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Organonitrogen compounds identified in degraded wheat straw by oxidation in a sodium hypochlorite aqueous solution

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HIGHLIGHTS

- NaOCl is an effective oxidant for wheat straw degradation under mild conditions.
- Thirty-eight ONCs were identified in the extracts from the degraded wheat straw.
- Sequential extraction is a potential methodology for removing ONCs.
- CS_2 is effective for enriching unsaturated ONCs from the degraded wheat straw.

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ABSTRACT

Wheat straw (WS) was oxidized in a sodium hypochlorite (NaOCl) aqueous solution at 40 °C followed by sequential extraction of the water-soluble fraction (WSF) with petroleum ether, carbon disulfide (CDS), diethyl ether and ethyl acetate (EA). The EA-inextractable solution was acidized and filtrated. The filtration was also sequentially extracted with the same series of solvents. In total, 38 organonitrogen compounds (ONCs) were identified by GC/MS analysis from the extracts. The ONCs can be classified into amides, sulfonamides, amines, an amino acid, nitriles, an isocyanatoethane, chloro(nitro)methanes, an oxime, *N*-heterocyclic compounds (NHCCs, most of them are pyrrolidones) and a benzohydrazide, indicating the diversity of ONCs in WS. NHCCs, amides and nitriles are the most abundant among the ONCs, implying that these types of species might be main existing forms of nitrogen in the oxidized WS and even in WS itself to some extent. Most of the ONCs, especially amides and pyrrolidones, were enriched in the CDS-extractable fraction from the WSF because of the strong π–π interaction between C=S bond in CDS and C=O bonds in the ONCs. This investigation provides an effective approach for understanding the modes of ONC occurrences in WS.

1. Introduction

The fixed nitrogen species in living organisms are essential parts of the total nitrogen cycle on the Earth [1–3], where it is present as DNA, RNA, proteins, peptides and amino acids (AAs), etc. As the most abundant renewable resource, lignocellulosic biomass (LCBM) plays crucial role in the transformation of inorganic and organic fixed nitrogen and supplies human needs for energy and nutrition.

When LCBM is used as fuel for power generation, NH_3, N_2O, NO_x, HCN and HNCO are emitted to the atmosphere as the main gas-phase nitrogen species (GPNSs) [2–5], leading to acid rain, photochemical smog and greenhouse effects [6,7]. Total content of organic nitrogen in LCBM is easy to be determined either by the Kjeldahl method or by elemental analysis. However, most of the investigations did not give the structures and detailed characterization of organonitrogen compounds (ONCs) contained in biomass on molecular level, although investigations on the environmental effects of organonitrogen species were paid great attention [8–10].

Combusted LCBM is believed to be one of the largest sources of organic aerosol in the atmosphere [11]. Wheat straw (WS) is one of main agricultural wastes with *ca.* 530 Mt annual global production. However, it does not provide important use and commercial interests. Furthermore, the combustion of WS in the field during wheat harvest in rural area of China becomes more and more serious environmental problem with the emission of large amounts of biomass burning aerosol (BMBA) and GPNSs. Detailed investigations issued on characterization of ONCs in urban air [12] and BMBA [13] have been reported. Aliphatic and cyclic amides, arylamides, pyridino and amino types

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of ONCs and NHCCs were detected in BMBA [13–15]. Consequent natural biogenetic problems may arise due to their mutagenicity, carcinogenicity and toxicity [16]. Several NHCCs such as *N*-heterocyclic amines (NHCAs) and condensed arenes (CAs) are carcinogenic and toxic compounds, inducing cancers and malformations in aquatic animals and human beings [17–19]. The ONCs in BMBA as well as GPNSs result in serious environmental problems over the world. Furthermore, like CAs, ONCs contained in LCBM may undergo incomplete combustion and be partially oxidized or just volatilize with smoke to form BMBA. Therefore, it is essential to ascertain the structures of ONCs contained in LCBMs as well as their partially oxidized products to evaluate their environmental effects during the LCBMs are used as fuel. In a recent investigation, several ONCs such as lactams, amides and NHCCs were identified in the products from fast pyrolysis of sewage sludge [20]. The ONCs identified may be quite different from those in the sewage sludge itself because of the severe reaction conditions. Fractional extraction with different solvents has been successfully used for isolating ONCs in coals [21–23]. Catalytic hydroconversion was found to release ONCs more selectively and efficiently [24,25]. Therefore, the degradation of LCBMs under mild and selective decomposition conditions is desired for obtaining more exact compositional information of ONCs. Oxidation is often used as a pretreatment process in the degradation of biomass, especially lignin, in the papermaking industry and production of bioethanol [26]. Sodium hypochlorite (NaOCl) is an easy available and strong oxidizing reagent used as bleaching reagent and bactericide, and proved to be effective and selective for coal degradation [27].

In this study, mild oxidation with NaOCl aqueous solution was used to degrade WS followed by sequential extraction of the resulting water-soluble fraction (WSF) and subsequent analyses, especially with gas chromatography/mass spectrometry (GC/MS) to understand the modes of ONCs occurrences in WS.

