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Properties of natural cellulose fibers from hop stems

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ABSTRACT

This paper reports the development of natural cellulose fibers from hop stems with properties similar to that of hemp. Hop stems are currently considered as byproducts and have limited applications. Since hop belongs to the genus cannabis that also includes hemp, it should be possible to obtain natural cellulose fibers from the stems of hop plants with properties similar to that of hemp. A simple alkaline extraction was used to obtain fibers from the bark of hop stems. Fibers obtained have high cellulose content, low% crystallinity but show good orientation of the cellulose crystals to the fiber axis. The strength and modulus of the fibers are lower but elongation is higher than that of hemp. Based on the properties of the fibers, we expect that the hop stem fibers will be suitable for use in textiles and composites similar to the common cellulose fibers currently in use.

1. Introduction

Hop (Humulus lupulus L.) belongs to the family *Cannabaceae* and genus *cannabis* that includes hemp. Hemp plants are used to produce excellent fibers that have been used for textiles for centuries. However, cultivation of hemp has been prohibited in the United States due to the perceived narcotic effects of the plant. Hemp fibers are obtained from the bast of the plants and it is reasonable to expect that hop plants which belongs to the same genus should have stems with fibers similar to that of hemp. Currently, the stems of hop plants are considered byproducts and have limited applications. No reports are available on the use, production or properties of natural cellulose fibers from hop stems. However, the stems and leaves of several plants that are currently considered byproducts have been studied as sources for natural cellulose fibers. Examples of such byproducts considered as sources to obtain natural cellulose fibers include corn stover, rice and wheat straw, sorghum stalk and leaves, pineapple leaves and sugarcane stalks (Collier, Collier, Agarwal, & Lo, 1992; Doraiswamy & Chellamani, 1993; Reddy & Yang, 2005a, 2005b, 2005c; Reddy & Yang, 2006; Reddy & Yang, 2007a, 2007b, 2007c).

Utilizing agricultural byproducts as sources for natural cellulose fibers are becoming increasingly necessary due to concerns on both the future price and availability of the natural and synthetic fibers in current use. For instance, there is a considerable decrease in the cultivation and availability of the most common natural fiber, cotton. Cotton cultivation in the United States had decreased to about 10,000 acres in 2007 compared to about 15,000 acres in 2005 and 2006. This has led to a decline in cotton production in the United States to about 4.3 million tons in 2007 from 5.2 million tons produced in 2006 (http://www.nass.usda.gov/QuickStats/index2.jsp). The decline in cotton cultivation and production is mainly due to farmers shifting to higher income generating biofuel crops such as corn and soybeans. Similarly, the increasing price and decreasing availability of petroleum resources have led to the increase in polyester fiber prices that currently sell at more than twice the price in the last decade. Due to these limitations of the fibers in current use, efforts are being made to find alternative sources for fibers.

Byproducts generated from commodity crops are abundant, cheap and renewable resources that are suitable for fiber production. It has been estimated that about 2000 million tons of byproducts are generated every year world wide from the major crops such as corn, wheat, rice, soybeans, sorghum and sugarcane (Huda et al., 2007). All of these byproducts are composed of considerable amounts (35–40%) of cellulose that can be extracted in the form of fibers. The available byproducts from these major agricultural byproducts could be used to obtain about 390 million tons of natural cellulose fibers, more than five times the current total fiber consumption in the world at about 70 million tons (Huda et al., 2007). Such large availability of fibers from currently limited use and abundantly available byproducts will help the fiber industry to be sustainable and also add value and increase the income from the agricultural crops. In addition, problems associated with disposing the byproducts after harvest will also be reduced if the byproducts are used for industrial applications.

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About 30,000 acres of hop are grown each year in the United States producing about 28,000 tons of hops. Even assuming a 1:1 weight ratio of hops to stems would mean an availability of 28,000 tons of byproducts, mostly stems. Since hop belongs to the same botanical classification of hemp and hemp fibers are obtained from the stalk of the plant, it is reasonable to expect that hop stems could be used to obtain natural cellulose fibers. Using hop stems for fibers will provide an opportunity to develop natural cellulose fibers with properties similar to that of hemp. In this paper, we have used hop stems to extract natural cellulose fibers and studied the composition, structure and properties of the fibers obtained. The properties of hop stem fibers have been compared to cotton and hemp data reported in literature.

