



Role of different chain end types in pyrolysis of glucose-based anhydro-sugars and oligosaccharides

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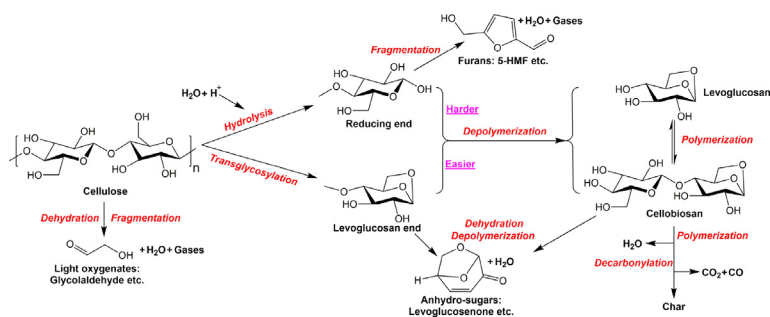
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GRAPHICAL ABSTRACT



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ABSTRACT

This study investigates the pyrolysis characteristics of glucose-based anhydro-sugars (maltosan and levoglucosan) and oligosaccharides (cellobiose, cyclodextrin and cellulose) using TG-FTIR-MS and the role of the reducing and levoglucosan ends in cellulose pyrolysis. During the slow pyrolysis of two disaccharides (cellobiose and maltosan), dehydration reactions were strongly promoted at low temperatures due to the polymerization, which led to the earlier decomposition of maltosan and cellobiose compared with other carbohydrates. Compared with the reducing end in cellobiose, the levoglucosan end in maltosan enhanced the cleavage of glycosidic bonds, which led to the maximum weight loss of maltosan at a lower temperature (i.e. 232 °C) than that of cellobiose (i.e. 299 °C). Furthermore, because of the stability of the levoglucosan end, a significantly higher char yield was obtained after an obvious carbonization process at the expense of gaseous volatiles. Fast pyrolysis of these samples at 500 °C was also conducted on Py-GC/MS and yields based on carbon of 28 products were identified. The results show that the reducing end prompted the rupture of pyran rings for furan species, while the stable structure of the levoglucosan end strongly promoted the formation of pyrans such as levoglucosenone. Finally, a mechanism for cellulose pyrolysis is proposed, which takes into consideration the effects of the different chain ends.

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1. Introduction

In last few decades, fossil fuels occupy the leading position of primary energy sources and ensure the operation of modern industry. However, accompanying concerns about the environmental pollutions and energy shortage pursue the gradual renewable clean substitution of conventional fossils. Biomass, as the only carbon based new energy resource, owns a huge global annual production and is a promising substitute resource for the traditional petrochemical industry [1]. The utilization of it make up a ‘carbon-neutral’ circle together with the photosynthesis. In consideration of the concerns of food security coming from first generation corn-based ethanol, lignocellulosic biomass has gained more and more interests in the recent years [2]. The conversion methods of lignocellulosic biomass can be generally divided into biochemical conversion methods and thermochemical conversion methods. In most thermochemical conversion processes including combustion, pyrolysis, gasification etc., pyrolysis is always the initial stage and a prominent technology for the production of chemicals and bio-oil [3]. However, the complicated pyrolysis chemistry involves numerous reactions, and the obtained products suffer from the low selectivity or the poor quality, which require further refinement and upgrading treatments [4]. Therefore, a clear understanding of the biomass pyrolysis mechanisms is critical for the optimization of pyrolysis conditions and subsequent treatments.

