analyze the evolution of typical products of the pyrolysis of the four model compounds. The corresponding pyrolytic routes were proposed and subsequent DFT calculations were performed.

## 2. Methods

### 2.1. Materials

The model compounds used in the study (D-xylan, D-mannose, D-galactose, and D-arabinose) were all purchased from Sigma-

Aldrich Corporation. Xylan is faint yellow whereas the other three monosaccharides are white. All of them are powders with an average particle diameter of 20 μm. Xylan, which is a polymer predominantly composed of xylose units, was extracted from beechwood. Table 1 shows the elemental analysis results of the four model compounds. The calculated molecular formulas are identical with the theoretical formulas of the monosaccharides. Because of its oxygen-rich groups in the side branches, xylan has a higher oxygen content than does xylose monomer.

### 2.2. Experimental methods

A thermogravimetric analyzer (Mettler–Toledo TGA/SDTA851e) coupled to FTIR spectroscopy (Nicolet NETXUS 670) (TG-FTIR) was used to study the pyrolysis behavior of the four model compounds. The experiment was carried out at a linear heating rate of 20 °C/min within the temperature range of ambient to 800 °C. To mitigate differences in heat and mass transfer, all of the sample weights were maintained at 10 mg. Nitrogen with purity of higher than 99.99% was used as carrier gas and kept in a steady flow of 40 mL/min to provide an inert atmosphere for pyrolysis. The volatiles released during pyrolysis were immediately swept to a gas cell through a Teflon tube. Both gas cell and Teflon tube were preheated to 180 °C to avoid condensation or adsorption of semi-volatile products. The volatiles were analyzed on a Nicolet NETXUS 670 FTIR equipped with a deuterated triglycine sulfate pyroelectric detector, which has the advantages of rapid response and low noise. The spectrum was obtained at 400–4000 cm<sup>-1</sup> at a resolution of 16 cm<sup>-1</sup>.

### 2.3. DFT calculations

The electronic structure calculations were performed using the Gaussian 03 program. The B3LYP functional with 6–31++G(d, p) basis set was used to optimize the geometries of the reactants, intermediates, transition states, and products (Wang et al., 2012b; Huang et al., 2012). The possible reaction intermediates and related elementary reactions were constructed according to the TG-FTIR analysis results. The reaction pathways were considered feasible only when there was no imaginary frequency in the optimized structures of reactants, intermediates, and products; and when transition states contained a single imaginary frequency. The activation energy, which was corrected by the zero-point energy, was defined as the difference in energies between the transition state and the reactant. All thermodynamic data were calculated as the relative values for products and reactants.

## 3. Results and discussion

### 3.1. Thermal analysis of the four model compounds

The pyrolysis behaviors of the four model compounds were studied by TG and differential thermogravimetry (DTG) at a heating rate of 20 °C/min. The results show that the four model compounds had the same trend of weight loss. The main degradation occurred at about 200 °C, and the weight loss rate reached a

**Table 1**  
Elemental analysis of the four model compounds.

| Sample    | C <sub>ad</sub> (wt.%) | H (wt.%) | O (wt.%) | Calculated molecular formula                        |
|-----------|------------------------|----------|----------|---|
| Xylan     | 36.00                  | 6.08     | 57.92    | C <sub>5</sub> H <sub>10.13</sub> O <sub>6.03</sub> |
| Arabinose | 40.01                  | 6.80     | 53.19    | C <sub>5</sub> H <sub>10.21</sub> O <sub>4.98</sub> |
| Mannose   | 39.65                  | 6.84     | 53.51    | C <sub>6</sub> H <sub>12.44</sub> O <sub>6.07</sub> |
| Galactose | 39.89                  | 6.83     | 53.28    | C <sub>6</sub> H <sub>12.34</sub> O <sub>6.02</sub> |

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