2. Experimental

2.1. Materials

WS was collected from the field in the vicinity of Xuzhou City, Jiangsu, China. It was washed with fresh water and then dried in sunlight for more than 2 months, chopped into small pieces, pulverized to pass through an 80-mesh sieve (<180 μm) and followed by desiccation in a vacuum drying oven (VDO) at 80 °C for 24 h. Table 1 shows the proximate and ultimate analyses of the dried WS sample. Analytical pure NaOCl (6% available chlorine) aqueous solution was used directly. The strength of the oxidant was determined by iodometric titration with $Na_2S_2O_3$ aqueous solution. All the organic reagents such as petroleum ether (PE), carbon disulfide (CDS), diethyl ether (DEE) and ethyl acetate (EA) were also analytical-pure reagents and distilled with a Büchi R-134 rotary evaporator prior to use to remove possibly present impurities, especially nitrogen-containing species.

Table 1
Proximate and ultimate analyses (wt.%) of WS sample.[a]

Proximate analysis			Ultimate analysis (daf)				
M_{ad}	A_d	V_{daf}	C	H	O[b]	N	S
8.0	8.2	70.2	42.3	6.6	50.2	0.3	0.6

[a] M, moisture; A, ash; V, volatile matter; ad, air-dried base; d, dry base; daf, dry and ash-free base.
[b] By difference.

2.2. General procedure

As shown in Fig. 1, 10 g WS and 100 mL NaOCl aqueous solution (the mass ratio of WS/NaOCl was *ca.* 0.79) were added to a 250 mL spherical flask and magnetically stirred at 40 °C for 24 h. Then reaction mixture was filtrated to afford filter cake 1 (FC_1,) and filtrate 1 (F_1). The FC_1 was dried in the VDO at 80 °C for 24 h and then weighed (7.18 g). The F_1 was sequentially extracted with PE, CDS, DEE and EA (100 mL of each solvent was used) in a separatory funnel to afford extraction solutions ES_{1-1}–ES_{1-4} and inextractable solutions IES_{1-1}–IES_{1-4} correspondingly, and extracts E_{1-1}–E_{1-4} were obtained by evaporating solvents in ES_{1-1}–ES_{1-4}, respectively. The IES_{1-4} was acidified with 35% of muriatic acid to pH 2–3 to convert —COONa to —COOH and filtrated to afford filter cake 2 (FC_2) and filtrate 2 (F_2). The FC_2 was dried in the VDO at 80 °C for 24 h and then weighed (0.01 g). Similar sequential extraction for F_2 isolation and subsequent solvent evaporation were conducted to afford extraction solutions ES_{2-1}–ES_{2-4}, corresponding extracts E_{2-1}–E_{2-4} and inextractable solutions IES_{2-1}–IES_{2-4}, as illustrated in Fig. 2. The IES_{2-4} was also evaporated to afford inextractable fraction (IEF). The E_{2-3}, E_{2-4} and IEF were esterified with CH_2N_2 to afford MEE_1, MEE_2 and MEIEF, respectively. The above experiments were repeatedly conducted. The mass ($m_{OM\ in\ F1}$) of organic matter (OM) transferred from WS to the F_1 was calculated according to the difference in OM mass between WS ($m_{OM\ in\ WS}$) and FC_1 ($m_{OM\ in\ FC1}$):

$$m_{OM\ in\ F1} = m_{OM\ in\ WS} - m_{OM\ in\ FC1}$$

The yields ($Y_{ONCs\ in\ F1/WS}$ and $Y_{ONCs\ in\ extract/WS}$) of ONCs enriched into organic matter (OM) in the F_1 and each extract based on OM in WS were calculated according to mass ratio of the ONCs ($m_{ONCs\ in\ F1}$ and $m_{ONCs\ in\ extract}$) detected to OM in WS:

$$Y_{ONCs\ in\ F1/WS} = m_{ONCs\ in\ F1}/m_{OM\ in\ WS}$$
$$Y_{ONCs\ in\ extract/WS} = m_{ONCs\ in\ extract}/m_{OM\ in\ WS}$$

Corresponding contents of nitrogen enriched into the F_1 based on OM in WS ($C_{N\ in\ F1/WS}$) and in OM transferred from WS to the F_1 ($C_{N\ in\ F1/F1}$) were calculated according to the following formula:

$$C_{NinF1/WS} = \sum(M_N.m_{ONC\ in\ F1}/M_{ONC})/m_{OM\ in\ WS}$$
$$C_{N\ in\ F1/F1} = \sum(M_N.m_{ONC\ in\ F1}/M_{ONC})/(m_{OM\ in\ WS} - m_{OM\ in\ FC1})$$

where M_N, $m_{ONC\ in\ F1}$ and M_{ONC} denote atomic mass of nitrogen, mass of individual ONC and molecular mass of individual ONC, respectively.

2.3. FTIR analysis

All the extracts were analyzed with a Nicolet Magna IR-560 Fourier transform infrared (FTIR) spectrometer using KBr pellet method. The spectra were recorded by collecting 50 scans at a resolution of 8 cm^{-1} in reflectance mode with measuring regions of 4000–500 cm^{-1}.

2.4. GC/MS analysis

A Hewlett–Packard 6890/5973 GC/MS system, which is equipped with a HP-5MS capillary column (crosslink 5% PH ME siloxane, 30 m × 0.32 mm i.d., 0.25 μm film thickness) and a quadrupole analyzer, was used for analyzing all the extracts. Mass spectra were obtained at an electron impact potential of 70 eV. Helium was used as the carrier gas. The column was heated first at a rate of 5 °C/min from 60 °C to 150 °C and then at a rate of 7 °C/min from 150 to 300 °C (and held for 15 min). Both injector and detector temperatures were set at 300 °C. The mass range scanned was from 30 to 500 *m/z*. The reproducibility of quantitative analysis for the