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Cell morphology and chemical characteristics of corn stover fractions

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ABSTRACT

This paper investigated cell morphology, chemical components, lignin distribution and inorganic elements distribution of corn stover fractions. Corn stover fractions, classified as stalk rind, stalk pith and leaf, had different tissues, cell morphology and chemical compositions. Corn stalk rind had good fiber morphological characteristics for papermaking, while stalk pith, having short fibers and high contents of parenchyma and vessel, was not suitable for papermaking. Stalk rind had the highest lignin and cellulose content but the lowest hemicellulose content among all the fractions. The major ash-forming elements in corn stover fractions were potassium, chlorine, silica, calcium, magnesium and sulfur. Potassium and chlorine took more than 86% of total inorganic elements in stalk rind while silica content was much higher in leaf and stalk pith than that in stalk rind. Perivascular sclerenchyma and subepidermal sclerenchyma of stalk rind were more lignified than the other tissues. The highest lignin concentration existed in cell middle lamella and corner. All corn stover fractions could be good biorefinery feedstock based on their main chemical compositions, though they are obviously heterogeneous in aspects of cell morphology and chemical characteristics.

1. Introduction

Current environmental and social pressures are limiting wood harvest volumes worldwide. Therefore wood supply is getting less and less for pulp and paper industry. Non-woody lignocellulosic biomass, such as wheat straw, rice straw and reed, has been an important fiber resource for decades in countries with a shortage of woods, like China. Meanwhile, lignocellulosic biomass is also a potential renewable feedstock for biofuels and biorefinery (Ragauskas et al., 2006). As a kind of abundant and renewable agricultural residue, corn (*Zea mays* L.) stover could be a low-cost and sustainable source for energy and chemicals in future. The term corn stover normally refers to combination of corn stalk (stem) and leaf.

Annual production of corn stover in China was about 200 million tons in 2008, which counted for one third of the total agricultural residues production in the country. In United States, since corn stover is the largest non-food biomass available source, it has been studied for biofuel process development at National Renewable Energy Laboratory (NREL) (Decker et al., 2007). Numerous studies have been undertaken to investigate pre-treatment and bioconversion of corn stover to biofuel (Akin et al., 2006; Kim and Lee, 2006; van Walsum and Shi, 2004; Weiss et al., 2010; Zhu et al., 2009).

Biomass is a complex heterogeneous mixture of organic components and, to a less extent, inorganic matter, containing various solid and fluid intimately associated phases or minerals with different origins (Vassilev and Vassileva, 2009). Corn stover always consists of stalks, leaves, husks and ears; and stalks are composed of stalk rind and pith. All these fractions have different tissue structures, fiber properties, and chemical compositions. Vassilev et al. (2010) indicated that there are two fundamental aspects relating to biomass usage for fuels and biorefinery materials: to extend and improve basic knowledge of the composition and properties and to apply this knowledge for the most advanced and environmentally safe utilization. The chemical composition of lignocellulosic feedstock is a key factor affecting efficiency of biofuel production during conversion processes (Hamelinck et al., 2005; Hames et al., 2003). Recently, an effective mechanical fractionation of corn stover into stalk rind, stalk pith, and leaves is realized (Sun, 2003). The wider utilization of corn stover as a source of fiber, biofuel and biochemicals requires a comprehensive understanding of the cells (including fibers) properties, chemical characteristics, lignin distribution and inorganic elements distribution.

Corn stover has been investigated as a fiber resource for pulp and papermaking since 1929 (Jahan et al., 2004). Corn stalk fibers showed good performance for papermaking (Ahmed and Zhu, 2006; Byrd et al., 2006; Cheng et al., 2008; Wiernik et al., 2002). However, corn stover has not yet been successfully commercialized for pulp production worldwide. The reason might come from two aspects: firstly, the abundant wood supply was the most

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convenient way for pulping industry in 20th century; secondly and maybe more importantly, the heterogeneity of corn stover fractions and their integrated harvest limit the application. However the situation starts changing significantly because of shortage of wood supply and technology development. Recent technology development has allowed the fraction separation by either mechanical or chemical methods. Therefore, corn stover is becoming an important feedstock for integrated biorefinery process to produce fibers and other valued biochemicals simultaneously.

Although fiber properties of corn stover have been studied for decades, no systematic investigation of cell morphology and fiber quality of different corn stover fractions is done so far. In this paper, the cell morphology and fiber quality of corn stalk rind, stalk pith, leaf blade and leaf sheath will be investigated systematically. Chemical components of corn stover fractions have been investigated in some studies. Ahmed and Zhu (2006) studied the contents of lignin, cellulose and pentosan in corn stalk rind and the sugar components of corn stalk. Hess et al. (2002) examined the chemical variations within the node, internode, and leaf sections of corn stover. Tortosa Masiá et al. (2007) characterized the ash components of corn stover. However, none of the above studies provided detailed and completed information of chemical components, sugar components and inorganic elements of individual corn stover fractions, which this paper will focus on. Furthermore, lignin distribution and inorganic elements distribution in corn stalk rind will also be investigated in this paper.

