Industrial Crops and Products 30 (2009) 344–350

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Studies on the macromolecular components of nonwood available in Bangladesh

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ARTICLE INFO

Article history:
Received 2 April 2009
Received in revised form 15 June 2009
Accepted 23 June 2009

Keywords:
Nonwood lignin
Syringyl
β-*O*-4 units
Nonwood cellulose
Crystallinity

ABSTRACT

The structural feature of macromolecular component of dhaincha, cotton stalks, jute fiber, rice straw and wheat straw, which are commonly used in paper pulp production in forest deficient countries, was thoroughly studied. Lignin was isolated by classical Bjorkman method and characterized by elemental and methoxyl analysis, alkaline nitrobenzene oxidation, FTIR and ^{1}H NMR spectroscopy. The C_9 formulas for cotton stalks, jute fiber, dhaincha, rice straw and wheat straw were $C_9H_{8.95}O_{3.53}(OCH_3)_{1.00}$, $C_9H_{8.12}O_{4.03}(OCH_3)_{1.65}$, $C_9H_{8.10}O_{4.65}(OCH_3)_{1.32}$, $C_9H_{8.58}O_{3.74}(OCH_3)_{1.23}$ and $C_9H_{8.31}O_{3.54}(OCH_3)_{1.23}$, respectively. The alkaline nitrobenzene oxidation products showed that syringyl to vanilin ratio of these nonwood varied from 1.1 to 2.9. Jute fiber showed the highest syringyl to vanilin ratio that are consistent with C_9 formula. The β-*O*-4 units in these nonwood lignins had predominately *erythro* stereochemistry type. The crystalline structure of these nonwood cellulose was also studied using X-ray diffraction and FTIR spectroscopy. The proportions of crystallinity, crystal size were varied from plant to plant. Jute fiber showed the highest proportion of crystallinity (73.4%) and crystal size (4.2 nm). The degree of polymerization of these nonwoods cellulose has also been studied. Degree of polymerization of jute cellulose was also the highest (3875). FTIR spectroscopy showed that these nonwoods cellulose was monoclinic unit cell structure (I_β). Carbohydrate analysis showed that the main sugar component in the hydrolyzates of these nonwoods were xylose apart from glucose.

1. Introduction

Forest deficient countries like Bangladesh are looking for alternative fibrous resources especially nonwood. In the past decades, fast growing plants have received particular attention as wood alternative sources of vegetable fibers. Despite the increasing importance and use of short rotation plant, information on the detailed chemical and structural analysis is quite scarce and dispersed. To the best of our knowledge, no comprehensive study on the detail chemical characterization of macromolecular components of nonwood of Bangladesh variety is reported.

The main constituents of lignocellulosic materials are cellulose, hemicellulose and lignin.

Lignin is one of the important chemical constituents of lignocellulosic materials like wood and nonwood. In softwood lignin, the network is formed primarily by coniferyl moieties (95%), the rest consisting of *p*-coumaryl alcohol-type units and only trace amounts of sinapyl alcohol moieties, while in hardwood and dicotyl crops like hemp and flax, various ratios of coniferyl/sinapyl have been reported (Dence, 1992). Lignins derived from monocotyl plants (grasses and cereal straw) contain also significant amounts of *p*-coumaryl alcohol residues (Dence, 1992). But, despite extensive investigation, the complex and irregular structure of lignin is not fully understood and their structures have not yet been completely elucidated (Ikeda et al., 2002; Puls and Schuseil, 1993). It varies, not only between different genera and species in the plant kingdom (Nimz et al., 1981) but also according to the method of isolation. Lignins contain several functional chemical groups, such as hydroxyl (phenolic or alcoholic), methoxyl, carbonyl and carboxyl, in various amounts, depending on origin and the applied isolation process (Gosselink et al., 2004; Sun et al., 2001). In fact, no method of isolation gives a highly representative and totally unaltered native lignin. The classical approach was established by Bjorkman (1956) which extracted lignin from ball milled wood with aqueous dioxane. The resulting ball milled wood lignin (MWL) is usually considered to be more or less representative of native lignin. In our previous investigation, lignin was extracted from nonwood by acidic dioxane (Jahan et al., 2007).

Hemicelluloses are the abundant natural polymeric materials, next to cellulose. Unlike most natural polymers, such as cellulose and starch, which consist of a single monomer and intermonomeric linkage, hemicellulose are heteroglycans, which consist of various

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doi:10.1016/j.indcrop.2009.06.006

different sugar units, arranged in different proportions and with different substituent. In particular, in contrast to wood hemicelluloses, there are a great variety of linkages and abundance of branching types in graminaceous hemicelluloses, depending on the species and the tissue within a single species, as well as on the age of the tissue (Nimz et al., 1981).

Cellulose, the most abundant renewable polymer available, is produced by nature at an annual rate of 10^{11}–10^{12} tons (Hon, 1994). If cellulose can be efficiently converted to monomeric sugars by hydrolytic processes, it can better compete with starch and play an important role to meet future energy needs. Hydrolytic processes are also used to remove amorphous cellulose in forming cellulose nanocrystals (Ranby, 1951). Cellulose nanocrystals have received increasing interest due to their natural, renewable origins and good mechanical properties (Podsiadlo et al., 2005). For example, cellulose nanocrystals are very attractive in making low cost, lightweight, and high-strength hybrid composites for multiple applications (Azizi et al., 2005).