2. Experimental

2.1. Materials

Hop stems were supplied by the Washington Hop Commission. The stems were air dried and leaves and other foreign materials were manually removed. The stems were then used for fiber extraction. All chemicals used in this study were reagent grade obtained from VWR International, Bristol, CT.

2.2. Fiber extraction

Hop stems were boiled in 0.5 N sodium hydroxide solution for 30 min with a material to solution ratio of 1:10. The outer bark of the stems had separated into fibers by the alkali treatment and the inner bark remained intact. The fibers formed were thoroughly washed first in warm and later in cold water, neutralized in dilute acetic acid solution to remove any remaining alkali and air dried.

Single cells or "ultimates" were obtained from the hop stems by maceration. Single cells are the smallest morphological units in fibers and measure a few millimeters in length. The single cells are used in the paper and pulp industry and commonly referred to as "ultimates or fibers" but are too small for high value fibrous applications. In this paper, fibers refer to a bundle of single cells held together by lignin and other binding materials.

Maceration of the hop stem fibers was done by treating the hop stem fibers in equal amounts of 10% (w/w) nitric acid and 10% (w/w) chromic acid solutions. Fibers were dipped in equal amounts of the solutions for about 24 h after initiating the reaction by heating the solution at 60 °C for 5 min (Ruzin, 1999). The treated fibers were thoroughly washed in water and dried after centrifuging in ethanol.

2.3. Fiber composition

The composition of the hop stem fibers in terms of the% cellulose, lignin and ash content was determined using standard test methods. Cellulose in the fibers was determined as the Acid Detergent Fiber (ADF) according to AOAC method 973.18 (Helrich, 1990). Lignin in the fibers was determined as Klason lignin according to ASTM method D1106-96 and ASTM method E1755-01 was used to determine the ash content in the fibers. Three replications were done for determining each component and the average and ± one standard deviation is reported.

2.4. Physical structure

The structure of the cellulose in the hop stem fibers was determined in terms of the% crystallinity and orientation of the microfibrils to the fiber axis in terms of the multifibrillar angle (MFA) using X-ray diffractometers. A Rigaku D-max/BΘ2Θ X-Ray diffractometer (Rigaku Americas, Woodlands, TX) with Bragg – Brentano parafocusing geometry, a diffracted beam monochromator, and a copper target X-ray tube set to 40 kV and 30 mA was used to determine the% crystallinity. Fibers were ground in a Wiley mill to pass through a 250 μm mesh and the powder was pressed into a pellet of about 5 mm thickness on a hydraulic press operated at a pressure of 138 GPa. Intensity measurements were taken on the pellet for a 2θ angle varying from 5° to 40°. The% crystallinity of the fiber was obtained by integrating the area under the crystalline peaks after subtracting the background and air scatter. Further details on calculating the% crystallinity of cellulose using the multi-peak method have been reported (Cave, 1997; Ward, 1950).

A Bruker D8 Discover model diffractometer (Bruker AXS Inc., Madison, WI) equipped with an area detector and GAADS software was used to determine the orientation of the microfibrils in the fiber to the fiber axis in terms of MFA and also to observe the diffraction pattern of the cellulose crystals in the fiber. The diffraction patterns were collected by mounting a bundle of fibers vertically in a specially designed sample holder. The diffraction patterns were collected for 10 min with the X-ray beam set to 40 kV and 30 mA. The 200 peak intensities in the diffraction patterns were fit into two Gaussian curves using a non linear least square algorithm with the software program Microcal ORIGIN to obtain the MFA. Details of the methods used to calculate the MFA have been previously reported (Cave, 1997; Hu & Hsieh, 1996).

2.5. Morphological studies

A Hitachi S3000N model variable pressure Scanning Electron Microscope (SEM) (Hitachi High Technologies America, Inc., Schaumburg, IL) was used to observe the longitudinal features of the untreated hop stems and fibers obtained from hop stems. The samples to be observed under the SEM were mounted on conductive adhesive tape, sputter coated with gold palladium and observed under the SEM. The widths of the single cells obtained by maceration as described earlier were measured from the SEM pictures and the lengths of the single cells were measured using a digital microscope. About 50 fibers were measured for the dimensions and the average and ± one standard deviations are reported.

2.6. Tensile properties

The fibers were conditioned in a standard testing atmosphere of 21 °C and 65% relative humidity for at least 24 h before conducting the tensile tests. The tensile tests were performed on an Instron tensile tester (Model 4000, Instron, Norwood, MA) to obtain the breaking tenacity, breaking elongation and Young's modulus of the fibers. A gauge length of 25 mm and a crosshead speed of 18 mm/min were used for the testing. About 100 fibers were tested and the average and standard deviations are reported.

2.7. Moisture regain

The moisture regain of the fibers was determined according to ASTM standard method 2654 using standard conditions of 21 °C and 65% relative humidity. Three replications were done for the moisture regain measurements and the average and ± one standard deviations are reported.

3. Results and discussion

3.1. Fiber composition

Hop stem fibers have cellulose content similar to cotton and higher than that of hemp fibers as given in Table 1. However, the

lignin and ash content in hop fibers is higher than that in cotton and hemp. The composition of the fibers depends on the variety, maturity of the plant, extraction conditions and methods used to determine the composition (Keller, Leupin, Mediavilla, & Wintermantel, 2001). Cotton is a single cell fiber and does not need lignin and other binding materials that are necessary to hold several single cells and form a fiber bundle as in the case of hop stem and the common bast fibers including hemp. Traditionally, hemp is extracted by natural retting and it is difficult to remove all the non-cellulosic substances by retting leading to slightly lower cellulose content in hemp compared to the cellulose content in chemically extracted hop stem fibers. The cellulose content of the hop stem fibers may increase further if stronger extraction conditions are used. However, stronger extraction conditions will remove lignin and other binding materials that could result in single cells that are not useful for high value fibrous applications. The amount of lignin and other binding materials to be removed should be determined by the properties of the fibers desired for an intended end use and the cost of extracting the fibers.

3.2. Physical structure

The crystallinity of cellulose in hop stem fibers is lower than that of cellulose in cotton and hemp as shown in Table 2. The MFA of cellulose fibrils in hop stem fibers is also lower than that of cotton but similar to that of most bast fibers including hemp. Fibers with low crystallinity will have relatively low strength and high chemical reactivity if the polymer and chemical compositions are the same, and fibers with low MFA will have lower elongation compared to fibers with high MFA (Howson, 1950). In addition to crystallinity, the amount of cellulose in the fibers, the degree of polymerization of the cellulose, length and width of single cells also influence fiber strength whereas the elongation is mostly influenced by the MFA. Hop stem fibers have MFA similar to that of hemp and other bast fibers and therefore could be expected to have elongation lower than that of cotton and similar to that of hemp and other bast fibers.

The diffraction patterns of cellulose in hop stem fibers are compared to hemp in Fig. 1a and b, respectively. As seen from the figure, cellulose in hop stem fiber produces diffraction bands very similar to that of hemp indicating that both the fibers have similar crystal structure. The diffracting arcs are sharp and short in hop and hemp unlike in cotton that has long diffracting arcs. This shows that cellulose crystallites in hop and hemp fibers are regularly distributed and are also parallel to the fiber axis and to each other (Bose & Ahmad, 1946). In addition to the typical equatorial reflections, the hop and hemp fibers also show the meridional reflections corresponding to the 004 plane of cellulose. The diffractogram of hop stem fibers shows that the intensity of peaks produced by the cellulose in hop fibers is much smaller than those produced by the cellulose in cotton and hemp as seen from Fig. 2. This is most likely due to the lower% crystallinity of cellulose in the hop fibers compared to cotton and hemp. In addition to the lower crystallinity, the presence of higher amounts of lignin and other non-cellulosic impurities in the fibers also influences the% crystallinity and physical structure of the cellulose in hop fibers (Thygesen, Oddershede, Lilholt, Thomsen, & Stahl, 2005). The presence of non-cellulosic substances in the hop fibers causes the overlapping of the $^{-}110$ and 110 peaks at 2θ angle between 13° and 17° whereas the two peaks are distinctly seen in cotton. Overall, the cellulose in hop stem fibers have lower% crystallinity but similar crystal structure to that of hemp fibers.