2. Materials and methods

2.1. Materials

The corn stover in this study was collected from Henan, China. The air-dried corn stover was manually fractionated into leaves and stalks firstly. Then the stalks were separated into rind and pith. Leaves included both leaf blades and leaf sheaths. Husks and cobs were not included in the study because they together just take less than 1% in weight percentage. The above separated fractions were stored in plastic bags for future use.

2.2. Methods

2.2.1. Weight percentage of corn stover fractions

About 5 kg of air-dried corn stover was manually separated into stalk rind, stalk pith and leaves. The separated fractions were weighed individually and their dryness contents were determined according to Technical Association of Pulp and Paper Industry (TAPPI) test method T258 om-02. Two batches of separation were conducted and the weight percentage of each fraction was calculated on oven-dry basis.

2.2.2. Cells morphology and their dimensions analysis

Four fractions, stalk rind, stalk pith, leaf blade and leaf sheath, were prepared for fiber morphology and quality analysis. The fractions were cut into 1 mm wide and 10 mm long strips manually followed by treatment with mixture of acetic acid and 30% hydrogen peroxide (1:1, v/v) at 60 °C for 72 h for cell dissociation. When the color of samples turned to white, the macerated cells were filtered and thoroughly washed with distilled water. The cells were stained with Graff C and the fiber morphological features were examined with Olympus BX51 research microscopy. The fibers were disintegrated with Metso handy disintegrator which does not introduce any mechanical damage to samples, and analyzed with Metso Kajaani-FiberLab FS-300 fiber quality analyzer. The fiber length (L), fiber diameter (D), cell wall thickness (W) and fines content were length weighted values. Fines were defined as fine fibers with a length smaller than 0.02 mm.

Three derived values, Runkel ratio, slenderness ratio and flexibility coefficient, were used to assess the suitability of plant raw materials for paper production (Saikia et al., 1997).

2.2.3. Chemical characterization

For chemical analysis, the 40–60 mesh fractions of stalk rind, stalk pith and leaves were prepared in accordance with TAPPI test method T257 cm-02. All chemical composition results were calculated based on oven-dried corn stover fractions.

The extractives and ash were analyzed according to TAPPI test method T204 cm-97 and T211 om-02 respectively. The holocellulose was obtained by treating the extractive-free samples with $NaClO_2$ and acetic acid to remove lignin, and then the α-cellulose content was determined by further treating holocellulose with 17.5% NaOH to remove the hemicellulose (Han and Rowell, 1996). Klason lignin content was determined according to TAPPI test method T222 om-02. Acid-soluble lignin content was determined by a spectrophotometric method based on absorption of ultraviolet radiation (Schoening and Johansson, 1965). Acetyl and formyl contents were determined by hydrolysis with NaOH and IC analysis (Anttila et al., 2007). Nitrogen content was determined according to the Kjeldahl method. The crude protein content was calculated from nitrogen content by multiplying a coefficient of 6.25.

2.2.4. Sugar analysis of hemicellulose and pectins

The sugar components of hemicellulose and pectins were determined by acid methanolysis and gas chromatography (GC) (Sundberg et al., 1996). About 10–20 mg of freeze dried sample was weighted in a conical bottle with cap. Acid methanolysis was performed with 2 ml of 2 M anhydrous HCl/MeOH at 100 °C for 3 h. After cooling in room temperature for 15 min, the sample was neutralized with 300 μl of pyridine. Additionally, 4 ml of sorbitol standard (0.10 mg/ml) was added as internal standard. Accurate 1 ml of the clear upper phase was transferred to another conical bottle and evaporated to dryness with nitrogen. Derivation was conducted by adding 200 μl of pyridine, 300 μl of hexamethylsilazane (HMDS) and 200 μl of trimethylchlorosilane (TMCS). The derived sugars were analyzed by Varian 3900 GC with FactorFour capillary column VF-1ms.

2.2.5. Inorganic components analysis

The silica content was determined according to related TAPPI test method T244 cm-99 for acid-insoluble ash determination. To determine the contents of sodium, potassium, calcium, magnesium, manganese, iron, copper, phosphorus, sulfur, aluminum and zinc, the 40–60 mesh fractions were digested in microwave digester by adding 7 ml of HNO_3 and 1 ml of H_2O_2. The digested samples were then washed into a 50-ml volumetric flask and diluted to the mark with 18-MΩ ultrapure water. The elements were determined by Thermo Scientific iCAP 6000 ICP-OES.

For chloride content determination, samples were boiled in distilled water for 1.5 h and then filtered. The filtrate was analyzed for chloride by ICS-1000 with IonPac AS23 anion-exchange column.

2.2.6. Inorganic elements distribution in stalk rind

The stalk rind was cut into 3 mm wide and 10 mm long strips manually. The strips were extracted with benzene–ethanol (2:1, v/v) for 24 h and then dehydrated with graded ethanol solutions. Then the samples were embedded in epoxy resin and polished with Struers LaboPol-5 polisher. The polished samples, coated with carbon by JEC-560 auto carbon coater, were examined with a JEOL 6009 analytical scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDXA).