



Full Length Article

Real-time monitoring biomass pyrolysis via on-line photoionization ultrahigh-resolution mass spectrometry



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ABSTRACT

Identification of pyrolysis intermediates and products is of great significance to better understanding of a pyrolysis process and therefore its further upgrade to practical fuels. We hereby report a real-time analysis of pyrolysis volatiles of biomass in a micro fixed-bed reactor via an on-line near-atmospheric pressure photoionization Orbitrap mass spectrometry (nAPPI Orbitrap MS). The mass spectra suggest the pyrolysis products bear a molecular weight in the range of m/z 50–300. The oxygenated compounds having between 1 and 5 oxygen atoms and with double bond equivalent (DBE) values ranging from 2 to 7 account for more than 90% of the identified peaks, indicating that significant upgrading should be developed towards applications. Pyrolysis products could be clearly distinguished from different components of biomass in the van Krevelen diagrams and DBE versus carbon number plots. The results from the nAPPI Orbitrap MS are further compared to those of off-line pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) and on-line single photoionization mass spectrometry (SPI-MS). The nAPPI Orbitrap MS is a powerful on-line approach with high sensitivity, ultrahigh-resolution, and no condensation or preparation. This analytical protocol is expected to be helpful in complicated thermochemical conversion studies, e.g. pyrolysis of biomass.

1. Introduction

Lignocellulosic biomass, consisting of cellulose, hemicellulose, and lignin, is considered to be the only carbon-based renewable energy on the Earth and has the potential to partially replace fossil fuels [1–7]. In recent decades, the thermochemical conversion of lignocellulosic biomass to biofuels or value-added chemicals has attracted considerable interest [8–12]. Among various thermochemical conversion techniques, pyrolysis is considered to be the simplest and economical way to obtain liquid bio-oil. Compared with traditional fossil fuels, bio-oil has been characterized by low calorific value, high acidity, strong corrosion and high instability caused by high-oxygen content, restricting its practical application in current petroleum oil infrastructures [13]. Thus, upgrading is necessary before processing with conventional petroleum oil refinery.

The chemical components of bio-oil are incredibly complex, and the main compositions are oxygenated compounds including phenols, carbohydrates, carboxylic acids, ketones, aldehydes, etc. [14–16], conferring the poor properties of bio-oil. Understanding the composition of pyrolysis products is of great significance to better understand the pyrolysis process itself and further refine the crude pyrolysis products into practical fuels [17,18]. As pyrolysis products are closely related to

the process conditions, a real-time and rapid characterization technique for pyrolysis of biomass is needed.

There are many well established analytical methodologies for analyzing pyrolysis products of biomass, and most of them are based on pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) due to its good separation capability and large mass spectral database [19–21]. Electron ionization (EI) with 70 eV electrons is typically employed to ionize molecules for MS analysis, which produces significant fragmentations that can be used to search mass spectra database for compound identification. Two-dimensional gas chromatography (GC × GC) considerably increases the separation capability of this method [22–24]. However, Py-GC/MS method suffers from the fact that it only permits the determination of relatively volatile and thermally stable compounds, which means that not all compounds in the pyrolysis products can be detected by GC/MS, such as compounds with high boiling points. Furthermore, statistical database searching based on fragmentation is not as useful for unknown compounds that are absent in database. It is still a significant challenge to study bio-oil at the molecular level with conventional methods.

To overcome the limitations of the off-line measurements, there has been much effort to develop and improve on-line measurement methods. Recently, single photoionization mass spectrometry (SPI-MS)

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has been widely used for on-line characterization of fuel combustion [25,26] and pyrolysis of solid fuels [27–32]. VUV light emitted from lamps, lasers, and synchrotron radiation was usually used for “soft” ionization of analyte, which prevents the formation of extensive fragmentation and improves the analysis of fragile molecules. Most reports regarding with on-line SPI-MS for pyrolysis used a time-of-flight mass spectrometer (TOF-MS) with a resolution of only a few thousand, which is far from enough to analyze the complex pyrolysis products of biomass [15,33,34].

Ultrahigh-resolution mass spectrometry has proved as a powerful tool for molecular characterization of complex samples with direct chemical composition analysis of thousands of molecular components. In recent years, ultrahigh-resolution mass spectrometry including Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), and Orbitrap mass spectrometry (Orbitrap MS) has been used for petroleomic analysis of different bio-oil [14,15,34–37]. Various soft ionization techniques including electrospray ionization (ESI), atmospheric pressure photoionization (APPI), atmospheric pressure laser ionization (APLI), atmospheric pressure chemical ionization (APCI) have been used to reduce fragmentations, increasing the suitability of this method for bio-oil analysis [14]. Accurate mass accuracy and ultrahigh-resolution have allowed for precise assignment of elemental composition to each mass peak, which is especially useful in characterizing oxygen-rich components in bio-oil. Currently, ultrahigh-resolution mass spectrometry is commonly used for analyzing bio-oil through direct infusion or after pre-separation by either GC or liquid chromatography (LC) [14], reports regarding the on-line analysis of pyrolysis products via ultrahigh-resolution mass spectrometry in real-time is still rare [38].

