Investigation of volatile chemicals and their distributions from pyrolysis of chitin by FT-IR and GC–MS

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A R T I C L E I N F O

A B S T R A C T

This article is focused on investigation of volatile chemicals and their distributions from pyrolysis of chitin. Thermogravimetric analyzer (TG) equipped with differential scanning calorimeter (DSC) was used to investigate the pyrolysis behavior of chitin, and the evolved volatiles were on-line characterized by Fourier transform infrared spectroscopy (FT-IR). Gas chromatography/mass spectrometry (GC–MS) was employed to further identify the volatile chemicals. The main volatiles evolved from the pyrolysis of chitin in vacuum were acetamide, furans and pyrroles, and acetamide was the major product. Pyrolysis temperature in the range of 260–360 °C has litter influence on concentrations and distributions of volatile compounds, which indicated that acetamide was produced by splitting of side constituents at the early stage of pyrolysis. The major volatile compound from pyrolysis of chitin in the presence of oxygen was also acetamide, whereas the distribution of volatile compounds became complicated and the concentration of acetamide decreased.

1. Introduction

Depletion of worldwide fossil fuel and the environmental risks derived from their use are the main reasons for increasing interest on search for alternative and renewable energy sources [1,2]. Among the potential renewable energy sources, biomass is an important source because of its low cost, extensive source and pollution reduction. Chitin is the second abundant natural polysaccharide in nature after cellulose [3], which is composed of 2-acetamido-2-deoxy-D-glucopyranose (N-acetyl-D-glucosamine). Due to their unique chemical and biological properties, chitin and its de-acetylation product chitosan has been widely used in the fields of agriculture, medicine, pharmaceuticals, functional food, environmental protection and biotechnology in the last 20 years [4–6]. Beside, good property of chitosan makes this biopolymers applicable textile industry [7]. Chitin is present in the shells of crustaceans, crustacean resting eggs, Arachnida, insect cuticles, and the cell walls of fungi [8–11]. It is estimated that annually 10^{11} t of this biopolymer is synthesized [8]. Disposal of shellfish is an intractable task for most of the shellfish-producing countries [12].

Biomass pyrolysis is a fundamental thermochemical conversion process that is of special importance in both industry and ecology. Through pyrolysis, the molecules of biomass are broken down to low molecular weight gases, liquids and solid char. Some researchers reported that cellulose could be transformed into anhydro-levoglucosan and furans by pyrolysis [13–15]. In our previous study, it was found that chitosan was transformed into pyrazine derivatives and pyridine derivatives upon pyrolysis [16]. As one of the most abundant natural polysaccharide in nature, the thermal degradation kinetics of chitin has been extensively investigated [17–20], but the volatile compounds and their distributions from the pyrolysis of chitin are rarely explored [21].

The main aim of this work is to investigate the volatile compounds and their distributions from thermal degradation of chitin. Thermogravimetric analyzer (TG) equipped with differential scanning calorimeter (DSC) has been recognized as a powerful tool for monitoring the pyrolysis behavior of natural and synthetic polymers. For characterization of species evolved from the pyrolysis of polymers, Fourier transform infrared spectroscopy (FT-IR) has turned out to be an important technique [21]. This method is non-destructive and can simultaneously on-line measure multiple gas phase compounds in a complex mixture. In this work, we employed TG equipped with DSC to investigate the pyrolysis behavior of chitin in nitrogen atmosphere, and the evolved volatiles were online identified by FT-IR connected to a thermal analyzer via a heated line. Gas chromatography in combination with mass spectrometer (GC/MS)

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was employed to further identify the volatiles from the pyrolysis of chitin. Moreover, we investigated the effect of pyrolysis temperature and oxygen on the concentrations and distribution of volatile compounds generated from the pyrolysis of chitin.

2. Experimental

2.1. Materials

Chitin was supplied by Golden-shell Biochemical Co., Ltd., China, and used directly without any further purification. Other chemicals were purchased from Sigma–Aldrich Corporation.

2.2. Non-isothermal pyrolysis of chitin and FT-IR characterization of gas products

Simultaneous TG-DSC coupled with FT-IR was performed on a thermal analyzer (SDT-Q600) connected to a Fourier transform infrared spectrometer (Thermo Nicolet 380).

5.0 mg dry chitin was loaded into an open alumina crucible. The heating rate of TG furnace was set as 10.0 °C/min, and nitrogen gas (purity > 99.999%) was used as carrier gas with a flow rate of 200 mL/min. The transfer line used to connect TG and FTIR was a 1.0 m long stainless steel tube with internal diameter of 2 mm, and the temperature was maintained at 200 °C. Accessory of the IR spectrometer was used, which has a 45 mL gas cell with path length of 200 mm and was also kept at 200 °C. The IR spectra were collected at 8 cm^{-1} resolution, co-adding 32 scans per spectrum. Lag time was about 7 s for gas products from furnace to gas cell.

2.3. Off-line pyrolysis of chitin in vacuum

An exactly weighed amount of 100 mg dry chitin was loaded into a stainless flask, and then the inner atmosphere was reduced to vacuum by oil-pump. The flask was put in an electrical heater, and pyrolysed at 260 °C for 1 h at the maximum heating rate. After cooling to room temperature, the evolved products were retrieved from the charring residue and the glass tube by dissolution into 10 mL of CH$_3$OH. This volume was found to be adequate for the quantitative desorption of volatile products. The solution was spiked with 0.50 mL of an internal standard solution (500 mg/L 4-chlorobenzaldehyde in MeOH) and analyzed by GC/MS.

2.4. Off-line pyrolysis of chitin in the presence of oxygen

An exactly weighed amount of 100 mg dry chitin was loaded into a two-necked flask. Then, a condenser with a stopper at the top was fixed onto the flask and circularly condensed by ethanol (temperature was −20 °C). A small exit was remained at the stopper for release of oxygen and carbon dioxide. A glass tube was inserted into the flask from one neck, and oxygen at the flow of 100 mL/min was fluxed from the glass tube. The flask was put in an electrical heater and pyrolyzed at 260 °C for 1 h at the maximum heating rate. After cooling to room temperature, the evolved products were retrieved from the charring residue and the glass tube by dissolution into 10 mL of CH$_3$OH. This volume was found to be adequate for the quantitative desorption of volatile products. The solution was spiked with 0.50 mL of an internal standard solution (500 mg/L 4-chlorobenzaldehyde in MeOH) and analyzed by GC/MS [22,23].

2.5. Gas chromatography/mass spectrometry (GC/MS) analysis

The gas chromatography was performed on Agilen 7890A-5975C equipped with a flame ionization detector (FID) and a non-polar fused silica capillary column (DB-1, 30 m × 0.25 mm (i. d.), 0.25 μm film thickness: J&W Scientific, Folsom, CA). The column

temperature was programmed from 80 °C to 270 °C at heating rate of 3.0 °C/min. The injector and detector temperature were maintained at 270 °C. The flow rate of helium carrier gas was 1 mL/min. The volume of the injected sample was 1 μL, and the spilt ratio was 25:1. GC/MS analysis was performed using an Agilen 7890A coupled with an Agilen 5975C mass-selective detector. The capillary column and temperature program were the same as in the GC analysis. Mass spectra were obtained by electron ionization at 70 eV and m/z scan from 33 to 500. The volatile compounds were identified based on their mass spectral characteristics, GC retention time, Wiley mass spectra library and some publications [24–26].

2.6. Quantification

The quantity of volatile compounds was calculated from the corresponding GC peak area (A_v) of volatile compound, the weight (W_{is}) of the internal standard and \\its peak area A_{is}, and the quantity Q of pyrolyzed sample: $Y = fW_{is}A_v/A_{is}Q$, where f was the response factor with respect to the internal standard. The mean response factor f was determined as follows: 1.00 ml of volatile compound (500 mg/L in MeOH) and 1.00 ml of 4-chlorobenzaldehyde (500 mg/L in MeOH, internal standard) were mixed, which were analyzed by GC/MS. The response factor f was calculated from the peak areas of internal standard (A_{is}) and volatile compound (A_v): $f = A_{is}/A_v$. In this study, 4-chlorobenzaldehyde was used as an internal standard for the quantification of different kind of compounds from pyrolysis of chitin, because its structure was much similar to that of the identified volatile compounds.

For each sample, the experiments were conducted at least three times to confirm the reproducibility of our procedures. Moreover, the standard deviation values were also calculated.

3. Results and discussion

3.1. Non-isothermal pyrolysis of chitin

3.1.1. TG and DSC analysis of chitin

The pyrolysis behavior of chitin in dynamic nitrogen atmosphere was investigated by TG-DSC, and the corresponding TG and DSC curves were shown in Fig. 1. Chitin was substantially decomposed between 254 and 380 °C with a weight-loss about 70.12%, suggesting that chitin started to decompose and produced some volatiles at 254 °C. The degradation of chitin should be composed of a set of concurrent and consecutive reactions, such as the degradation of main chain and deacetylation [27,28]. The exothermic peak in Fig. 1 was mainly attributed to charring of chitin.
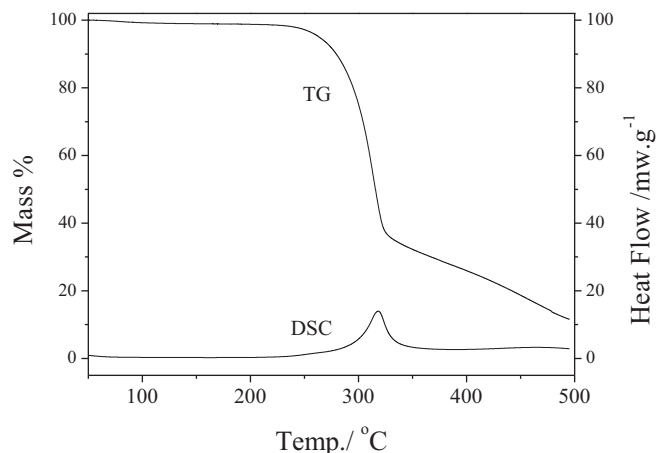

Fig. 1. TG and DSC curves of chitin in dynamic nitrogen.