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Mechanism of cellulose fast pyrolysis: The role of characteristic chain ends and dehydrated units

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ABSTRACT

Understanding the fundamental reactions and mechanisms during biomass fast pyrolysis is essential for the development of efficient pyrolysis techniques. In this work, quantum chemistry calculation, kinetic analysis and fast pyrolysis experiment were combined to reveal the cellulose pyrolysis mechanism. During cellulose pyrolysis, the indigenous interior units, reducing end (RE end) and non-reducing end (NR end) initially form various characteristic chain ends and dehydrated units which then evolve into different pyrolytic products. As the rising of the degree of polymerization (DP), reactions occurring at the interior unit and NR end are more competitive than those taking place at the RE end, resulting in distinct pyrolytic product distribution for cellulose and glucose-based carbohydrates. The reactions occurring at the three indigenous units of cellulose chain all favor the formation of levoglucosan-terminated end (LG end) and/or NR end, which then generate levoglucosan (LG). The acyclic D-glucose end (AG end), which mainly derives from the RE end, is essential for the formation of 1,6-anhydro-β-D-glucofuranose (AGF), 1,4:3,6-dianhydro-α-D-glucopyranose (DGP), furfural (FF), 5-hydroxymethyl furfural (5-HMF) and hydroxyacetaldehyde (HAA). Compared with the chain ends, the dehydrated units are not feasible to be generated, and their decomposition favors the formation of HAA.

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1. Introduction

Biomass is an important renewable organic resource which can be converted into various fuels and chemicals by different technologies, to alleviate the severe energy shortage and environmental pollution problems. Fast pyrolysis is a green and efficient way to convert biomass materials mainly into liquid products which can be utilized as liquid fuels for thermal and power generation or as raw materials for chemicals extraction and production [1,2]. During biomass fast pyrolysis process, various competing pyrolytic reactions take place, complicating the pyrolysis mechanism and product distribution. A deep insight into the pyrolysis mechanism can help develop efficient pyrolysis techniques towards valuable products [3].

Cellulose is usually the most abundant component of lignocellulosic biomass. Its fast pyrolytic bio-oil mainly consists of water, anhydrosugars, furan derivatives and light oxygenated compounds. The major organic compounds include levoglucosan (LG), levoglucosenone (LGO), 1,6-anhydro-β-D-glucofuranose (AGF), 1,4:3,6-dianhydro-α-D-glucopyranose (DGP), 1,5-anhydro-4-deoxy-D–glycero–hex–1-en-3-ulose (APP), 1–hydroxy–3,6-dioxabicyclo[3.2.1]octan-2-one (LAC), 5-hydroxymethyl furfural (5-HMF), furfural (FF), hydroxyacetaldehyde (HAA), hydroxyacetone (HA), acetic acid (AA) and formic acid (FA), etc. [4,5]. LG is usually the most abundant anhydrosugar and also the most abundant organic liquid product in bio-oil [6,7]. Its formation mechanism has been widely investigated. The most accepted viewpoint was that LG derived from the levoglucosan-terminated end (LG end) or the non-reducing end (NR end) through continuous depolymerization (transglycosylation) [8–10]. However, less attention has been paid to other anhydrosugars. LGO, AGF and DGP were previously regarded as the secondary decomposition product of LG [11,12]. Later studies implied that these minor anhydrosugars should be mainly formed in parallel pathways of LG [13,14]. In terms of furan derivatives and light oxygenated compounds, their formation relies on the occurrence of acyclic structures (reducing sugar), which mainly come from the reducing end (RE end) [15,16].

So far, different experimental and theoretical approaches have been applied to reveal cellulose pyrolysis mechanism. Particularly, the application of quantum chemistry methods offers a promising way to deepen the insight into the chemical reactions in fast pyrolysis at atomic/molecular level. Due to the high degree of poly-

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merization (DP) of cellulose, it is necessary to select proper model compounds for pyrolysis mechanism investigation using quantum chemistry methods [17]. Glucose is the basic unit of cellulose and has been widely used to analyze the chemical reactions mechanism in cellulose fast pyrolysis [18–21]. However, glucose does not contain glycosidic bonds and the yields of glucose pyrolytic products differ remarkably from those of cellulose [6,15]. Given the limitation of glucose as the cellulose model compound, cellobiose (dimer) and cellotriose (trimer) are more suitable to be employed as cellulose representatives. Currently, few theoretical studies have been performed on them as compared with glucose. During the pyrolysis of cellulose and glucose-based carbohydrates, the initial decomposition process forms various characteristic chain ends and dehydrated units, which then evolve into different pyrolytic products. Broadbelt et al. [10] and Zhou et al. [22,23] emphasized the importance of the distinct chain ends and dehydrated units for the final pyrolytic product distribution. However, the role of chain ends and dehydrated units has not been well investigated by theoretical methods. Moreover, distinct theoretical methods were adopted in previous literatures which brought difficulties in comparison of the formation reactions for each product.

In this study, quantum chemistry calculation was performed based on density functional theory (DFT) [24] which has already been employed in pyrolysis mechanism study [25–27]. Both cellobiose and cellotriose were selected as the model compounds to reveal their primary pyrolysis mechanism to form the characteristic chain ends i.e., LG end, RE end, NR end, acyclic D-glucose end (AG end), 2,5-anhydro-D-mannose end (ADM end) and unsaturated end (US end) as well as dehydrated units. Afterwards, the evolution pathways and pyrolysis mechanisms of these chain ends and dehydrated units were explored to reveal their effects on final product distribution based on the kinetic parameters of elementary reactions. In addition, the theoretical results were compared with the fast pyrolysis experimental results of glucose-based carbohydrates and cellulose to give a systematical insight into cellulose fast pyrolysis mechanism.

2. Methods

2.1. Computational section

All the calculations were performed by using Gaussian 09 D.01 software [28]. According to Mayes et al. [8], fast pyrolysis of cellulose mainly followed the concerted mechanism, rather than homolytic or heterolytic mechanism. Hence, all the calculations were based on concerted reactions. Firstly, M06-2X functional [29] and combined 6-31 + G(d,p) basis set were employed to optimize the geometries for all compounds (reactants, transition states, intermediates and products). Afterwards, vibrational analysis was conducted to confirm the reliability of the above geometries. Every transition state had exactly one imaginary frequency which had a proper vibration pattern. And there were no imaginary frequencies existing for the other compounds. Thermodynamic parameters (i.e., enthalpy, Gibbs free energy, etc.) were also obtained by vibrational analysis. Furthermore, intrinsic reaction coordinate (IRC) analysis was conducted to prove that the transition state corresponded to the proper reactant and product for each elementary reaction. Detailed structures and atomic coordinates of all the compounds involved in the pyrolytic reactions are shown in the Supplementary Materials (*Section* S9).

Based on the quantum chemistry calculation results, kinetic analysis was performed to obtain the rate constant k, the pre-exponential factor A, and the activation energy E_a. Kinetic parameters were calculated by using transition state theory (TST) [30] with detailed information shown in the Supplementary Materials (*Section* S1).

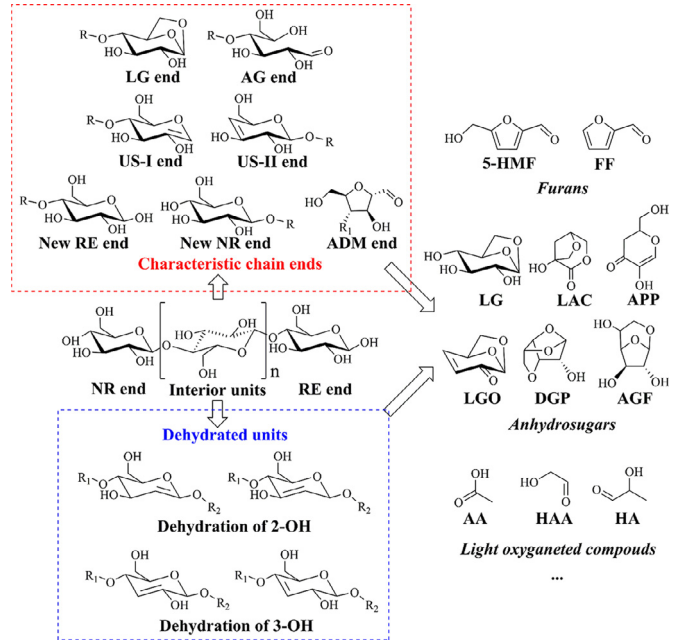

Fig. 1. Schematic diagram of the cellulose pyrolysis process.

Fast pyrolysis usually performs at medium temperatures around 500 °C. Therefore, the activation free energies and rate constants ($\triangle G^{\neq}_{500\,°C}$ and $k_{500\,°C}$) are all reported with the values obtained at 500 °C in this study.

2.2. Experimental section

Three glucose-based carbohydrates and cellulose were used for fast pyrolysis experiments. The three carbohydrates were D-(+)-glucose (≥99.5%, GC), D-(+)-cellobiose (98%) and D-(+)-cellotriose (>95.0%, HPLC), which were purchased from Aladdin, Macklin and TCI, respectively. Microcrystalline cellulose (Avicel PH-101) was purchased from Sigma.

Analytical pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) experiments were conducted using the connected CDS Pyroprobe 5200HP pyrolyzer (Chemical Data Systems) and the Perkin Elmer GC/MS (Clarus 560). The detailed experimental process has been reported in our previous work [31]. To be brief, fast pyrolysis was performed at 500 °C for 20 s with a fast heating rate of 20 °C/ms. The carrier gas was helium (He, 99.999%) with a flow rate of 80 mL/min. In each experiment, the sample weight was strictly 0.20 mg. The experiments for each sample were repeated for at least three times, and peak area and peak area% values were recorded for each product.

3. Results and discussion

Each cellulose chain has one RE end, one NR end and hundreds or thousands of interior units. During the initial pyrolysis process, the cellulose chain undergoes complex depolymerization (transglycosylation, hydrogen shift), dehydration, ring-opening and other reactions to generate various characteristic chain ends, including new RE end, new NR end, LG end, AG end, ADM end, US-I end (US end with C1 = C2 bond), US-II end (US end with C3 = C4 bond), as shown in Fig. 1. In addition, dehydration reactions of free hydroxyl groups (2-OH and 3-OH) result in the formation of dehydrated units. These characteristic chain ends and dehydrated units then evolve into various pyrolytic products (anhydrosugars, furan derivatives and light molecular compounds) through different pathways. Based on this fact, the formation of characteristic

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