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Twenty-two compositional characterizations and theoretical energy potentials of extensively diversified China's crop residues

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ABSTRACT

Knowledge of the compositional properties of crop residues feedstocks is important for process control and handling of co-products and waste from energy utilization. In this study, 1076 crop residues were collected from 326 sites across China. Chemical analysis of five organic chemical compositions, four proximate compositions, five ultimate compositions and eight mineral elements were conducted. Energy potentials of crop residues in China were quantified based on their compositional characterization. Results showed that the compositional characteristics of wheat straw, rice straw, corn stover, rape stalk and cotton stalk were shown to be significant different ($p < 0.05$) and highly variable. The coefficients of variation were negatively correlated with the means of crop residues compositions. Principal component analysis reflected that the compositions could explain several variations and clustering rules of the five crop residues. The correlations among parameters could be briefly summarized as hemicelluloses/ash −cellulose/lignin/water soluble carbohydrates/crude protein/P, water soluble carbohydrates−crude protein, crude protein−N−P−Mg−Cu, volatile matter−ash−fixed carbon, C−H−O−N−S, P−K−Na−Ca and ash−C/H/O/K ($p < 0.01$). The energy potentials of the five substrates were also significantly different ($p < 0.05$). The higher heating values, theoretical ethanol yields, and theoretical biomethane yields of the crop residues were 12.97−18.58 MJ/kg, 336.69−658.25 g/kg, and 151.48−288.45 L/kg, respectively.

1. Introduction

Crop residue is one of the main biomass energy resources, is available in large quantities with widespread distribution at low cost, is easy to procure, and is frequently renewed. The annual world output of crop residues contains a surprising amount of energy [1–3]. Compared with fossil fuels, the effective utilization of crop residues could help realize the sustainable and ecologically sound development, and reduce the emissions of CO_x, NO_x, and SO_x atmospheric pollutants [4,5]. For this reason, alternatives to the disposal of crop residues are being increasingly considered attractive approaches for coping with both environmental issues and the increasing global demand for energy over the past decades in the worldwide [6,7].

Crop residues can be used in a variety of ways for energy production, including combustion, ethanol conversion, and biomethane conversion [7,8]. However, compositional characterization of crop residues is imperative as the compositions affect the energy potentials by affecting the conversion processes [9–12]. For example, cellulose, hemicellulose, lignin, WSC (water-soluble carbohydrates), and CP (crude protein) constitute the organic carbon materials produced by photosynthesis, and their contents and structures directly affect the thermochemical and biochemical conversion processes, products, and yields [13–15]. During the thermochemical conversion process of crop residues, the ultimate compositions (C, H, O, N and S), proximate compositions (moisture (Moist), ash, VM(volatile matter), and FC (fixed carbon)), and mineral elements (P, K, Na, Ca, Mg, Fe, Cu, and Zn) differentially affect the calorific value, slagging and combustion performance of the fuel [16–20]. With the complex compositions of crop residues, the conversion yields of heat energy, ethanol, biomethane, and other energy potentials can be predicted [20–22]. Several studies have shown that the crop varieties, agricultural systems, soil and irrigation in different regions may vary the

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Nomenclature

CP	crude protein
DM	dry matter
FC	fixed carbon
HHV	higher heating value
Moist	moisture
Mt	million tons
PCA	principal component analysis
VM	volatile matter
WSC	water soluble carbohydrates.

compositions and energy characteristics of crop residues [23–25]. The characteristics of crop residues depend on local climate and agricultural conditions.

China is one of the largest global agricultural producers and the production of crop residues was 842 million tons (Mt) in 2010, which included 153.62 Mt wheat straw, 119.55 Mt rice straw, 331.83 Mt corn stover, 24.26 Mt rape stalk, and 22.48 Mt cotton stalk [26–28]. China has diverse and complex climate conditions, planting environment and planting patterns compared with other countries. Thus, a better understanding of the basic compositional characteristics of extensively diversified Chinese crop residues is critical and imperative for their successful energy application perspectives, including conversion processes, quality control, economic value, and eventually the safe disposal of waste [6,8,26]. However, such understanding on a national scale to date is largely limited. Thus, the present study: (1) investigated a wide variety of crop residues which were extensively collected across different areas of China to present their variation and correlation in compositional properties, and (2) evaluated the energy potentials of the crop residues as feedstock for the production of thermal energy, ethanol, and biomethanol based on their characterization.

2. Materials and methods

2.1. Samples collection and preparation

Based on the planting areas and distributions of crops in China, crop residue samples were selected considering different species and locations. Wheat straw, rice straw, corn stover, rape stalk and cotton stalk samples were collected at the fully ripe stage during 2011–2014. The regional distributions of the collected samples are shown in Fig. 1. Sampling was conducted at 326 sites in 32 provinces, cities, and autonomous regions in China [28]. A total of 1076 specimens were collected, comprising 328 wheat straw, 142 rice straw, 341 corn stover, 130 rape stalk, and 135 cotton stalk samples. Each crop residue sample was taken from different plots in the field. The samples had the grains and roots removed and the middle part retained. Then, the samples were thoroughly mixed to obtain a representative batch of approximately 2 kg.

According to ASTM (American Society for Testing and Materials) E1757-01, the collected crop residue samples were dried in a forced-air drying oven at 45 °C for 36–48 h, fed into a ZM100 mill (Retsch GmbH & Company, Germany), and milled through a 0.90 mm sieve. Then, the samples were stored in bags prior for compositional analysis.

2.2. Compositional and higher heating value analyses

All the experiments were performed in duplicate and the recorded results are the averages of two parallel samples, and the results are expressed on a DM (dry matter) basis after 45 °C oven dried.

2.2.1. Organic chemical compositions

Cellulose, hemicellulose, and lignin were measured according to the National Renewable Energy Laboratory method [29]. A crop residue sample (0.30 g) and deionized water (10 mL) were combined in a high-pressure tube and extracted in a boiling water bath for 1 h to remove soluble sugar, then hydrolyzed with 72% H_2SO_4 (3 mL) at 30 °C for 2 h. Then, the mixture was diluted to 4% H_2SO_4 with deionized water (84 mL) and placed in an autoclave at 121 °C for 1 h. After cooling to room temperature, a portion of the supernatant (20 mL) was neutralized to pH 5–6 by adding 0.82–0.85 g $CaCO_3$ and then filtered. The monosaccharide compositions of the hemicelluloses in the neutralized, filtered liquid were determined by High Performance Liquid Chromatography using the Aminex HPX-87P column (Bio-Rad) with a refractive index detector (HITACHI, L-2490) to obtain cellulose and hemicellulose, whereas lignin was determined by the residue remaining after combustion in a 575 ± 25 °C muffle furnace for 3 h [29]. WSC was determined using the UV-2550 spectrophotometer according to the anthrone sulfuric acid method. CP was analyzed using the Kjeltec 2300 auto-analyzer (FOSS Tecator AB, Sweden) according to the Association of Official Analytical Chemists method [30].

2.2.2. Proximate compositions

Moist was determined in a 105 °C oven according to the weight difference before and after heating. The ash content was measured after burning the samples to a constant weight in a muffle furnace at 575 ± 25 °C for 3 h [31]. VM was analyzed at 900 °C after 7 min combustion in a muffle furnace, and FC was determined by using Eq. (1) [32]:

$$FC = 100\% - Moist - VM - Ash \quad (1)$$

2.2.3. Ultimate compositions

The C, H, N and S contents were determined using the Elementar Vario EL II (Vario Macro, Germany). The O content was obtained by using Eq. (2) [18,33]:

$$O = 100\% - Ash - (C + N + H + S) \quad (2)$$

2.2.4. Mineral elements

Crop residue samples were digested using an advanced microwave digestion instrument (Milestone Ethos Touch Control, equipped with an HPR 1000/6S rotor) with a 1200 W microwave oven. The crop residue sample (0.50 g) was digested in concentrated HNO_3 (7 mL) in a closed reactor in the microwave oven. Then, the reactor was heated at 160 °C on a hot plate to remove the acid, and the digested liquid was transferred to a 100 mL volumetric flask. After the preparation of standard curves, inductively coupled plasma-mass spectrometry (ICP-MS, Analytik Jena AG, Jena, Germany) was used for P, K, Na, Ca, Mg, Fe, Cu and Zn analyses.

2.2.5. Higher heating value

HHV (Higher heating value) was determined by bomb calorimetry according to ASTM E-711 [34]. A crop residue sample (1.00 g) was placed in the bomb, and the HHV was determined by the oxygen-bomb combustion method.

2.3. Calculation of the theoretical energy potentials of crop residues

2.3.1. Theoretical thermal energy conversion

The annual production of wheat straw, rice straw, corn stover, rape stalk, and cotton stalk in China in 2014 was estimated by multiplying the crop grain outputs in the China statistical yearbook by the ratios of crop residue to grain [27,28]. The thermal energy conversion potentials of the five crop residues in 2014 were