



# Identification of organic nitrogen compounds in methanol-soluble portion from sweet sorghum stalk methanolysis

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## ABSTRACT

Understanding the chemical composition of organic nitrogen compounds (ONCs) in biomass and its derived liquids is important because of their negative impacts on the environment during biomass utilization as fuel. In this study, X-ray photoelectron spectrometer (XPS) was used to identify the nitrogen forms on sweet sorghum stalk (SSS) surface and gas chromatograph/mass spectrometer (GC/MS) together with electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometer (FTICRMS) were employed to analyze ONCs in methanol-soluble portion (MSP) from SSS methanolysis. Analysis with XPS shows that the nitrogen forms on SSS surface mainly include pyrrolic, amino, and quaternary nitrogen species. GC/MS identified 14 ONCs in MSP, including 3 pyrroles, 3 indoles, 2 imidazoles, 3-methoxypyridine, 1-(hex-5-enyl)-1-methylhydrazine, cyclohexanecarbohydrazide, *N*-pyridin-3-ylacetamide, 1,3,4-trimethyl-1*H*-pyrazol-5(4*H*)-one, and pyridin-3-amine. According to analysis with negative-ion ESI FTICRMS,  $N_1O_n$  class species are the main neutral nitrogen compounds (NNCs) in MSP.  $N_1O_3$  class species are the most abundant NNCs, followed by  $N_1O_4$  and  $N_1O_5$  class species. Pyrroles and indoles should be dominant NNCs based on double bond equivalent (DBE) distributions. In positive-ion mode, most of the detected basic nitrogen compounds in MSP are  $N_2O_n$  class species, in which  $N_2O_2$ – $N_2O_4$  class species with DBE = 8–12 and carbon atom numbers of 19–28 are the most abundant.  $N_2O_n$  class species with DBE < 4 are likely to be diamines, hydrazines, hydrazides, imidazoles, and/or pyrazoles, while those with DBE ≥ 4 could be ascribed to pyridinamine, pyrazines, pyrimidines, benzoimidazoles, indazoles, and/or isoquinolinamines.

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## 1. Introduction

Biomass-derived liquids (BDLs) obtained from biomass conversion are complex mixtures consisting of numerous organic species. During BDL utilization as fuel, organic nitrogen compounds (ONCs) can be converted to  $\text{NO}_x$ , which contributes to environmental problems caused by acid rain, photochemical smog, and greenhouse effects [1–3]. Amides, nitriles, and *N*-heterocyclics are typical ONCs and nitrogen content of different biomass and BDLs is usually distinct. For example, nitrogen content of the liquid derived from wood or agricultural biomass is generally lower than that from macroalgae or sewage sludge [4,5]. To meet environmental regulations and upgrade the quality of BDLs, catalytically removing nitrogen is necessary. However, ONCs play a key role in catalyst deactivation by forming coke on the catalyst surface [6,7]. Therefore, a detailed knowledge of the molecular compositions of ONCs has profound implications for nitrogen removal from biomass.

Many efforts have been made to identify ONCs in biomass and BDLs using gas chromatograph/mass spectrometer (GC/MS), X-ray

photoelectron spectrometer (XPS), and  $^{15}\text{N}$  nuclear magnetic resonance [8–10]. Although XPS has successfully characterized the occurrence forms of nitrogen in biomass, the results cannot provide detailed information on the molecular compositions of ONCs in biomass. GC/MS has succeeded in analyzing some ONCs in BDLs [11,12], but failed to detect polar and/or less volatile ONCs. As a fast developed instrument, Fourier transform ion cyclotron resonance mass spectrometer (FTICRMS) proved to be powerful for molecular characterization of extremely complex mixtures, such as petroleum [13,14], coal-derived liquids [15,16], and pyrolysis BDLs [17,18]. It possesses ultrahigh resolving power and mass accuracy (< 1 ppm), allowing for distinct assignment of unique elemental composition to each mass spectral peak. In addition, electrospray ionization (ESI), a soft ionization technique, allows ionization of polar molecules. Negative-ion ESI favors the ionization of acidic oxygen-containing species and neutral nitrogen compounds (NNCs) [19], while positive-ion ESI facilitates the formation of protonated basic nitrogen compounds (BNCs) [20]. Therefore, ESI coupled to FTICRMS is useful for analyzing ONCs.

Among many technologies for converting biomass into useful products, fast pyrolysis, wherein biomass is subjected to rapid heating to high temperatures (400–1000 °C) under an inert atmosphere, was widely used to produce BDLs on an industrial scale [21]. Supercritical

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**Table 1**

Proximate, ultimate, and group composition analyses (wt%) of SSS.

Proximate analysis			Ultimate analysis (daf)				$S_{t,d}$	Group composition (daf)		
$M_{ad}$	$A_d$	$VM_{daf}$	C	H	N	O <sup>a</sup>		Cellulose	Hemicellulose	Lignin
6.0	2.9	89.9	50.7	6.7	0.6	> 41.9	0.1	42.4	37.7	13.7

daf: dry and ash-free base;  $M_{ad}$ : moisture (air dried base);  $A_d$ : ash (dry base);  $VM_{daf}$ : volatile matter (dry and ash-free base).<sup>a</sup> By difference;  $S_{t,d}$ : total sulfur (dry base).

depolymerization may be an alternative technology due to relatively low reaction temperature [22–24]. In our recent investigation [25], sweet sorghum stalk (SSS) was subjected to methanolysis under different conditions and the maximum yield of methanol-soluble portion (MSP) is 40.5% at 300 °C for 0.5 h.

