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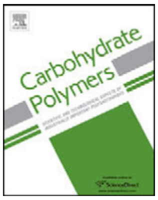

Volatile compounds formed from the pyrolysis of chitosan

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ABSTRACT

Chitosan is a renewable resource for the production of nitrogen-containing aromatic heterocyclics. It was found that chitosan started to decompose and produce some volatile compounds at around 525 K in a nitrogen atmosphere, the volatiles were characterized by Fourier transform infrared spectrometer. The apparent activation energy for the thermal degradation of chitosan was determined. To further investigate the degradation, chitosan was pyrolyzed under vacuum at 553 K for 1 h, and the volatile compounds were analyzed by gas chromatography/mass spectrometry. The volatile compounds included aromatic heterocyclics such as pyrazines, pyridines, pyrroles and furans, and the pyrazines were the major products. The pyrolysis mechanism of chitosan was also proposed.

1. Introduction

Chitosan, a widely available polysaccharide, is mainly composed of 2-amino-2-deoxy-D-glucopyranose (D-glucosamine, GlcN) units with some degree of 2-acetamido-2-deoxy-D-glucopyranose. Due to their special chemical and biological properties, chitosan and their derivatives have been widely used in food industry, agriculture, pharmacy, medicine and waste water treatment (Kumar, Muzzarelli, Muzzarelli, Sashiwa, & Domb, 2004).

As an environmental-friendly and renewable resource, chitosan and its degradation behavior in environment have been extensively investigated. The degradation of chitosan in various environmental conditions leads to breaking of chains and release of volatile products (Nieto, Peniche-Covas, & Padrón, 1991; Peniche-Covas, Argüelles-Monal, & Román, 1993). At high temperature, chitosan usually produces char and some volatile compounds (López, Mercê, Alguacil, López-Delgado, 2008; Zawadzki & Kaczmarek, 2010). Although kinetics of thermal degradation of chitosan is largely explored (Britto & Campana-Filho, 2007; Sato et al., 2002; Tang, Wang, & Chen, 2005), there is still very limited knowledge of the pyrolysis of chitosan for production of fine chemicals. It has been reported previously that the monomer of chitosan, glucosamine, was pyrolyzed to produce aromatic volatile compounds such as pyrazines, pyridines, pyrroles and furans (Chen & Ho, 1998). Thus, it is reasonably assumed that chitosan would be an abundant source to produce aromatic heterocyclics. To utilize this widely available biomass to produce some fine chemicals, it is very necessary to investigate the pyrolysis behavior of chitosan and the formed volatiles.

The main aim of this work is to investigate the pyrolysis of chitosan for production of fine chemicals. Thermal analysis methods, such as thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC), have been well established in monitoring the pyrolysis of natural 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. So, in this work, we employed TGA equipped with DSC to investigate the pyrolysis behavior of chitosan in nitrogen atmosphere. The volatiles evolved from the pyrolysis of chitosan were online identified by FT-IR connected to a thermal analyzer via a heated line. To further identify the volatiles from the pyrolysis of chitosan in vacuum, gas chromatography coupled with mass spectrometer (GC/MS) was employed. It was found that the volatiles evolved from the pyrolysis of chitosan were aromatic heterocyclics such as pyrazines, pyridines, pyrroles and furans.

2. Experimental

2.1. Materials

Chitosan with degree of deacetylation (DD = 85.5%) and Mw 7.60×10^5, was supplied by Golden-shell Biochemical Co., Ltd., China, and used directly without any further purification. Other chemicals were purchased from Sigma Chemical Co.

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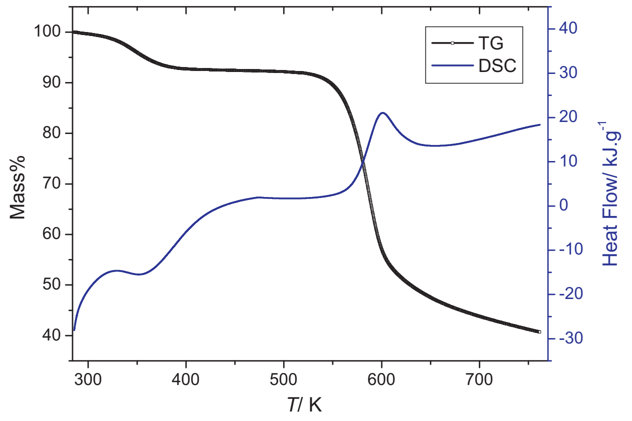

Fig. 1. TG and DSC curves of chitosan.

