



## A new horizon on effects of alkalis metal ions during biomass pyrolysis based on density function theory study

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### ABSTRACT

In this work, a local pyrolytic model was brought up firstly to understand better the pyrolysis mechanism of cellulose with alkalis metal, and density function theory (DFT) was employed to investigate eight reaction pathways of  $\beta$ -D-glucopyranose. The mechanism of levoglucosan formation was based on the concerted mechanism, and that of other small molecular structures, such as hydroxyacetaldehyde acetol, acetic acid, etc., referred to in our previous work. All thermodynamic and kinetic parameters were calculated using Gaussian method at B3LYP level based on 6-31G (d, p) basis set. According to calculation results, the formation of levoglucosan was restrained remarkably by adding alkalis mental ions, which indicated the validity of the local pyrolytic model and also demonstrated that it was indeed suitable to describe the process of levoglucosan formation through concerted mechanism. On the other hand, the yields of other small molecules were enhanced with  $K^+$  and  $Na^+$ . All results above were consistent with related experimental conclusions. So the local pyrolytic model is an appropriate tool to study the effect of catalyst and a feasible way to search a new high-efficiency catalyst on the biomass pyrolysis in the future.

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### 1. Introduction

Recently, due to the shortage of fossil fuel and the worsening environmental problem, exploring new and renewable energy has become increasingly significant. As one of the most important renewable resources, biomass energy has been playing a pivotal role in conquering the challenges mentioned above. Bio-oil, which can be obtained by liquefaction technology from pyrolysis of biomass, has many advantages like easy storage, transportation and high energy density. Therefore, biomass liquefaction technology was considered as a promising way to utilize biomass energy. Cellulose is the main composition of the biomass, so it is of vital importance to study mechanism of cellulose pyrolysis to reveal bio-oil formation mechanism.

Amounts of work have been completed to unveil the mechanism of cellulose pyrolysis [1–5] by experimental and theoretical methods. B-S pyrolytic model [6] was regarded as an appropriate way to explain effects of exterior conditions and corresponding changes in products of tar, gas and coke, which indicated that the transition from cellulose to active cellulose happened firstly

under low temperature through depolymerization, then char, gas and volatile ingredients were generated during further pyrolysis of active cellulose. Based on this model, several improved models were developed to better fit in the experimental phenomena [7–10]. Levoglucosan (LG) was a significant and common outcome during cellulose pyrolysis and also was the main component of bio-oil. Hence, numerous efforts were paid to it and large numbers of literature have provided detailed mechanisms of LG formation and degradation [1,2,4,5,11]. Huber et al. held the view that the first procedure of cellulose pyrolysis yields LG and anhydrosugar polymers, after that the dehydration of anhydrosugars leads to furanoses and hydroxyacetaldehyde. Hydroxyacetone and glyceraldehyde could be produced from retroaldol condensation of anhydrosuga [12]. According to the experimental results, Shanks et al. proposed the mechanism that levoglucosan and low molecular weight compounds were formed through competitive reactions rather than sequential pyrolytic reactions [13], which was in accordance with other work conducted by Luo et al. [14] and Yang et al. [15]. Most scholars asserted that LG comes from active cellulose [8,16,17]. Although levoglucosan could be generated from cellulose through heterolysis or homolysis ways, it was more considerable to accept that the concerted mechanism was the main reaction channel because of its relatively low energy barrier [5,18]. During the pyrolysis of cellulose, hydroxyacetaldehyde (HAA) was

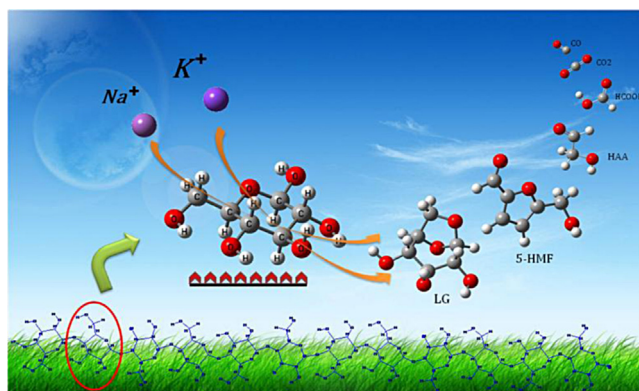
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another main product compared with other small molecular outcomes [8,16,17,19]. Some experimental results indicated that the formation of HAA was derived from the immediate product pyrolysis such as the active cellulose [3,7,9]. How to convert cellulose to HAA and other products in small proportion, such as acetol, formic acid and furfural is still unclear. In our previous work, seven concrete chemical reactions were discussed with an emphasis on formation of HAA by DFT method to illustrate how these outcomes were generated [20]. And results indicated that HAA can be generated from monosaccharide or produced directly from cellulose chain, which were in accordance with relevant experimental results [3,11,21,22].