The objectives of this study were to elucidate the variation of macromolecular components among these nonwood. In this study, (1) lignin was isolated from dhaincha, cotton stalks, jute fiber, rice straw and wheat straw by classical Bjorkman (1956) method, and lignin preparations were studied by methoxyl and elemental analysis, alkaline nitrobenzene oxidation, Fourier transform infrared (FTIR), ^{1}H NMR spectroscopy. (2) The cellulose crystallinity, crystal size and crystal structure of dhaincha, cotton stalks, jute fiber, rice straw and wheat straw cellulose were investigated by X-ray diffractometry, FTIR spectroscopy. The degree of polymerization (DP) of dhaincha, cotton stalks, jute fiber, rice straw and wheat straw cellulose was also investigated. (3) The hemicelluloses compositions among these nonwood species were investigated.

2. Experimental

Dhaincha, cotton stalks, jute fiber, rice straw and wheat straw were collected from Dhaka region, and ground in a Wiley mill, extracted with acetone and dried in vacuum over P_2O_5.

2.1. Preparation of milled wood lignin (MWL)

Following the Bjorkman (1956) the extracted meal were ground in a vibratory ball mill for 100 h. The milling proceeded for 12 h per day. Milled wood was mixed with dioxane:water (9:1) and extracted inside vibratory ball mill for 24 h. The solution was centrifuged and supernatant was evaporated to dryness under reduce pressure. The residue was dissolved in acetic acid:water (9:1) and the solution was then added drop wise by small needle dropper to water with constant stirring. A precipitate was formed. The solution was centrifuged and residue was dried in vacuum over P_2O_5. The dried residue was dispersed in 1,2 dichlorethane:ethanol (2:1), which was then centrifuged. The clear supernatant was added dropwise to anhydrous diethyl ether and a precipitate was formed, which was centrifuged and residue was dried in vacuum over P_2O_5. The yield of MWL was calculated based on Klason lignin. The lignin yields were 28.7%, 29.1%, 25.9%, 30.3%, and 30.7%, for dhaincha, cotton stalks, jute fiber, rice straw and wheat straw, respectively.

2.2. Acetylation of MWL

100 mg MWL was added in 1.5 ml of dry pyridine:acetic anhydride (1:1) and kept it for 72 h at room temperature. The solution was added to a 10-fold volume of ice-cold water whereupon the acetylated sample was recovered as a precipitate, which was purified by successive washing with water and dried under vacuum over P_2O_5.

2.3. Elemental analysis

C, H and N analyses were carried out in analytical in analytical research division of BCSIR Laboratories, Dhaka. The methoxyl content in MWL was determined in accordance to Japan International Standard Methods (JIS P8013 1972).

2.4. Spectroscopy

FTIR: Infrared spectra were recorded by using a Shimadzu FTIR spectrometer model 8201PC.The dried samples were embedded in KBr pellets in the concentration of about 1 mg/100 mg KBr. The spectra were recorded in the absorption band mode in the range 4000–400 cm^{-1}.

For the cellulose crystallinity determination, the powder of extractive free dhaincha, cotton stalks, jute fiber, rice straw and wheat straw was used for FTIR spectroscopy measurements. The dried samples were embedded in KBr pellets, and were analyzed by using a Shimadzu FTIR spectrometer model 8201PC. The spectra were recorded in the absorption band mode in the range 900–400 cm^{-1}.

^{1}H NMR: Spectra of lignin solution (100 mg of acetylated lignin contained in 0.5 ml $CDCl_3$) were recorded in a Bruker 400 spectrometer. Solvent was used as internal standard (7.25 ppm). 128 scans and 1.3 s of time were acquired to complete relaxation of all protons. For quantification of protons, the signal in specified regions of the spectrum were integrated with respect to a spectrum-wide baseline drawn at the level of the background noise, and the results were referred to the signal for methoxyl protons, whose average number per C_9 unit was established as described above.

2.5. Alkaline nitrobenzene oxidation

Alkaline nitrobenzene oxidation of dhaincha, cotton stalks, jute fiber, rice straw and wheat straw was carried out according to Mun's modified method (Mun and Wi, 1991). GC analysis was conducted using a Shimatzu GC 17A gas chromatograph equipped with Neutrabond 1 capillary column (30 m × 0.53 mm). Conditions used were as follows: column temperature was programmed to increase from 150 to 250 °C at the rate of 5 °C/min; injection and detection temperature were 220 and 250 °C, respectively; column flow was rate 6 ml/min and split ratio 30.

2.6. Sugar analysis

The carbohydrates composition of these nonwoods were determined according to Tappi test methods (T249 cm00). Middle part of all raw materials was taken for sugar analysis. Jute consists of bark (fiber) and core (wood). In this study, we used middle part of the jute fiber (bark).

2.7. α-Cellulose preparation

For the removal of lignin, dhaincha, cotton stalks, jute fiber, rice straw and wheat straw meal was treated with Na-chlorite solution (Browning, 1967). The pH of the solution was maintained at 4 by acetate buffer. α-Cellulose was extracted from Na-chlorite treated nonwood meal in 17.5% NaOH (T 203 om-88).

2.8. Degree of polymerization

Single point viscosities of dhaincha, cotton stalks, jute fiber, rice straw and wheat straw cellulose at 0.5% concentration in cupriethylenediamine were determined according to Tappi test methods (T 230 om-99). Intrinsic viscosities (η_{int}) were calculated from the