

Dependence of chemical and crystalline structure of alkali sulfite pulp on cooking temperature and time

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Abstract

This study investigates the change in chemical and crystalline structure of pulp samples during alkali sulfite process at different cooking temperatures and time. TAPPI and SCAN standard test methods and X-ray diffraction and FT-IR spectroscopy were used. It was shown that the crystalline structure of cellulose in hemp (*Cannabis sativa* L.) bast fibers was very strong and stable. Crystallinity of alkali sulfite pulp samples obtained from processing at 140 up to 180 °C increased, but then decreased at 200 °C. The crystallite size of cellulose in alkali sulfite pulp samples increased with cooking temperature. The crystalline allomorph of cellulose in alkali sulfite pulp samples obtained at 200 °C changed from monoclinic structure to triclinic structure. Crystalline structure of cellulose in alkali sulfite pulp samples was little affected by changing cooking time. It was concluded that cooking temperature during alkaline sulfite pulping process had more effect on carbohydrate components and crystalline structure of pulp samples than cooking time.

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1. Introduction

Cellulose is a water-insoluble polysaccharide whose mostly extended individual chains of β -1,4-glucosyl units are coalesced into arrays held together by Van der Waals forces and hydrogen bonds. These arrays, with varying degrees of crystalline perfection and lattice type, are responsible for many of the desirable properties of the polymer in nature. In cellulosic materials, these crystalline regions are generally dispersed in a random and continuous fashion throughout the fiber, and the degree of crystallinity is normally quantified by the so-called relative crystallinity index (CrI). Because different methods of measuring CrI yield different values for the same substrate, CrI values do not truly quantify the fraction of glucosyl units that are ordered into a crystalline array, nor do they provide

information on how crystallinity is distributed throughout the fibers. Nevertheless, CrI values are useful for rank-ordering the average crystallinity of different celluloses and for determining how crystallinity is affected by various physical and chemical treatments (Weimer, Hackney, & French, 1995).

The linear cellulose molecules are linked laterally by hydrogen bonds to form linear bundles, giving rise to a crystalline structure. The crystalline regions are interrupted every 60 nm with non-crystalline amorphous regions. Crystalline regions may contain occasional kinks or folds in the polymer chain, called defects. The type and the number of defects vary with the origin of cellulose. If amorphous domains of cellulose are degraded chemically there is an increase in the relative degree of crystallinity. At the same time, there is also the possibility that random cleavage of the cellulose occurs in the accessible chains within the crystalline domains. The chains at the outer portions of the crystallites can cleavage randomly and protrude from crystalline domain. The accessible chains can then be

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considered amorphous, since they are not part of the crystallite. A significant increase in the total amorphous character of the cellulose would decrease the relative degree of crystallinity (De Souza, Bouchard, Methot, Berry, & Argyropoulos, 2002; Fengel & Wegener, 1984; Gardner & Blackwell, 1974).

The mechanical strength of cellulosic materials is intrinsically related to the interactions between the cellulose molecules and an understanding of the molecular structure of cellulose is therefore extremely important (Hinterstoisser & Salmen, 1999). A lot of effort has been made to characterize the crystalline structure of native cellulose, mainly using X-ray diffraction technique, for a long time. Nevertheless, the detailed structure of cellulose has not been clarified as yet, and the reason for the difficulty has only recently been partly understood (Horii, 2001).

The purpose of this study was to examine systematically how carbohydrate components and lignin content in hemp bast fibers are affected by alkaline sulfite pulping process related to cooking temperature and time. A second purpose of the study was to determine how crystallinity, crystallite size, and crystalline allomorphs of cellulose in hemp bast fibers are changed during alkali sulfite pulping process obtained at different cooking temperatures and time by using X-ray diffractometer and FT-IR spectroscopy methods.

2. Experimental

2.1. Material

Hemp (*Cannabis sativa* L.) bast fibers were used as raw material. These were obtained from the Taskopru-Kastamonu region of Northern Turkey. The alkali sulfite process was used at different cooking temperatures and times to produce the pulp samples. Cooking trials were made in a batch type digester rotating four times per min with automatic temperature control. Hemp bast fibers' charge (grams oven dry basis) was 500 g for each cook. Pulp yields were determined based on the oven dry weight of hemp bast fibers initially loaded into the digester. The conditions of alkali sulfite pulping are given in Table 1. When the cooking temperature was selected as a variable factor, the cooking time was 90 min. When cooking time was the variable, the cooking temperature used was 180 °C.

Table 1
Alkali sulfite pulping conditions

Cooking parameters	
Na ₂ SO ₃ (%)	14
NaOH (%)	3.5
Na ₂ SO ₃ /NaOH	4/1
Liquor/raw material	5/1
Temperature ^a (°C)	140, 160, 180, 200
Time ^a (min)	60, 90, 120, 150

^a Cooking temperature and time was selected as variable factors.

2.2. Determination of chemical properties

Carbohydrate components, solubility experiments, yields, and viscosity were done on raw material and pulp samples using the following standard methods (Scan Test Methods; TAPPI Standards, 1992):

Carbohydrates components	Standard methods
Holocellulose	Wise's chlorite method
Cellulose	Kurschner–Hoffner method
α-Cellulose	TAPPI T203 cm-99
Lignin	TAPPI T211 om-88
<i>Others</i>	
Viscosity	SCAN-C 15:62
Yield	SCAN-C 3:63

Kappa number method was used for the determination of the lignin content in alkali sulfite pulp samples, but hemp bast fibers in pulp samples were not defibrillated during the experimental procedure. In this contact, the kappa number method was not used. Because of this, the classical sulfuric acid method for lignin content was used, but hemp bast fibers in pulp samples were not hydrolyzed completely, according to the classical sulfuric acid method (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 based on S. Yaşar's Ph.D. thesis, respectively (Yaşar, 1999). Finally, the Klason lignin method was used.

2.3. X-ray diffraction method

Pulp samples, which were obtained from alkali sulfite pulping processes at different cooking temperatures and time, were used for X-ray diffractometer analysis. All samples were ground in a Wiley mill and all powders were then screened by 60 mesh prior to pressing. Pressing of sample powders was carried out under axial force about 7.5 tons for 30 s to fill a circular hole with diameter of 13 mm.

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

2.3.1. Determination of crystallinity and crystallite size

Crystallinity of cellulose in alkali sulfite pulp samples was calculated from diffraction intensity data using two different methods. The first one is Ruland's method. This method was developed to take into account the diffuse scattering due to thermal vibrations and lattice imperfections in crystalline part of a substance. The crystallinity (X_{cr}), according to Ruland's method, was calculated by the

following equation (Balta-Calleja & Vonk, 1989; Ruland, 1961).

$$X_{\text{cr}} = X_{\text{cr}}^I \times k, \quad (1)$$

$$X_{\text{cr}} = \frac{\int_0^\infty s^2 I_c(s) ds}{\int_0^\infty s^2 I(s) ds} \times \frac{\int_0^\infty s^2 \overline{f^2} ds}{\int_0^\infty s^2 \overline{f^2} D ds}, \quad (2)$$

where X_{cr} is the crystallinity index, $s = 2 \sin \theta / \lambda$, θ is the angle between the atomic plane and both incident and reflected beams, λ is the wavelength of X-rays, $I_c(s)$ and $I(s)$ are the coherent scattering intensities at s in the crystalline and total region, respectively, $\overline{f^2}$ is the mean squared amplitude of the atomic scattering factor ($\overline{f^2} = \sum N_i f_i^2 / \sum N_i$), N_i and f_i are the number of atoms of type i and the atomic scattering factor, respectively, and D is the disorder function (Vonk, 1973).

D is expressed as follows:

$$D = \exp(-ks^2), \quad (3)$$

$$k = k_r + k_1 + k_2, \quad (4)$$

where k express the disorder parameter, k_r is the thermal motion, and k_1 and k_2 are the lattice imperfections of the first and second kinds.

The second approach was the empirical method proposed by Segal, Creely, Martin, and Conrad (1959) for native cellulose:

$$\text{CrI} = [(I_{002} - I_{\text{Amorph}}) / I_{002}] \times 100, \quad (5)$$

where CrI is the crystalline index, I_{002} is the maximum intensity of the (002) lattice diffraction, and I_{Amorph} is the intensity diffraction at 18° 2θ degrees (Gümüşkaya, Usta, & Kırıcı, 2003).

The average size of crystallite was calculated from the Scherrer equation method. This method is based on the width of the diffraction patterns occurred in the X-ray reflected crystalline region. In this study, the crystallite sizes of the pulp samples were determined by using the diffraction pattern obtained from the 101, 10–1, 002, and 040 lattice planes (Ahtee, Hattula, Mangs, & Paakkari, 1988).

$$D_{(\text{hkl})} = \frac{k\lambda}{B_{(\text{hkl})} \cos \theta}, \quad (6)$$

where $D_{(\text{hkl})}$ is the size of crystallite, k is the Scherrer constant (0.84), λ is the X-ray wavelength, $B_{(\text{hkl})}$ is the FWHM (full width half maximum) of the reflection hkl measured in 2θ is corresponding to Bragg angle.

2.4. FT-IR spectroscopy

The carbohydrate components of hemp bast fibers and alkali sulfite pulp samples were used for FT-IR spectroscopy measurement. The dried samples were embedded in KBr pellets and were analyzed by using a Perkin-Elmer Spectrum One FT-IR spectroscopy Model 2000. They were recorded in the absorption mode in the range 4000–400 cm^{-1} with an accumulation of 32 scans, resolution of 2 cm^{-1} , and normalized C–O–C band at 2900 cm^{-1} .

3. Results and discussion

3.1. Chemical properties of samples

The chemical compositions for hemp (*C. sativa* L.) bast fiber were determined by using TAPPI and SCAN test methods in this study. The carbohydrate content of hemp bast fibers were found to be higher than those of wood species and some annual plants used in pulp and paper industry, and the lignin content was lower, as can be seen in Table 2. In particular, the α -cellulose content for hemp bast fibers was much higher, compared to wood species (Fengel & Wegener, 1984).

The neutral and alkali sulfite pulping process offers many advantages compared to the Kraft process. Some of them are higher pulping yield, higher brightness of unbleached pulp, and easier to bleach high brightness (less bleaching stages). Many papermaking properties of them are exceptionally good despite the high yield (Tikka, Tulpala, & Virkola, 1982). The pulps have higher viscosity and bleach much more readily to higher brightness and strength than Kraft pulps (Ingruber, Stradal, & Histed, 1982). Alkali sulfite pulping system is created which combines the benefits of both Kraft and sulfite pulping, in particular the universal applicability of the Kraft process and Kraft-like strength properties with the easy bleachability of sulfite pulps (Kordsachia & Patt, 1991).

Yield, viscosity, and carbohydrate components of alkali sulfite pulp samples depending on cooking temperature were reported in Table 3. As can be seen in Table 3, it was found that yield and viscosity for alkali sulfite pulp samples decreased, when carbohydrate components increased in rising cooking temperature. It was determined that α -cellulose ratio in pulp samples obtained from alkali sulfite process at 200 $^\circ\text{C}$ closed to cellulose content.

When the lignin content was determined in pulp samples, hot water solubility, acetone solubility, and NaOH 17% solubility fulfilled on samples, respectively. At last, Klason method carried out the determination of lignin content based on Yaşar (1999). The values in Table 4 show the effects of cooking temperature on solubilities and lignin content of alkali sulfite pulp samples. As can be seen in

Table 2
Chemical components of hemp bast fiber as raw material

Chemical components in hemp bast fibers	Content (%)
<i>Main cell wall components</i>	
Holocellulose	86.93
Cellulose	71.41
Lignin	6.59
α -Cellulose	63.77
<i>Solubility</i>	
Cold water solubility	7.75
Hot water solubility	9.06
NaOH 1% solubility	29.55
Alcohol–benzene solubility	4.23

Table 3
Chemical components of alkali sulfite pulp samples obtained from different cooking temperatures

