



# A thermal decomposition study of pine wood under ambient pressure using thermogravimetry combined with synchrotron vacuum ultraviolet photoionization mass spectrometry

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## Abstract

As pyrolysis is the initial step involved in thermochemical processes of biomass, understanding of the pyrolytic behavior of biomass is crucial to biomass thermochemical conversions. This work presents a new facility for studying the pyrolysis behavior of solid fuels. The experimental setup contains a thermogravimetry system connected with a home-made reflectron time-of-flight mass spectrometer via a single-stage molecular beam sampling interface, and a tunable vacuum ultraviolet (VUV) light generated from synchrotron source is used for soft photoionization. Evolution of the gaseous products of pine wood pyrolysis was examined at a heating rate of 20°C/min in a nitrogen environment at atmospheric pressure. Experiments were performed at the photon energies of 10.0, 10.5 and 11.0 eV, and mass spectra of gaseous products were recorded by the time-of-flight mass analyzer every five seconds. Species with the mass range of  $m/z$  20–220 are presented and possible formation pathways of typical products are discussed.

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## 1. Introduction

Lignocellulosic biomass, such as wood, straws, and agricultural residues, has gained extensive in-

terests as a renewable source of energy and chemicals. Biofuel converted from biomass is one of important substitutes of conventional fossil fuels [1–5]. Thermochemical conversion of biomass is one of the most promising routes to convert bulk biomass feedstock into marketable fuels and chemicals. As the pyrolysis process is always an initial step of thermochemical process, understanding of

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the thermal decomposition behavior during pyrolysis is crucial to optimize the conversion process and control the composition of end products.

Thermogravimetry is an important method for studying pyrolysis kinetics of biomass [6–8]. Although thermogravimetry can provide accurate information for global mass loss kinetics, it cannot analyze pyrolysis products qualitatively. Thus, thermogravimetry is usually coupled with spectroscopy, gas chromatography (GC), or mass spectrometer (MS) by capillary. However, quenching of reactive species and condensation of stable components in capillaries limit the accuracy of detection. Molecular-beam sampling is a high-sensitive technique, the integrity of the sampled products is preserved during the free-jet expansion since chemical reactions are effectively prevented and condensation is inhibited [9–14]. Kaisersberger et al. introduced a two-stage molecular beam sampling interface to replace the capillary in the coupling of thermogravimetry and mass spectrometry [15,16]. This new combination features online detection and minimizes sample condensation. The ionization source used in their work was the widely used electron impact ionization which, despite its reliability and high sensitivity, has the disadvantage of fragmentation caused by the 70 eV electrons used. Fragmentation of molecules leads to overlapping of peaks, which makes it difficult or impossible to interpret the spectra, especially for pyrolysis of biomass. This disadvantage leads to a demand for “soft” ionization technique with less fragmentation. As the ionization energies of most organic compound are in the range from 7 to 12 eV, photoionization with VUV light is a good choice. Recently, Zimmermann et al. [17] used VUV-light generated by electron beam pumped rare gas excimer as ionization source to study diesel and polymers. The interpretation of mass spectra is eased as the fragmentation is minimized with the soft photoionization method. Rare electron beam pumped gas excimer is a kind of VUV lamp with high-photon flux and the typical photon energy is 9.8 eV with a narrow distribution. However, fixed photon energies of VUV lamps cannot easily realize threshold ionization of organic molecules. Synchrotron radiation light sources can produce tunable and intense VUV light in the energy range of 6–14 eV. It can be tuned continuously to achieve the near-threshold ionization of molecules without fragmentation [18,19].

In this paper we report an experimental system based on molecular beam sampling and synchrotron VUV photoionization technique. A thermogravimetry is connected with a home-made reflectron time-of-flight mass spectrometer via a single-stage molecular beam sampling interface, and the synchrotron VUV light source was employed for soft photoionization. Pyrolysis behavior of pine wood was studied with the new facility.

## 2. Experimental method

The experiment was performed at National Synchrotron Radiation Laboratory (NSRL), University of Science and Technology of China, Hefei, China. The characteristics of the VUV beamline used for photoionization has been fully described elsewhere [20]. Briefly, VUV light delivered by a new undulator beamline is used for the photoionization source. The optical system of the beamline contains two toroidal mirrors with the grazing incidence angle of  $7^\circ$  and a planar grating with the including angle of  $152^\circ$ . The photon flux of the 200 l/mm grating is higher than  $1 \times 10^{13}$  photons/s in the energy range of 6–13 eV. For the 400 l/mm grating, the photon flux is around  $(3\sim 10) \times 10^{12}$  photons/s in the energy range of 11–21 eV. The high-order harmonic radiation is eliminated by a gas filter filled with argon, neon or helium.

Figure 1 shows the sketch of the experimental setup to study biomass pyrolysis which consists of a thermal gravimetric analyzer (TGA), a photoionization chamber with a single-stage sampling nozzle and a home-made reflectron time-of-flight mass spectrometer.

The quartz sampling nozzle with included angel of  $25^\circ$ , thickness of  $\sim 1$  mm and total length of 60 mm had a small aperture of  $\sim 70$   $\mu\text{m}$  diameter, that ensures the vacuum in the ionization chamber in the order of  $10^{-1}$  Pa while the reactor was kept at atmospheric pressure. The distance between the aperture and the crucible of the thermogravimetric analyzer was about 2 mm. The sampled species were ionized by the synchrotron VUV light and detected by the home-made time-of-flight mass spectrometer.

The white pine wood used in the experiment was obtained from Northern China. Before the experiments, the pine wood was pulverized into small pieces and air-dried in ambient condition. The approximate chemical formula of the pine wood is  $\text{C}_{3.8}\text{H}_{6.3}\text{O}_{3.8}$  based on elemental analysis. An analytical balance was used to weight 10 mg of pine wood scraps for each experiment. The heating rate of each run was kept at  $20^\circ\text{C}/\text{min}$ , and the furnace oven was kept at atmosphere pressure with nitrogen flow at a rate of 100 ml/min. The time-of-flight mass analyzer recorded mass spectra every five seconds (one cycle).

## 3. Results and discussion

### 3.1. Thermogravimetric analysis and mass spectra of major thermal decomposition products

In our experiments, the TG and derivative thermogravimetric (DTG) curves were obtained for the pine wood pyrolysis at the heating rate of  $20^\circ\text{C}/\text{min}$ . The TG cycles were performed under the same condition for each selected photon energy.

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