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

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

5.0 mg chitosan was loaded into an open alumina crucible. The heating rate of TG furnace was 10.0 K/min and nitrogen gas (purity > 99.999%) with a flow rate of 100 mL/min was used as carrier gas. 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 473 K. Accessory of the IR spectrometer was used, which has a 45 mL gas cell with 200 mm path length and was also kept at 473 K. The IR spectra were collected at 8 cm^{-1} resolution, co-adding 32 scans per spectrum. This resulted in a temporal resolution of 4.32 s. Lag time that the gas products went from furnace to gas cell was about 7 s.

The pyrolysis of chitosan was also studied by using simultaneous TG and DSC in nitrogen atmosphere when the heating rate of TG furnace was 2.5, 5.0 and 20.0 K/min, respectively.

2.3. Isothermal pyrolysis of chitosan and gas chromatography/mass spectrometry (GC/MS) analysis

1.0 g dry chitosan was loaded into a 100 mL stainless flask and the inner atmosphere was reduced to vacuum by oil-pump, then the flask was sealed. The flask was put in an oil bath and heated at 553 K for 1 h. After cooling to 283 K, 3 × 10 mL CH_2Cl_2 was added to the flask to extract the products generated from chitosan. The organic phase was dried over anhydrous magnesium sulfate, then filtered and concentrated to approximately 0.5 mL under a gentle stream of nitrogen gas. The concentrated sample was ready for GC–MS analysis.

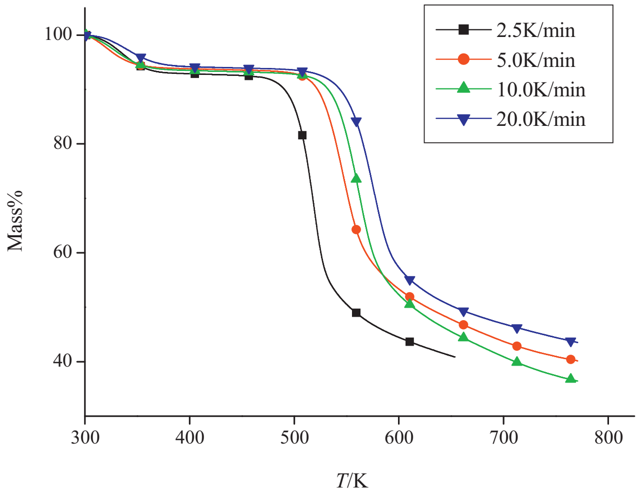

Fig. 2. The TG curves of chitosan at different heating rates.

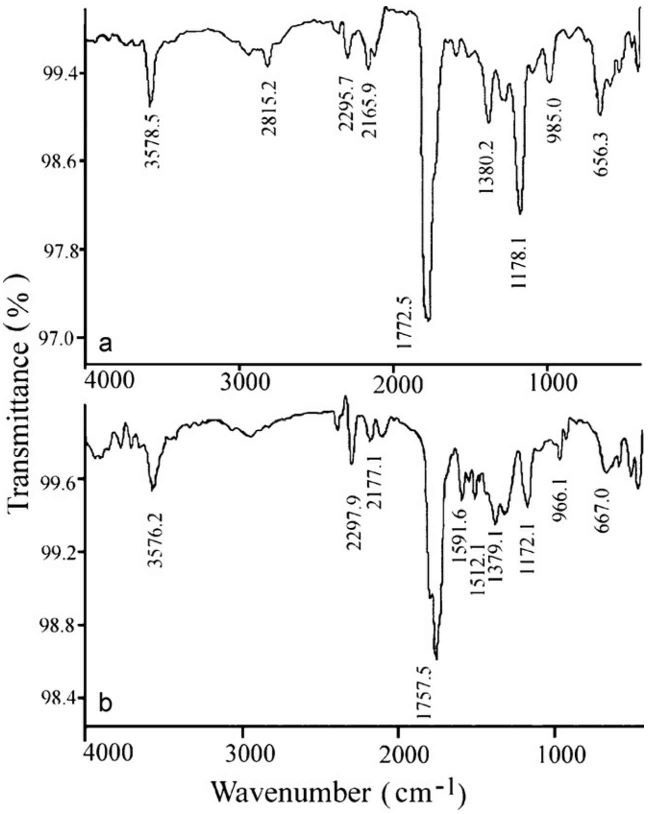

Fig. 3. FT-IR spectra of the gas products from thermal degradation of chitosan. (a) 26.8 min; (b) 35.4 min.

The gas chromatograph was performed on a Varian Model 3400 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 room temperature to 543 K at heating rate of 3 K/min. The injector and detector temperature were maintained at 543 K. 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 HP Model 5790 GC coupled with an HP 5970A 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 a mass scan from 33 to 500. Quantification was based on GC/FID data, and compound identification was based on mass spectra obtained from the GC/MS. Identification of compounds referred to Wiley mass spectra library.

3. Results and discussion

3.1. Non-isothermal pyrolysis of chitosan

3.1.1. TG and DSC analysis of chitosan

To investigate the pyrolysis behavior of chitosan, it was heated from room temperature to 823 K in dynamic nitrogen atmosphere, and the corresponding TG and DSC curves were showed in Fig. 1. The first thermal event was a wide endothermic peak in the range of 320–385 K coupled with weight-loss about 7%. This thermal event

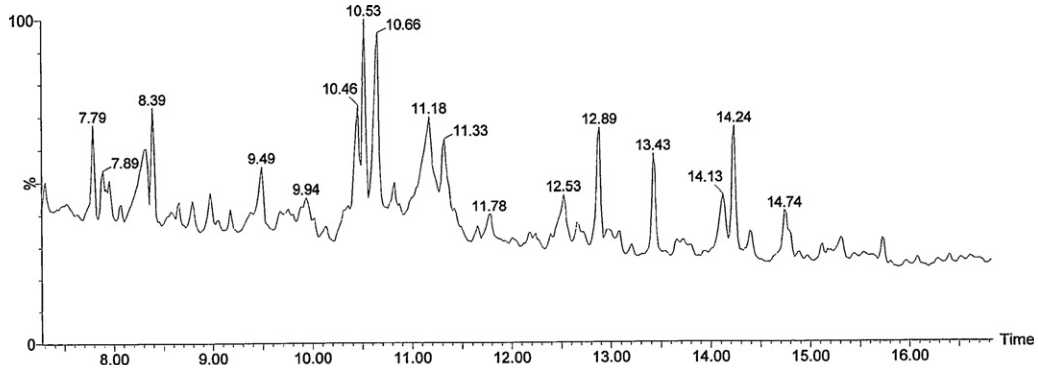

Fig. 4. Gas chromatography of volatile compounds generated from pyrolysis of chitosan.

was associated with evaporation of water absorbed in the samples (Qin, Du, Zong, Zeng, & Liu 2003). The second thermal event for chitosan was a wide exothermic peak coupled with a weight-loss about 48% between 525 and 650 K, suggesting that chitosan started to decompose and produce some volatiles at 525 K. The exothermic effect might result from cross-linking reactions during the thermal degradation of chitosan. The second decomposition step, which appeared at higher temperature, might result from the thermal degradation of the new cross-linked materials that have formed in the first degradation process (Pawlak & Mucha, 2003).

3.1.2. *Determination of apparent activation energy*

The Ea for the thermal degradation of chitosan was determined from the TG curves using iso-conversional method proposed by Ozawa–Flynn–Wall (Britto & Campana-Filho, 2007; Tang, Wang, & Chen, 2005). This iso-conversional method is based on the assumption that the reaction model is independent of the heating program. According to this method, a set of experiments are carried out at different heating programs, the activation energy is determined at a specific extent of conversion value by linear fitting the following equation:

$$\log \beta = \log\left[\frac{A\,\mathrm{Ea}}{g(\alpha)R}\right] - 1.0573\frac{\mathrm{Ea}}{RT}$$

where α is the extent of conversion, R is the gas constant, A is the pre-exponential factor, T is reaction temperature, and $g(\alpha)$ is a temperature-independent function that represents the reaction model. Therefore, a set of experiments were run at different heating rates β (Fig. 2), then the value of Ea was obtained from the plot of $\log\beta$ against $1/T$ for a fixed degree of conversion. The Ea was 137 kJ/mol ($\alpha = 0.30$).

The knowledge of the thermal pyrolysis kinetics of chitosan may help better understanding and planning of the industrial process because adequate kinetic description of chemical and physical processes can be profitably applied for process design and optimization.

3.1.3. *FT-IR characterization of gas products*

The gas products evolved from thermal degradation of chitosan were online analyzed by FT-IR. Fig. 3 recorded the corresponding infrared spectra of gas products at the 26.8 min (568 K) and 35.4 min (654 K), respectively. The most characteristic bands were the strong and sharp peaks around 1750–1780 cm^{-1}, which were corresponding to the aldehyde carbonyl group. The sharp peaks around 1591and 1512 cm^{-1} are very characteristic of aromatic heterocyclics.

3.2. *Isothermal pyrolysis of chitosan and GC/MS analysis of the volatile products*

The volatile products evolved from pyrolysis of chitosan at 553 K should be examined by GC–MS. Fig. 4 showed the gas chromatography of volatiles generated from pyrolysis of chitosan, and the volatiles were listed in Table 1. A total of 13 compounds were identified, including furans, pyridines, pyrroles and pyrazines. The major compounds were methylpyrazine, 2-(2-furyl)-(6)-methylpyrazine, 2-acetyl pyridine, 2,5-di(2-furyl)pyrazine, 2-(2-furyl)pyrazine, 2-acetyl-6-(2-furyl)pyrazine, 2-acetylfuran and 2-acetylpyrrole in decreasing order.

3.3. *Discussion*

Polysaccharides represent the largest fraction of biomass and previous work in understanding the polysaccharides pyrolysis mechanisms and kinetics have been well reported in the literatures (Aléna, Kuoppalab, & Oeschb, 1996; Antal & Varhegyi, 1995;

Table 1
Volatile compounds identified in the pyrolysis of chitosan at 553 K.

Retention time (min)	*m*/*z*	RI (area)	Compounds	Reference
6.73	41.03	515	Acetonitrile	Lib
7.79	93.06	1070	2-Methylpyridine	Lib
7.89	122.17	1226	Trimethylpyrazine	Lib
8.30	212.06	3067	2,5-Di(2-furyl)pyrazine	Lib
8.39	146.05	3000	2-(2-Furyl)pyrazine	Lib
9.02	108.14	784	2-Ethylpyrazine	Lib
9.49	109.05	1620	2-Acetylpyrrole	Lib
9.94	125.05	1494	2-Acetamidofuran	Lib
10.46	121.05	4250	2-Acetylpyridine	Lib
10.53	160.06	6250	2-(2-Furyl)-5(6)-methylpyrazine	Chen and Ho (1998)
10.66	94.11	10,138	Methylpyrazine	Lib
11.18	188.06	2983	2-Acetyl-6-(2-furyl)pyrazine	Chen and Ho (1998)
11.33	118.05	1692	4-Cyanic-2-methylpyridine	Lib
13.43	135.07	1268	2-Acetyl-3-methylpyridine	Lib