In this investigation, pyrolysis products of camphor wood were investigated via an Orbitrap MS equipped with a micro-fixed bed pyrolysis reactor and a newly developed on-line near-atmospheric pressure photoionization (nAPPI) source. Meanwhile, characterizations of pyrolysis products with both off-line Py-GC/MS and on-line SPI-MS were also conducted and compared with the results of nAPPI Orbitrap MS.

2. Material and methods

2.1. Feedstock and characterization

The camphor wood was obtained in the Minhang campus of Shanghai Jiao Tong University, and was ground into fine powders (< 0.1 mm). The wood powder was dehydrated at 100 °C for five hours in the air before the experiment.

The proximate analysis was performed using a TGA (TG Discovery, TA Instrument). The amounts of carbon, hydrogen, nitrogen, and sulfur in camphor wood were determined using a Vario EL Cube instrument (Elementar Analysensysteme GmbH), and the amount of oxygen was calculated by the difference. The amounts of other elements were determined by an inductively coupled plasma optical emission spectroscopy (iCAP7600, Thermo Scientific). Table 1 summarizes the results of proximate and ultimate analysis of the camphor wood.

2.2. Pyrolysis experiments

The pyrolysis experiments were performed using a micro fixed-bed reactor consisting of an electrical-heated furnace, a quartz tube, and a quartz sample boat. The inner diameter of the quartz tube is 20 mm. Before pyrolysis, the furnace was maintained at 500 °C. The temperature distribution along the central axis of the reactor is displayed in Fig. A1. The quartz tube was flushed with nitrogen at a flow rate of 200 mL/min for 20 min to ensure excluding the interference of air. Then, the flow of nitrogen was switched to 50 mL/min, and after 2 min of stabilization, the quartz boat with 10 mg wood sample was inserted into the center of the reactor. Experiments with Py-GC/MS and SPI-MS are detailed in the Supporting Information (Figs. A6–A8).

Table 1

The composition of camphor wood powder.

Property	Measured value
<i>Proximate analysis</i>	
Moisture (%)	1.43
Volatiles (%)	73.64
Ash (%)	8.12
Fixed carbon (%) ^a	16.81
<i>Ultimate analysis</i>	
C (wt%)	45.17
H (wt%)	5.51
N (wt%)	0.25
O (wt%) ^b	40.96
H/C	1.46
O/C	0.68
S (wt%)	0.0780
P (wt%)	0.0683
K (wt%)	0.3158
Na (wt%)	0.6838
Ca (wt%)	0.5896
Mn (wt%)	0.0028
Mg (wt%)	0.1456
Fe (wt%)	0.1352

^a Calculated by the difference.

^b O% = 100%–Ash%–C%–H%–N%.

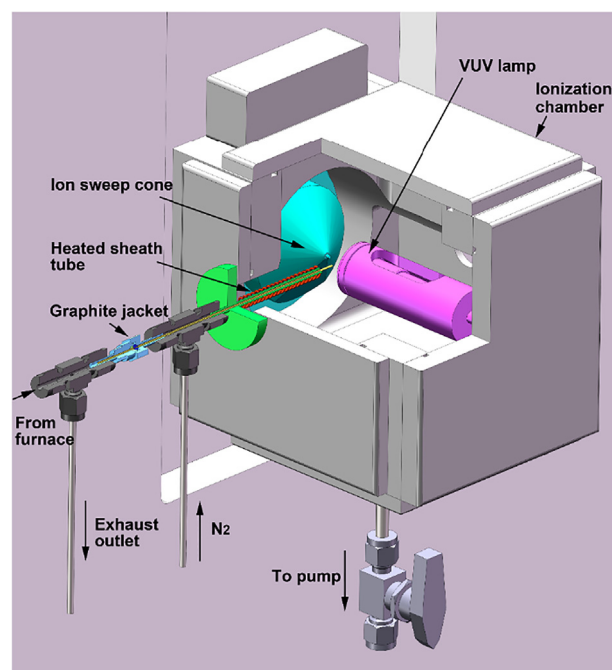


Fig. 1. Cutaway diagram of the near atmospheric pressure photoionization (nAPPI) source.

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.fuel.2018.08.098>.

2.3. On-line nAPPI Orbitrap MS

Fig. 1 depicts a cutaway diagram of the nAPPI source developed for on-line analysis of pyrolysis products. The connection fittings including two union tees, a graphite jacket, a sheath tube and a fused silica capillary with an inner diameter of 150 μm were used to combine the pyrolysis furnace and the ionization chamber, and the total length of the transfer line was approximately 120 mm. The pyrolysis products were sampled in the first union tee by the capillary and delivered into the ionization zone directly. A VUV lamp (PKS106, Heraeus, Ltd.) with

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