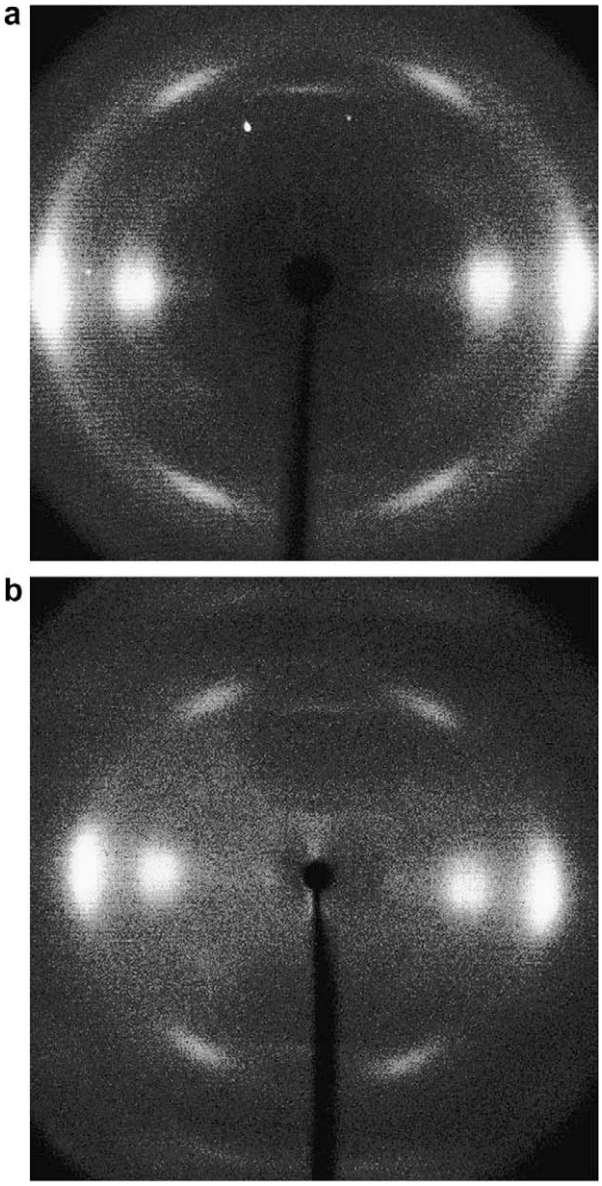

Fig. 1. Diffraction pattern of hop stem fibers and hemp show bright and short diffracting arcs indicating good orientation of the cellulose crystals in the fiber. The fibers also show the distinct equatorial and meridional reflections.

Table 1
Comparison of the composition (% by weight) of hop stems fibers with cotton and hemp. Data for cotton and hemp are from literature (Batra, 1998). Errors are ± one standard deviation.

Material	Cellulose	Lignin	Ash
Hop fibers	84 ± 1.6	6.0 ± 0.2	2.0 ± 0.1
Cotton	85–90	0.7–1.6	0.8–2.0
Hemp	55–72	2–5	1

Table 2
Comparison of the morphological and physical properties of hop stems fibers with cotton and hemp. Data for cotton and hemp are from literature (Batra, 1998). Errors are ± one standard deviation.