The pyrolysis of cellulose was complex in view of inner and extra factors. Thus, it is meaningful to investigate these external conditions, like catalyst, to further understand cellulose pyrolysis mechanisms and to achieve more target products. Alkali metal ions like sodium and potassium ions are necessary elements during biomass growing process, and also have significant influence in cellulose pyrolysis. In 1996, according to experimental results, Szabo et al. concluded that the presence of the mineral salts increases the char yield highly and amounts of light volatiles, but decreases the amount of the tar fraction [23]. Jones also got a similar result that adding potassium ion can increase char formation [24]. Similarly, the proportion of HAA and other small molecule components were also enhanced by catalytic effects of metallic salts in the work of Wang et al. [25]. Large numbers of literature also came to an agreement on conclusions aforementioned [26–29]. Nevertheless, previous studies concentrated merely on experimental phenomena caused by these catalysts, few reports focused on how these alkalis metal ions worked to alter the proportions of pyrolytic products. DFT method was a proper tool to probe into the mechanism of cellulose at micro scale and calculation results are also widely accepted in this field by using DFT. Many literature have explained detailed mechanisms of cellulose pyrolysis including formations of LG, HAA, furan and other gas outcomes under non-catalyst condition by this method [5,30–32]. However, few efforts were allocated to explore effects of catalysts during pyrolytic processes on molecular level. In 2012, Jones et al. employed *ab initio* calculation to investigate effects of catalysts for the first time, and their results indicated that the metal ions form multiple interactions with hydroxyl and ether groups in the cellulose structure [33], while concrete chemical reactions with metal ions were not discussed in their work. For the purpose of understanding the effect of catalysts and seeking appropriate catalysts to enhance the proportion of target products at micro scale, unveiling the mechanism of cellulose pyrolysis with catalyst is of significant importance.

## 2. Calculation model

Choosing an appropriate model compound is of crucial importance by using DFT method. As one of the minor products of cellulose,  $\beta$ -D-glucopyranose has many specific characteristics: firstly, it is a cyclic monomer of cellulose chains, which contains all chemical bonds in pyran ring such as C–C bonds, C–O bonds and hydroxyl groups. Another advantage is that the pyrolysis of  $\beta$ -D-glucopyranose can also reflect chemical reaction processes at the end of cellulose chains. Experimental results revealed that compositions of products from fast pyrolysis of glucose and cellobiose were similar to that from cellulose [34]. Other literature also illustrated mechanisms of cellulose by using the glucose, even smaller model compounds, and results obtained were all consistent with related experiments [35–38]. Therefore, it was reasonable to employ  $\beta$ -D-glucopyranose as a model structure to investigate the principles of cellulose pyrolysis.



Scheme 1. Main products of  $\beta$ -D-glucopyranose pyrolysis.

Chemical reactions with catalyst were relatively complicated and traditional experimental methods could not figure out how the catalyst works during pyrolytic reactions; while DFT method has advantages in presenting what happens during concrete reactions. In order to study these extremely complex catalytic processes, an appropriate simplification was necessary on the condition of non-missing reality. A simplified catalytic model called local catalyst model was brought up in this work, which described that the main atoms merely participating in reaction should be taken into consideration during a concrete catalytic reaction. These atoms belonged to a local small reaction system with certain electric charge. And these main atoms were selected after calculations and analyses. Specifically, metal ions ( $K^+$  and  $Na^+$ ) and  $\beta$ -D-glucopyranose structure were main parts constituting the system, and concrete catalytic reactions were based on these main atoms. Although this model cannot represent all conditions in reality, it can give us a clear description of catalyst working during cellulose pyrolysis from molecular level. Also this model will be helpful to research effects of other catalysts and explore new catalysts by simulated calculation in the future.

## 3. Calculation details

### 3.1. Design of reaction pathways

In order to have a full investigation on pyrolytic ways of  $\beta$ -D-glucopyranose and shed light on the effect induced by metal ions, main products were studied as shown in Scheme 1. For the formation of LG, the concerted mechanism was investigated in this work. The formation of other small molecular structures, such as HAA, acetol, formic acid, formaldehyde and glyoxal, were mainly based on reactions in our previous work [20], also all parameters under the condition of pure pyrolysis referred to it. The details of each reaction pathways can be referred in supporting information.

### 3.2. Calculation methods

The DFT method based on quantum mechanisms was employed. The equilibrium geometries of all reactants, intermediates, transition states and products involved in every chemical reaction was performed at B3LYP level with 6-31G (d,p) basis set, which was a proper choice of a model chemistry for most systems, especially for organic molecules, because it can provide accurate geometrical parameters and energies with low computational costs. All the calculations were performed in the state of ground. The transition states were located by TS method and were confirmed by frequency analysis and intrinsic reaction coordinate (IRC) calculations. With the same basis set, all the energies of structures were obtained after zero-point energy (ZPE) correction and that of optimizations

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