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Value-added organonitrogen chemicals evolution from the pyrolysis of chitin and chitosan

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ABSTRACT

Thermogravimetric characteristics of chitin and chitosan and their potentials to produce value-added organonitrogen chemicals were separately evaluated via TG/DSC-FTIR and Py-GC/MS. Results shown that chitin had the better thermal stability and higher activation energy than chitosan because of the abundant acetamido group. Furthermore, the dominated volatilization in active pyrolysis of chitin contributed to its endothermic property, whereas the charring in chitosan led to the exothermal. During fast pyrolysis, the acetamido group in chitin and chitosan was converted into acetic acid or acetamide. Typical products from chitosan pyrolysis were aza-heterocyclic chemicals, i.e. pyridines, pyrazines, and pyrroles, with the total selectivity of 50.50% at 600 °C. Herein, selectivity of pyrazine compounds was up to 22.99%. These aza-heterocyclic chemicals came from the nucleophilic addition reaction of primary amine and carbonyl. However, main reaction during chitin pyrolysis was ring-opening degradation, which led to the formation of acetamido chemicals, especially acetamido acetaldehyde with the highest selectivity of 27.27% at 450 °C. In summary, chitosan had the potential to produce aza-heterocyclic chemicals, and chitin to acetamido chemicals.

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1. Introduction

Chitin is the second most abundant biopolymer on earth after cellulose, and the annual production is up to 10^{11} tonnes. It widely exists in the exoskeleton of crustacean and insects, the cell walls of fungi, etc., and is polymerized by N-acetyl-D-glucosamine with the β-(1 → 4)-glucosidic bonds (Baran & Menteş, 2015; Baran, Menteş, & Arslan, 2015; Zeng, Hu, Gu, Fu, & Qin, 2015). On account of the distinctive structure and properties, chitin and its deacetylated product, viz. chitosan, are widely applied in the fields of agriculture, environmental protection, functional food, biomedical and biotechnology engineering, and textile industry, especially prepared as hydrogels and drug delivery materials (Baran, Açıksöz, & Menteş, 2016 Baran, Inanan, & Menteş, 2016; Kumar, 2010; Kumar, Muzzarelli, Muzzarelli, Sashiwa, & Domd, 2004). Recently, in order to reduce the dependence on fossil resources, various biomass (including cellulose, hemicellulose, and lignin) were converted into value-added bio-chemicals, such as furan compounds (Mettler et al., 2012; Wang, Ren, Li, Deng, & Sun, 2015) and phenol compounds (Hu, Shen, Xiao, Wu, & Zhang, 2013; Singh & Ekhe, 2014). However, less attention has been paid on the conversion and utilization of chitin and chitosan.

Previous research reported that chitin can be directly transformed to 3-acetamido-5-acetylfuran in solution with catalysts by the reconstruction of the pyranose ring (Chen, Chew, Kerton, & Yan, 2014; Chen, Gao, Wang, Chen, & Yan, 2015). However, these obtained furan derivatives did not perform much more difference with that derived from cellulose and hemicellulose. Apart from solvolysis, pyrolysis is another promising thermochemical technology (Bridgwater, Meier, & Radlein, 1999), which could convert biomass into value-added bio-fuel and bio-chemical rapidly. Initially, pyrolysis was used to detect the chitin in fossil arthropods (Bierstedt, Stankiewicz, Briggs, & Evershed, 1998) and molluscan shells (Furuhashi et al., 2009), and determine the amine content or the degree of acetylation of chitosan (Lal & Hayes, 1984; Sato et al., 1998). Afterwards, pyrolysis was used to investigate the thermogravimetric characteristics and kinetics of chitin and chitosan according to various dynamic models (Stolarek & Ledakowicz, 2005; Tang, Wang, & Chen, 2005; Zeng, Qin, Wang, & Li, 2011). Recently, research on chitin and chitosan pyrolysis turns to focus on their thermal conversion. Zeng et al. (2011, 2015) and Qiao et al. (2015) detected the volatiles from the thermogravimetric processes of chitin and chitosan using TG-FTIR and TG-MS respectively.

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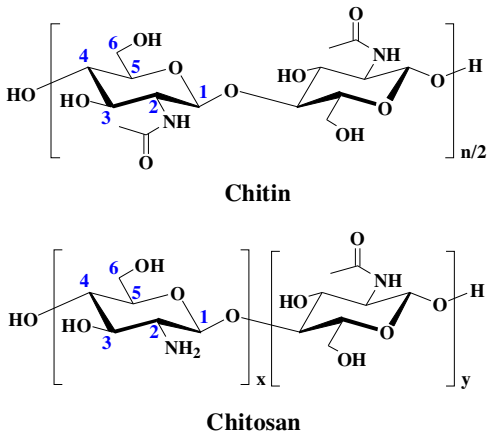

Fig. 1. Chemical structural formulas of chitin and chitosan: n, x, and y: degree of polymerization; x: y equals 17: 3.

Furthermore, bio-oil from the fast pyrolysis of chitin and chitosan was off-line identified (Zeng et al., 2011; Zeng et al., 2015). Herein, major product from chitin pyrolysis was acetamide, whereas those from chitosan pyrolysis were pyrazines. These organonitrogen chemicals are important intermediates in the chemical and pharmaceutical industries, and have substantially greater market value than chitin or chitosan.

However, previous reports on pyrolysis of chitin or chitosan only exhibited their individual properties, but could not present their distinction, as well as the relevance between their thermal conversions. Hence, systematic comparative studies of chitin and chitosan on their thermal stability, kinetics, products distribution, as well as pyrolysis mechanism, were carried out using the thermogravimetric analyzer and analytical pyrolyzer to evaluate the potentials of these two natural amino polysaccharides to produce value-added organonitrogen chemicals.

2. Materials and methods

2.1. Materials

Materials used in this study were chitin and chitosan, whose chemical structural formulas were shown in Fig. 1. Chitin was separated from shrimp shell, and purchased from Aladdin Industrial Corporation (Shanghai, China). Chitosan, prepared from crab shell, was supplied by Jinan Haidebei Marine Bioengineering Co., Ltd. (Jinan, China). Its degree of deacetylation determined by acid-base titration (Kasaai, 2009) was 85%, and weight-average molecular weight measured by gel permeation chromatography method (Li et al., 2012) was 2.5×10^5 g/mol. The two materials were only dried again in a vacuum oven at room temperature for 24 h before using.

2.2. TG/DSC-FTIR

TG/DSC-FTIR experiments were carried out on a STA 449 F3 Jupiter thermogravimetric analyzer (NETZSCH, Germany) coupled with a TENSOR 27 Fourier transformation infrared spectrometer (Bruker, Germany). High-purity nitrogen (99.999%) was used as the carrier gas with a flow rate of 20 mL/min. In each case, about 5 mg of sample was loaded in the ceramic crucible, and heated from 40 °C to 850 °C with a heating rate of 20 °C/min. Volatiles released from the pyrolysis were quickly swept into a Fourier transform infrared spectrometer gas cell by nitrogen. Moreover, before each experiment, the FTIR gas cell and the pipe were already preheated to 150 °C. The spectrum scope was located in the range from 4000 cm^{-1} to 667 cm^{-1} and the resolution factor was set at 4 cm^{-1}.

2.3. Char characterization

Char residues from the thermogravimetric processes of chitin and chitosan were characterized by the Fourier transform infrared (FTIR) spectrometry and the solid-state cross-polarization magic angle spinning (CP/MAS) ^{13}C-nuclear magnetic resonance (NMR). FTIR was programmed on a VECTOR 22 FTIR spectrometer (Bruker, Germany). Samples were pressed into a KBr disc with a mass ratio of 1:50. The spectra were scanned in the range from 4000 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1}. Solid-state CP/MAS ^{13}C NMR was carried out on an AVANCE III HD 400 superconducting Fourier transform NMR spectrometer (Bruker, Germany) at 100 MHz acquired in cross-polarization conditions with a spinning rate of 5 kHz, and the spectra were composed of 2000 scans.

2.4. Fast pyrolysis

Fast pyrolysis of chitin and chitosan were investigated on a CDS 5200 analytical pyrolyzer (CDS Analytical, USA) coupled with a 7890A gas chromatography and a 5975C mass spectrometry (Agilent Technologies, USA) (Py-GC/MS). Samples (~0.5 mg) were loaded in the pyrolysis tube and pyrolyzed at 350, 450, and 600 °C for 20 s with a heating rate of 10000 °C/s. The split ratio was 50:1, and the flow rate of helium (carrier gas) was 1.00 mL/min. The injector, detector, and interface temperatures of GC/MS were all set at 250 °C. An HP-INNOWax capillary column (30 m × 0.25 mm × 0.25 μm) was selected as the separation column. The column temperature was programmed from 50 °C to 250 °C (10 min) with a heating rate of 5 °C/min. The mass spectrometer was set at an ionizing voltage of 70 eV, and the mass range from m/z 5 to 400 was scanned with a speed of 1.0 s/decade. Data processing was performed using Perkin Elmer NIST Spectral Version 5 software (USA).

3. Results and discussion

3.1. TG, DSC, and kinetics

The thermogravimetry (TG) and differential thermogravimetry (DTG) curves of chitin and chitosan with the heating rate of 20 °C/min were presented in Fig. 2. Three degradation stages can be recognized in the thermogravimetric processes of both chitin and chitosan (Liang et al., 2015; Yang, Yan, Chen, Lee, & Zheng, 2007). The first stage was the dehydration process, which basically occurred before 150 °C. The second stage was known as the active pyrolysis process. In this stage, feedstock degradation and volatile releasing occurred heavily. The third stage was the positive pyrolysis process, which benefited from the redecomposition and carbonization of the char residue. As summarized in Table 1, the degradation parameters of the two samples were different. T_{oneset} of chitosan was 203 °C, which was 25 °C lower than that of chitin. T_{peak} of chitosan was 312 °C, whereas T_{peak} of chitin was 388 °C. Furthermore, R_{peak} of chitosan (-1.252% $°C^{-1}$) was lower than that of chitin (-0.973% $°C^{-1}$) as well. During the whole process, the mass loss of chitin was 77.06 wt.%, and that of chitosan was 65.97 wt.%. All those differences between chitin and chitosan were in consisted with the literatures (Qiao et al., 2015; Tang et al., 2005), which were caused by the different chemical structures, mainly the different contents of the amino and acetamido group.

Fig. 2 also displayed the differential scanning calorimetry (DSC) curves of chitin and chitosan with the heating rate of 20 °C/min. As can be seen from the DSC carves, when temperature was lower than 200 °C, there was an obviously endothermic peak. This attributed to the energy required to evaporate the absorbed water (Yang et al., 2007). With temperature rising up, the DSC profile of chitin showed

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