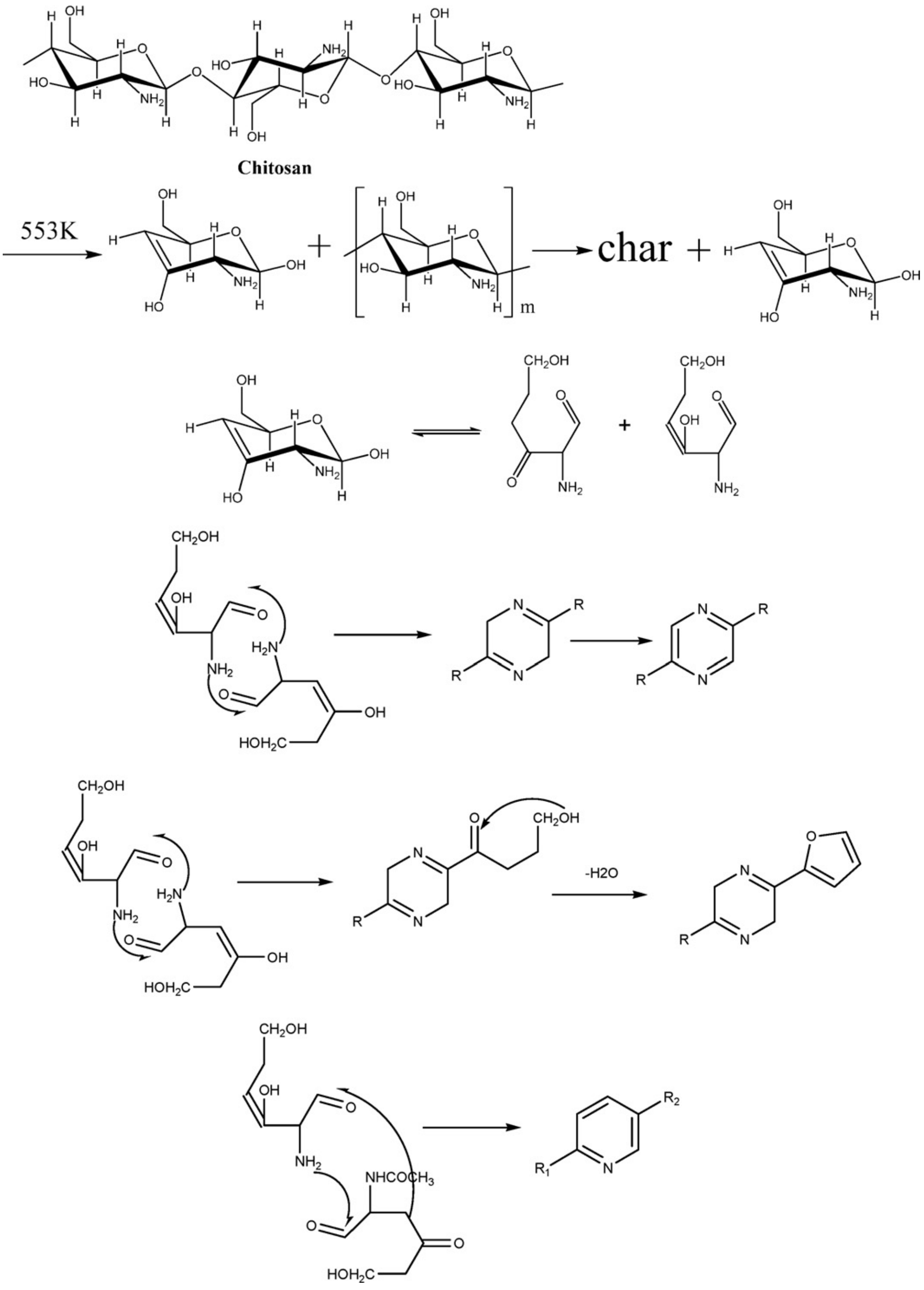

Fig. 5. The proposed mechanisms for pyrolysis of chitosan and formation of volatile compounds.

Bridgwater, 1999; Patwardhan, Satrio, Brown, & Shanks, 2009; Ponder & Richards, 1994).

Volatile compounds such as pyrazines, pyridines, pyrroles and furans are generated from the pyrolysis of glucosamine. Pyrazine compounds are the most important products among the volatiles identified. The furan ring was suggested as a result of the dehydration reaction from the intermediate polyhydroxypyrazines, which were dimerization products of glucosamine (Chen & Ho, 1998). When chitin was pyrolyzed at over 300 °C, acetamide and a series of methyl-substituted pyrazines were generated (Knorr, Wampler, & Teutonico, 1985). Pyrazine compounds are widely distributed in food systems, especially when foods are processed at high temperatures and under dry conditions. The extensive reviews on pyrazines in food were published (Maga, 1992).

Pyrazines were the most important products in the pyrolysis of chitosan, which was similar to the decomposition of glucosamine. Pyrozines are widely distributed in food systems, especially when foods are processed at high temperatures and under dry conditions. There are several precursors and pathways for the generation of pyrazine compound. The α-amino carbonyls, which can be formed from the degradation of chitosan, were generally considered to be the precursors of pyrazine compounds. The proposed pathway for formation of pyrazines was illustrated in Fig. 5. Glucosamine has α-amino carbonyl structure, which can react with each other to form pyrazine compounds (Chen & Ho, 1998; Wang & Odell, 1998). Pyridine derivatives also generated when chitosan was pyrolyzed.

4. Conclusions

In this study, chitosan was found to decompose and char when the temperature reached to 525 K. The volatile products included pyrazines, pyridines, pyrroles and furans, and pyrazines were the major volatile aromatic products. Chitosan is the potential biomass source to produce nitrogen-containing aromatic heterocyclics. The process conditions should be further investigated for utilizing chitosan to produce the chemicals.

Acknowledgements

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