In this study, we focus on the characterization of ONCs in MSP from SSS methanolysis. XPS was adopted to characterize nitrogen forms on the surface of SSS and GC/MS together with ESI FTICRMS were employed to analyze ONCs in MSP. Molecular-level understanding of ONCs in MSP will provide scientific basis for removing nitrogen and obtaining value-added chemicals from SSS.

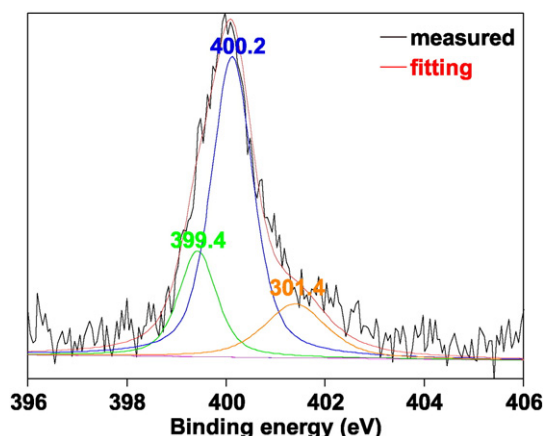
## 2. Experimental

### 2.1. Materials

SSS was provided by China Agricultural University. After air-drying for a week, the feedstock was pulverized to pass through an 80-mesh sieve followed by desiccation in a vacuum at 80 °C for 24 h before use. Table 1 lists proximate, ultimate, and group composition analyses of the sample. Solvents used in the experiments are commercial analytical reagents and were purified by distillation prior to use. MSP was obtained from SSS methanolysis as reported in our recent study [25] and described in Fig. S1 of the Supporting information.

### 2.2. Analysis of SSS with XPS

The occurrence forms of nitrogen on the surface of SSS was determined with a Thermo Fisher ESCALAB 250Xi XPS, which was equipped with a monochromatized Al K $\alpha$  X-ray source operated at 150 W. The analysis with XPS was run at a fixed analyzer transmission mode, and calibration for binding energy of nitrogen was referred to the main C 1s peak at 284.8 eV. XPS PeakFit software was used for peak fitting and semi-quantitation of XPS N 1s spectrum. The corresponding N 1s spectrum was curve resolved using 50% Lorentzian–Gaussian line shape.

**Fig. 1.** XPS N 1s spectrum and its fitting curves of SSS.**Table 2**

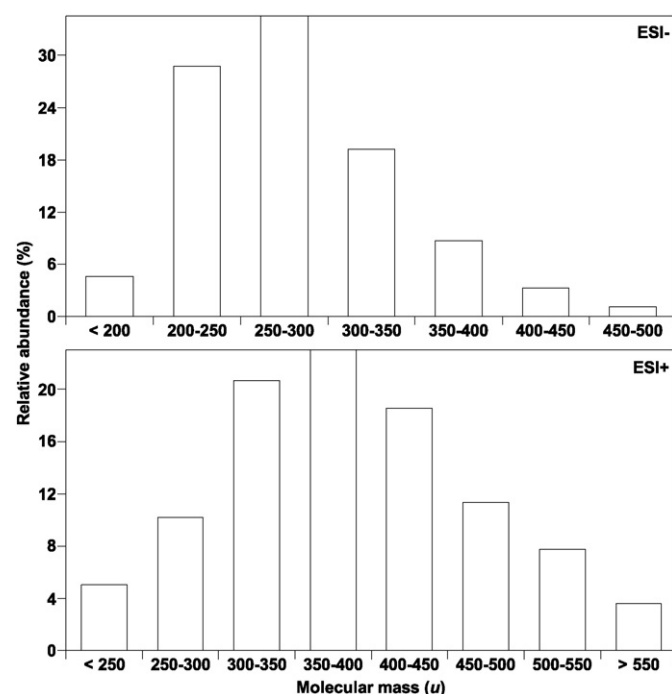
Distribution of nitrogen forms in SSS analyzed with XPS.

Binding energy (eV)	Nitrogen form	Molar content (%)
398.6	Pyridinic	< 1.0
399.4	Amino	28.0
400.2	Pyrolic	58.3
401.4	Quaternary	13.3
402.0	Chemisorbed	< 1.0

### 2.3. Analyses of MSP with GC/MS and ESI FTICRMS

MSP was analyzed with an Agilent 7890/5975 GC/MS equipped with a HP-5MS capillary column (60 m length, 0.25 mm inner diameter, 0.25  $\mu$ m film thickness) and a quadrupole analyzer with a  $m/z$  range from 33 to 500 and operated in electron impact (70 eV) mode. The column temperature was programmed from 60 to 240 °C at 3 °C min<sup>-1</sup>, then raised to 300 °C at 10 °C min<sup>-1</sup> and held at that temperature for 5 min. The compounds were identified by comparing mass spectra with NIST11 library data.

MSP was also analyzed with a 9.4 T Bruker apex-ultra ESI FTICRMS both in negative- and positive-ion modes. The sample solution was infused through an Apollo II ESI source with a syringe pump. In ESI source, the voltages at the emitter, capillary column front end, and capillary column end for negative-ion (positive-ion) were set to 4.0 (–3.5) kV, 4.5

**Fig. 2.** Distributions on molecular mass of the compounds in MSP analyzed with ESI FTICRMS.

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