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Reaction pathways of hemicellulose and mechanism of biomass pyrolysis in hydrogen plasma: A density functional theory study

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ABSTRACT

In this work, the reaction pathways of hemicellulose were investigated for a complete understanding of the mechanism of biomass pyrolysis in thermal plasma. Energies of the possible reaction pathways of three model compounds of hemicellulose, xylose, *O*-acetyl xylose and 4-*O*-MeGlcA, in hydrogen plasma were estimated through density functional theory (DFT), and the most favorable reaction routes were proposed. Combining with our previous work, the effects of the biomass composition on their pyrolysis behavior in hydrogen plasma were discussed, and the production distribution was predicted. The reaction mechanism of biomass pyrolysis in hydrogen plasma was clarified finally, which indicated that active H• in plasma played a very important role in dehydrogenation reactions.

1. Introduction

Biomass, as a typical renewable energy and carbon carrier, has been drawing more and more interests. It can be converted into chemicals and fuels [1,2], which can significantly eliminate the negative effects of fossil energy consumption on the environment. Among all the utilization ways of biomass, thermal pyrolysis is an attractive one, and it can be an alternative for the production of syngas [3,4]. Thermal plasma is a working media, usually generated by arc discharge in gases, consisting of a mixture of electrons, ions and neutral particles [5]. Due to its unique properties, such as super high temperature and high density of active species, thermal plasma has been considered as a promising method to conduct thermo chemical process recently [5]. Comparing to conventional thermal pyrolysis, plasma pyrolysis can give higher biomass conversion rate and lower bio-oil content in product. When biomass is pyrolyzed via thermal plasma, CO and H_2 can be obtained as main products after fast quench [6–9]. And some light hydrocarbons (methane, ethane, acetylene, and etc.) are also produced simultaneously. Biomass conversion using thermal plasma is also considered to be economic and energy efficient, according to Tang and Shie's analysis [7,8].

Cellulose, hemicellulose and lignin are the three main components of lignocellulosic biomass, and their contributions to the thermal pyrolysis behavior of biomass are different [10–12]. As the most abundant constituent in biomass, cellulose's pyrolysis mechanism can basically explain the pyrolysis behavior of biomass. The pyrolysis mechanism of cellulose has been extensively studied [13]. It is widely accepted that the pyrolysis of cellulose undergoes two steps [13]. Firstly, cellulose turns into active cellulose, and then active cellulose decomposes to produce light gas (mainly CO and H_2) and small organic molecules such as hydroxyacetaldehyde (HAA), hydroxyactone (HA), pyruvic aldehyde (PA), acetaldehyde and formaldehyde. Secondly, volatiles from primary pyrolysis further decompose into smaller products, such as CO and H_2, and this step is called secondary pyrolysis. Regarding the pyrolysis mechanism of cellulose in thermal plasma, it has been discussed in our previous work using density functional theory (DFT) method [14]. The most possible reaction pathways of cellulose were gained using β-D-glucopyranose as the model compound, and it was concluded that the main product of cellulose pyrolysis in hydrogen plasma was syngas [14].

Lignin is commonly considered as the second abundant component in biomass and its effect on biomass pyrolysis behavior is different from cellulose due to the difference of their chemical

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structures. As for the regular thermal pyrolysis of lignin, it has been investigated experimentally and theoretically in many studies [15–18]. The pyrolysis of lignin also proceeds through two steps, just like cellulose. Lignin decomposes into styrene and phenol in the first step, and then styrene and phenol continue to pyrolysis, producing the final products [15–18]. The pyrolysis of lignin in hydrogen plasma was studied also through DFT calculations in our previous work [19]. Phenethyl phenyl ether (PPE) was chosen as the model compound, and the most possible reaction pathways of PPE were identified. According to these pathways, the main products of lignin pyrolysis in hydrogen plasma were syngas and acetylene [19].

As the third component of biomass, hemicellulose has not drawn too much attention yet, and studies on its pyrolysis mechanism are few. Shen et al. [20] investigated the conventional thermal pyrolysis mechanism of hemicellulose, and then they proposed the possible routes for the formation of main products. They believed that all the products originated from the decomposition of three types of structural units in hemicellulose and the subsequent reactions of fragments from primary pyrolysis [20]. But these researches are still not enough since lots of important information, such as reaction enthalpy and activation energy, is missing, let alone the reaction mechanism in thermal plasma. This may be due to the complicated chemical structure of hemicellulose on one hand. On the other hand, the severe reaction condition such as high temperature (2000–3500 °C) in thermal plasma makes it harder to gain better insight into pyrolysis mechanism through experimental studies.