	Hop stem fibers	Cotton	Hemp
Single cell dimensions			
Length, mm	2.0 ± 1.0	15–56	5–55
Width, μm	16.5 ± 5.5	12–25	10–51
Physical structure			
Crystallinity,%	44 ± 5	65–70	81–89
MFA, deg	8 ± 0.7	20–30	–

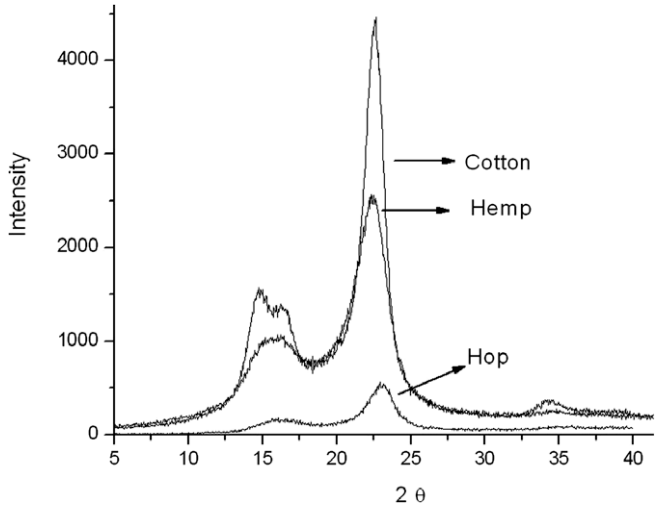

Fig. 2. Diffractograms of hop stem fibers compared to cotton and hemp. Cellulose crystals in hop stem fibers shows distinct crystal reflections of 200 and 004 planes at 2θ angle of 22° and 35°, respectively. However, the characteristic $^{-}$110 and 110 peaks found in cotton (2θ between 13° and 17°) are not distinct in the hop stem fibers.

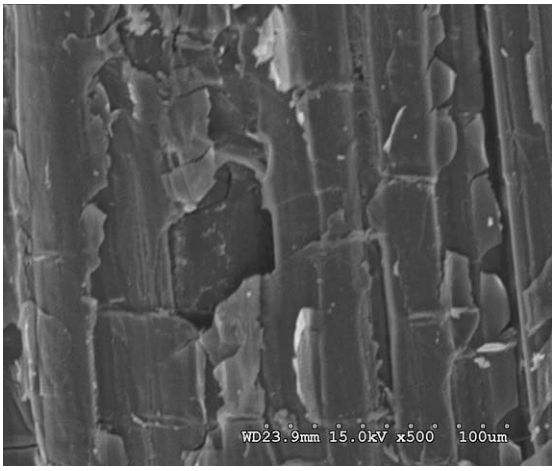

Fig. 3. Surface of an untreated hop stem is irregular and has layer of deposits probably composed of lignin, hemicellulose and other non-cellulosic substances.

3.3. Morphological structure

The single cells in hop stem fibers are much smaller than those in both cotton and hemp as seen from Table 2. The width of the single cells is similar to that of cotton and in the lower range of widths of single cells in hemp fibers. The length and width of the single cells in the fibers will mainly influence the fineness and strength of the fibers. Shorter single cells mean more number of single cells per unit length of the fibers compared to a fiber composed of longer length single cells. The higher number of single cells not only means an increase in fineness but also higher number of binding spots. The binding spots are the weak places that break easily during tensile testing and therefore, fibers with shorter single cells will have lower tensile strength.

The surface of the hop stems before treatment is irregular and is coated with non-cellulosic substances as seen from Fig. 3. Most of the non-cellulosic substances are removed during fiber extraction resulting in smooth and clean fiber surfaces as seen from Fig. 4.

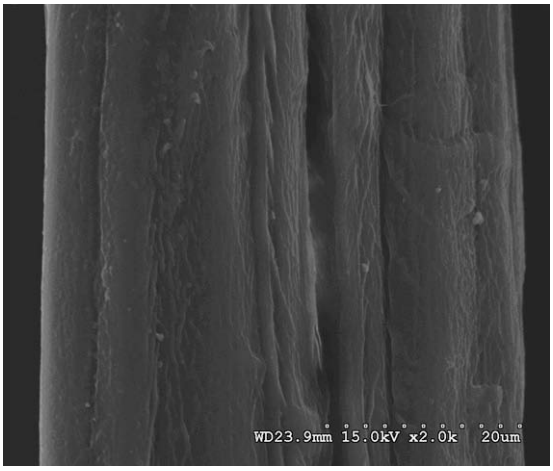

Fig. 4. SEM image of a fiber obtained from hop stems showing that the fibers have a relatively smooth and clean surface.

Table 3
Fineness, mechanical properties and moisture regain of hop stem fibers compared to cotton and hemp. Data for cotton and hemp are from Batra, 1998. Errors indicate ± one standard deviation.

Fiber properties	Hop stem fibers	Cotton	Hemp
Fineness, Denier	48 ± 19	3–8	–
Length, cm	11.5 ± 2.9	1.5–5.6	–
Strength, g/den	4.1 ± 1.9	2.7–3.5	5.2–6.8
Elongation,%	3.3 ± 1.2	6.0–9.0	1.7–2.6
Modulus, g/den	161 ± 57	55–90	203–245
Moisture regain,%	8.3 ± 0.4	7.5–8.0	12

3.4. Fiber properties

Fibers obtained from hop stems are coarser than cotton and hemp as shown in Table 3. However, the average length of hop stem fibers is much higher than that of cotton and in the range of lengths reported for various bast fibers including hemp (Batra, 1998). The long length of hop stem fibers allows them to be processable on the long staple spinning machinery similar to hemp and linen. The hop fibers can be cut to shorter lengths and processed on the short staple machines similar to cotton. Stronger treatment conditions, use of delignifying agents are some of the approaches that could be used to obtain hop fibers with fineness similar to that of hemp and other bast fibers.

Breaking tenacity of the hop stem fibers is higher than that of cotton and close to that of the hemp fibers. Shorter single cells and low crystallinity of cellulose in the fibers should be the major reasons for the lower breaking tenacity of hop fibers compared to hemp. Elongation of the hop stem fibers is lower than that of cotton but higher than the elongation of hemp fibers. The low MFA of hop fibers compared to cotton makes the fibers less flexible with respect to the fiber axis and therefore the fibers have low elongation as seen from Table 3 and from the stress–strain curve in Fig. 5. Modulus of hop stem fibers is between that of cotton and hemp indicating that the fibers will be stiffer than cotton but similar to that of hemp if the fiber fineness are similar. The high denier of the hop stem fibers compared to cotton and hemp is also responsible for the high modulus of the hop stem fibers. However, the high modulus of hop stem fibers makes the fibers stiff and suitable for use in applications such as carpets and composites whereas finer denier hop stem fibers would be more suitable for apparel and other applications. Moisture regain of hop stem fibers is similar to that of cotton and slightly lower than that of hemp. The lower

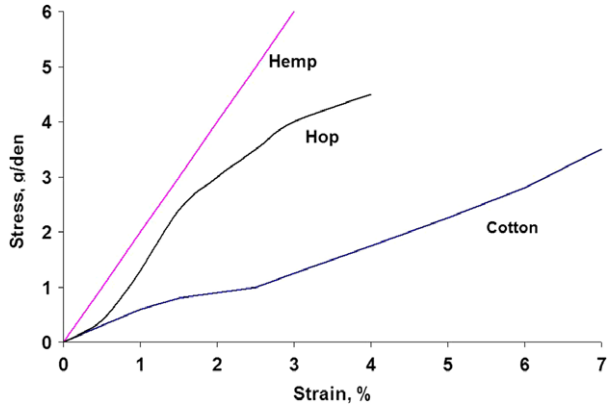

Fig. 5. Stress strain curve of hop stem fibers compared to cotton and hemp.

moisture regain for hop stem fibers compared to hemp should mainly be due to the difference in the composition of the fibers.

4. Conclusions

Hop stems have been used to obtain natural cellulose fibers with properties similar to that of hemp. The hop stem fibers have high cellulose content and relatively low lignin content whereas single cells in hop stem fibers are much shorter and wider than that in cotton and hemp. Hop stem fibers also have low% crystallinity but the cellulose in the fibers is well oriented to the fiber axis providing the fibers with good strength but low elongations compared to cotton. Modulus of the hop stem fibers is in between that of cotton and hemp. Overall, fibers obtained from hop stems have excellent properties and the fibers obtained from hop stems could be suitable for use in textile, composite and other fibrous applications.

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