Lignocellulosic biomass comprises three main components, i.e. cellulose (40–50 wt%), hemicellulose (25–35 wt%) and lignin (16–33 wt%) [5]. Cellulose molecular chain results from the polymerization of glucose monomers in β -1,4-glycosidic bonds. Numerous chains are connected by intra-molecular and inter-molecular hydrogen bonds leading to cellulose fibres, which further constitute macro cellulose substance [6]. The pyrolysis characteristics of cellulose can partially reflect the regularity of lignocellulosic biomass pyrolysis [7]. Extensive work has been done related to cellulose pyrolysis and draw various conclusions [1,8,9]. At the initial stage, the hydrogen bonds network changes as the temperature increases [10–12]. Following it, liquid intermediates are observed probably coming from the depolymerization of the original cellulose chain and the drop of short chain from cellulose [13,14]. It was suggested that the intermediates mainly consist of oligosaccharides (degree of polymerization, DP = 1 ~ 15) and anhydro-sugars (DP = 1 ~ 11) [15,16]. After the stage, the intermediates further depolymerizes and fragments into anhydro-sugars, furan/pyran derivatives and C2–C4 low molecular weight products (LMWPs), concerning two kinds of reactions, depolymerization and ring scission [17]. Related to depolymerization of cellulose, efforts have been made by many researchers and resulted into several possible reaction pathways including hydrolysis, transglycosylation, homolysis, heterolysis etc. [18–21] Zhang et al. compared four mechanisms for the formation of levoglucosan through quantum chemical calculations and proposed that levoglucosan chain-end (LG-end) mechanism which happens via two transglycosylation steps is the most reasonable pathway [22]. A recent work by Zhu et al. [23] used α -cyclodextrin as the kinetic surrogate for cellulose and studied its initial breakdown kinetics from 385 °C to 505 °C on a millisecond, thin-film reactor. The results show two kinetic regimes with apparent energetics of 23.2 kcal·mol⁻¹ at low temperature and 53.7 kcal·mol⁻¹ at high temperature, respectively comparable to hydrolysis and transglycosylation. These two processes can lead a non-reducing end (NR-end) and a reducing end (RD-end) or a LG-end. In previous work [24–27], RD-end is proved to affect the products distribution of the cellulose pyrolysis. Reactive RD-end was suggested to be sensitive to temperature, and the degradation of it can provide H₂O and H⁺ for the acceleration of the following pyrolysis reactions [24,27]. NR-end, which can interact with RD-end through glycosylation, can stabilize the cellulose against discoloration and weight-loss [28]. As to LG-end, to the best of our knowledge, there is no experimental study available on the role of it in the cellulose pyrolysis. Furthermore, as suggested in our previous works [15,29], anhydro-

sugars such as levoglucosan and cellobiosan are the main primary products of the cellulose pyrolysis, which contain the LG-end. Their secondary degradation is of critical importance to the cellulose pyrolysis mechanism, and model compounds were often used to explore the pyrolysis mechanism of biomass [25,30–33]. Previous works [25,34] studied the fast and slow pyrolysis of cellobiose and maltose using Py-GC/MS and TG-MS, respectively. The results suggested that the pyrolysis characteristics of two disaccharides were not strongly influenced by the different conformation of 1,4-glycosidic bonds. Although cellobiosan was proposed as one of the primary products during cellulose pyrolysis, maltosan had an appreciable yield during pyrolysis in fluidized bed with serious secondary reactions [35]. Therefore, in this work, in consideration of the unavailability of cellobiosan with an acceptable purity, maltosan with a α -1,4-glycosidic bond was used as a representative of anhydro-sugars. The slow and fast pyrolysis of it was conducted on the TG-FTIR-MS and Py-GC/MS together with the pyrolysis of levoglucosan and several oligosaccharides.

2. Materials and methods

2.1. Samples used

Microcrystalline cellulose (Avicel PH-101), levoglucosan (1,6-anhydro- β -D-glucopyranose), α -cyclodextrin and cellobiose were all purchased from Sigma-Aldrich. Maltosan was obtained from Carbosynth Ltd. (England) with negligible amounts of impurities, as shown in Table 1S and Fig. 1S. Table 1 lists the chemical structures of these samples.

2.2. TG-FTIR-MS experiments

Slow pyrolysis experiments were conducted in the same device used by Zhang et al. [24]. In each experiment, ~15 mg of sample was heated from 35 to 700 °C at a heating rate of 10 °C/min in an inert atmosphere of argon, whose flow was 100 ml/min. To prevent condensation of volatiles, the connecting lines between the TGA and the FTIR and the MS were kept at 200 °C. The scanning ranges of the FTIR and MS were 4000–400 cm⁻¹ and 0–200 amu, respectively. Four selected ions (m/z = 18, 44, 60, 96) were monitored in this work corresponding to H₂O, CO₂, acetic acid and furfural. Each experiment was carried out for three times to verify the reproducibility, which was found adequate.

2.3. Py-GC/MS experiments

In the fast pyrolysis experiments, 3 μ L aqueous mixture of sample (10 wt%) was loaded in the middle of the quartz-tube between two layers of quartz wool and dried at 75 °C for 12 h. The sample amount was determined by weight difference of the tube before and after loading. Then the tube was loaded on a CDS5200 Pyroprobe (CDS Analytical, USA), equipped with a 7890A/5975C GC/MS (Agilent Technologies, USA). All the experiments were carried out at a heating rate of 10 °C/s to 500 °C and held for 20 s at the final temperature. A relatively low heating rate of 10 °C/s was chosen to minimize the difference between the set temperature and the sample temperature according to a previous work. Other pyrolysis parameters may be found elsewhere [24]. Each experiment was carried out for three times. Furthermore, according to the method of previous work [24,36], 27 compounds were identified, among which 12 main compounds were quantified by corresponding pure standards mainly through direct injection of their acetone solution into the GC/MS, while levoglucosan and glycolaldehyde depended on the pyrolysis of levoglucosan and glycolaldehyde dimer. The remaining 15 compounds were quantified only by MS according to the standard curve of certain compound with a similar molecular weight and structure. Table 2S shows the quantification information of the 27 compounds.

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