Available online at www.sciencedirect.com
ScienceDirect
Bioresource Technology 98 (2007) 491–497
BIORESOURCE TECHNOLOGY

Carbohydrate components and crystalline structure of organosolv hemp (*Cannabis sativa* L.) bast fibers pulp

Esat Gümüşkaya [a,*], Mustafa Usta [a], Mualla Balaban [b]

[a] *Karadeniz Technical University, Faculty of Forestry, The Department of Pulp and Paper, 61080 Trabzon, Turkey*
[b] *İstanbul University, Faculty of Forestry, The Department of Forest Industrial Engineering, Bahçeköy, İstanbul, Turkey*

Received 27 May 2004; received in revised form 13 May 2005; accepted 24 February 2006
Available online 6 June 2006

Abstract

Changes in carbohydrate components and crystalline structure of hemp bast fibers during organosolv pulping were investigated by X-ray diffractometry, FT-IR spectroscopy and high performance liquid chromatography (HPLC). The reasons for defibrillation and beating problems with organosolv hemp bast fiber pulp were investigated with reference to these properties of pulp samples. Hemp bast fibers and organosolv pulp samples had low hemicellulose contents and high cellulose contents. It was found that the disorder parameter of cellulose in hemp bast fibers was very low, when crystalline cellulose ratio was high and the crystalline structure of cellulose in hemp bast fibers was very stable. These properties affected defibrillation and beating of organosolv hemp bast fibers pulp negatively.

Keywords: Cellulose; Crystallinity; Pulping; Hemp; X-ray; FT-IR; HPLC

1. Introduction

Nonwood or agro-based fibers are a potential source of pulping material. However, these fibers have tremendous variations in chemical and physical properties compared to wood fibers. Hemp (*Cannabis sativa* L.) is a particularly interesting nonwood fiber material for pulping (Han, 1998). Hemp stems consist of about 65% woody core fibers and 35% bast fibers. The core fibers consist of 40–48% cellulose, 18–24% hemicellulose and 21–24% lignin. The bast fibers are 57–77% cellulose, 9–14% hemicellulose and 5–9% lignin. As the differences between these two fractions merit a separation into two separate materials, it is appropriate that research is carried out into this aspect (Capelle, 1996).

There are some disadvantages in the use of hemp woody core for pulping and papermaking (Krotov, 1995):

- The difficulty of delignification which is determined by the composition of the raw materials, i.e. there are high lignin contents in fiber cell walls and, in particular, the lignin content of hemp woody core approaches the lignin content in soft wood.
- Unbleached hemp woody core pulps produced using a conventional pulping process have lower yields and higher kappa number as compared to hardwood pulps.
- Pulps produced from hemp woody core fibers have small length fibres which are 2–3 times shorter than hardwood pulp fibers.
- Extremely low drainage rate of pulps produced from the hemp woody core fibers by conventional methods.
- Low papermaking and mechanical pulp properties of pulp produced from hemp woody core by conventional methods.
- Possible recovery problems due to higher ash content and silica compounds present in the ash.

When chemical and physical properties of hemp bast fibers and woody core were investigated in previous

* Corresponding author. Tel.: +90 462 377 34 99; fax: +90 462 32574 99.
E-mail address: gkaya@ktu.edu.tr (E. Gümüşkaya).

0960-8524/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2006.02.031

studies, it could be said that hemp bast fibers were appropriate for pulping and papermaking. There are two important problems for bast fibers during paper making: defibrillation and beating (Abel, 1980). Bast fibers are composed of numerous thick-walled cells with tapering ends that are joined principally by lignin and pectins (Van der Werf, 1994).

While hemp (*C. sativa* L.) woody core fiber length varies between 2 and 5 mm, bast fiber length varies between 5 and 55 mm (Han, 1998; Capelle, 1996).

Hemp bast fibers have some advantages for pulping as a wood alternative:

- Hemp is an annual fiber crop that could replace the need for wood used in manufacturing paper products, thereby reducing or eliminating the environmentally detrimental practice of deforestation.
- Hemp, as a nonwood fiber, is claimed to be easier to pulp and bleach, requiring less energy and chemicals.
- Quality hemp pulp could be produced without the use of environmentally dangerous chemicals such as sulfur and chlorine compounds (Johnson, 1999).

In this study, the reasons for beating and defibrillation difficulties with organosolv hemp bast fibers pulp were investigated. For this purpose, chemical and crystalline structures of organosolv hemp bast fibers pulp were examined by using standard test methods, X-ray diffractometry, FT-IR spectroscopy and high performance liquid chromatography (HPLC).

2. Methods

2.1. Pulping

Hemp (*C. sativa* L.) bast fibers used as raw material were taken from the Taskopru–Kastamonu region in the northern part of Turkey. Pulps were produced by using organosolv processes with different cooking times. Cooking trials were carried out in a batch type digester rotating 4 times per min with automatic temperature control. The hemp bast fibers charge (oven dry basis) was 500 g per batch. Pulp yields were determined based on the oven dry weight of hemp bast fibers initially loaded into the digester. The conditions selected for organosolv pulping were 40/60 ethanol/water ratio, 0.25% H_2SO_4, 180 °C cooking temperature and 5:1 liquor:raw material ratio as invariable parameters. Residence times were 90 min for pulp 1 sample, 120 min for pulp 2 sample and 150 min for pulp 3 sample.

2.2. Determination of chemical properties

Carbohydrate component contents, solubility experiments, yields and viscosities were determined for raw material and pulp samples following standard methods (TAPPI Test Methods (2002–2003); Scan Test Methods (1959–1973)):

Carbohydrates components	Standard methods
Holocellulose	Wise's chlorite method
Cellulose	Kurschner–Hoffner method
α-Cellulose	TAPPI T203 cm-99
Lignin	Klason method (TAPPI T22 om-02)
Others	
Viscosity	SCAN-C 15:62
Yield	SCAN-C 3:63

The Kappa number method was not used for determination of lignin content in organosolv pulp samples, because hemp bast fibers in pulp samples were not defibrillated during the experimental procedure. After that, it was decided to use the classical sulfuric acid method for lignin content, but hemp bast fibers in pulp samples were not hydrolyzed completely (TAPPI T211 om-88). For these reasons, hot water, acetone and 17% NaOH solubility experiments were applied to pulp samples for determination of lignin content as described by Yaşar (1999). In the last stage, the Klason lignin method was used. These experimental procedures were carried out according to TAPPI Test Methods (2002–2003).

2.3. X-ray diffraction method

Pulp samples obtained from three different pulping processes were analyzed by X-ray diffraction. All samples were ground in a Wiley mill and all powders were then passed through a 60 mesh screen prior to pressing. Pressing of sample powders was carried out under an axial force of about 7.5 tons for 30 s to fill a circular hole with diameter of 13 mm.

X-ray diffraction was performed with a Rigaku 3D/Max series diffractometer. The radiation was Ni-filtered CuK_α of wavelength 0.1542 nm. The X-ray unit operated at 40 kV and 30 mA. Angular scanning was conducted from 3° to 45° at 1°/min and data were collected using a 2-step scan mode with angular intervals of 0.05°. All experiments were repeated twice and duplicate X-ray analyses were performed.

2.4. Determination of crystallinity and crystallite size

Crystallinity of cellulose in pulp samples was calculated from diffraction intensity data using Ruland's method. This method was developed to take into account the diffuse scattering due to thermal vibrations and lattice imperfections in the crystalline part of a substance. The crystallinity (X_{cr}), according to Ruland's method, was calculated from the equation below (Balta-Calleja and Vonk, 1989; Ruland, 1961):