As stated above, the pyrolysis mechanism of hemicellulose is needed to get full understanding of the reaction mechanism of biomass pyrolysis in thermal plasma. In this paper, density function theory is employed again to figure out the reaction mechanism of hemicellulose pyrolysis in hydrogen plasma, and then combining with our previous works [14,19] the effects of biomass composition on the production distribution are discussed. DFT is a quantum mechanical modeling method, which is widely used to determine the properties of a many-electron system [21]. Through DFT calculation, energies needed for reactions can be obtained, and the most favorable reaction pathways can be predicted [22,23]. Base on the study of Shen et al. [20], xylose, *O*-acetyl xylose and 4-*O*-MeGlcA are chosen as model compounds here, which present the three chemical structural units in hemicellulose, respectively. The chemical structures of these three model compounds are listed in Table S1 of Supporting information.

2. Theoretical approaches and computational details

Gaussian 09 suite of programs [24], the latest version of the Gaussian series of programs, was employed here to perform DFT calculations. Base on the fundamental laws of quantum mechanics, Gaussian 09 can give lots of useful information, such as the energies, molecular structures, vibrational frequencies of molecules and reactions in all kinds of chemical environments. Using the hybrid functional B3LYP with the 6-31G(d,p) basic set [25,26], geometries of reactants, products and transition states were optimized. To obtain zero-point energy (ZPE) corrections, vibrational frequencies of all species were computed at the same level of theory. Thus the ground state energies (E) of species were obtained. By calculating the relative energies between products and reactants, the reaction enthalpies can be gained. Transition states were found using QST2 and TS methods. Transition states were confirmed by inspecting the imaginary frequencies in Gaussian view and running intrinsic reaction coordinate (IRC) calculations. The relative energy between TS and reactant was defined as the activation energy of reaction.

3. Results and discussion

3.1. The generation of hydrogen plasma

The hydrogen plasma used here is generated by an electric arc between the cathode and anode of plasma generator. H_2, working gas of plasma generator, passes through the electric arc and is heated up to a temperature of 2000–3500 °C. At such high temperature, hydrogen molecules decompose into active hydrogen atoms ($H^{\bullet}$) very easily. After hydrogen plasma is generated, large quantities of hydrogen atoms are produced and the energy of electric arc transfers to the active hydrogen atoms in thermal plasma.

3.2. Primary pyrolysis

Although the studies on thermal pyrolysis mechanism of hemicellulose are not well clarified, it is widely agreed that just like cellulose, the pyrolysis of hemicellulose takes place via two steps (primary pyrolysis and secondary pyrolysis). In this section, the primary pyrolysis of three model compounds in plasma is discussed, base on the possible reaction routes proposed by Shen et al. [20].

3.2.1. Primary pyrolysis of xylose

The 1,6-hemiacetal bond in β-D-glucopyranose (monomer of cellulose) is considered to be very active under thermal condition [27]. In fact, the 1,4-hemiacetal bond in xylose is even more unstable [28], and it breaks very easily which results in the opening of pyran ring. Thus the pyrolysis reaction is initiated. According to our DFT calculations, this reaction is endothermic by only 9.9 kcal/mol, but it has to go through a transition state (TS1) with an activation energy of 44.0 kcal/mol. The product of ring-opening of xylose, $CH_2OHCHOHCHOHCHOHCHO$ (IM1), can decompose into small molecules (containing no more than 3 carbon atoms) through three different reaction pathways. The possible pathways of this primary pyrolysis are shown in Scheme S1. Fig. 1 presents the reaction energies along the three pathways of the primary pyrolysis of xylose.

As shown in the Fig. 1(a) and (b), IM1 decomposes into different C_2 and C_3 intermediates through C–C bond breakings and H shifts at different positions. Then C_2 and C_3 fragments continue to dehydrate and decarbonate, yielding smaller molecules. In the third path (Fig. 1(c)), IM1 turns into acetone finally through dehydration, isomerization and decarbonylation. To sum up, these three pathways are composed of the same kinds of reactions basically, so their required energies are at the same level. These reactions go through molecular reaction channels, and there are transition states in the reaction routes. In a word, these reactions are equally thermodynamically favorable during the primary pyrolysis of xylose. Some gases (mainly CO and CH_4) and evaporable liquid (HAA, CH_3CHO, CHOCHO, CH_3CH_2OH, HCHO, CH_3COCH_3) are the main products. The optimized geometries and important structure parameters of species involved in the primary pyrolysis of xylose are listed in Table S2.

3.2.2. Primary pyrolysis of O-acetyl xylose

Just like xylose, the primary pyrolysis of *O*-acetyl xylose also has three possible pathways, but there is difference in the first step. Instead of the opening of pyran ring, the pyrolysis of *O*-acetyl xylose starts with the decomposition of the CH3–CO–O- side group of the pyran ring, via losing small molecule. There are three different pathways; therefore different small molecules are produced during the initiation step. Then the intermediates from the first step can further pyrolyze via a series of reactions, including ring-opening, dehydration, isomerization, C–C bond breaking and