Cooking temperature (°C)	Yield (%)	Viscosity (cm ³ /g)	DP	Holocellulose (%)	Cellulose (%)	α -Cellulose (%)	NaOH %1 Sol. (%)
140	74.90	2204	3599	90.07	85.37	79.49	3.75
160	66.86	2049	3320	90.16	86.21	82.85	3.37
180	64.59	1696	2695	93.52	89.30	85.60	2.95
200	59.33	1258	1937	96.53	89.96	89.27	2.67

Table 4
Solubility and lignin content of alkali sulfite pulp samples obtained from different cooking temperatures

Cooking temperature (°C)	Hot water solubility (%)	Acetone solubility (%)		NaOH %17 solubility (%)		Lignin (%)
	I. step	II. step	Start ^a	III. step	Start ^a	
140	2.65	4.12	6.65	13.50	19.54	4.26
160	2.09	3.99	6.53	12.65	18.19	3.84
180	1.87	3.70	5.51	12.25	16.53	2.89
200	1.47	3.24	4.66	11.86	16.35	2.48

^a Solubility was calculated according to beginning sample weight (g).

Table 4, it was established that lignin content in alkaline sulfite pulp samples decreased with increasing cooking temperature.

An alternative to Kraft pulping, sulfite pulping, is somewhat older as a technical process and gives brighter and more easily bleached pulps. Pulping is carried out in an acidic solution containing sulfur dioxide and either calcium, sodium or magnesium ions at temperature in the range of 120–150 °C for 6–9 h. The sulfite process is more sensitive to wood species and the resulting fibers are somewhat weaker than those from the Kraft process. For special purposes, sulfite pulping of hardwood at a neutral or slightly alkaline pH is carried out. That process results in a high yield sulfite pulp used for making corrugated medium board (Gelerstedt, 2001).

In alkali sulfite cooking (cooking liquor mainly composed of NaOH and Na₂SO₃, cold pH 10–13.5), the active chemical charge strongly affected the rate of delignification. The use of anthraquinone in alkali sulfite cooking reduced the active chemical charge by 15–30%, but the heat consumption was still greater than in Kraft cooking. Alkali sulfite–anthraquinone cooking yield and the papermaking properties were equal to the Kraft pulping process (Kettunen, Virkola, & Yrjälä, 1979).

Yields, viscosity, and carbohydrate components of alkali sulfite pulp samples depending on cooking time are given in Table 5. When yields and viscosity of pulp samples decreased by extending cooking time, it was determined

Table 5
Chemical components of alkali sulfite pulp samples obtained from different cooking time

Cooking time (min)	Yield (%)	Viscosity (cm ³ /g)	DP	Holocellulose (%)	Cellulose (%)	α -Cellulose (%)	NaOH %1 Sol. (%)
60	64.84	1894	3044	93.28	91.21	84.32	4.55
90	64.59	1696	2695	93.52	89.30	85.60	2.95
120	64.08	1568	2471	94.04	89.11	84.72	3.40
150	61.95	1360	2111	94.83	88.71	87.92	3.04

that carbohydrate components increased in pulp samples. As can be seen in Table 5, it was determined that the α -cellulose content in alkali sulfite pulp samples become close to the total cellulose content.

Solubility values and lignin contents of alkali sulfite pulp samples depend on cooking time as shown in Table 6. Hot water, acetone, and NaOH 17% solubility values and lignin contents of pulp samples decreased by extending cooking time from 60 to 150 min.

3.2. X-ray measurements

Cellulosic materials from various sources and treatments differ considerably in their degree of crystallinity, as evidenced by a large number of investigative methods. Since the superstructure of cellulose (i.e., hydrogen-bonding system) has important consequences for the pulping, purification, and papermaking process, as well as for the cellulose reactivity in the end use, this part of the review will focus on it at some length (Awadel-Karim, Nazhad, & Pazner, 1999).

In this study, crystalline properties of carbohydrate components of hemp bast fibers as raw material were investigated and reported in Table 7. It was determined that crystallinity and disorder parameter of cellulose in hemp bast fiber were 51.0% and 0.8, respectively. As can be seen in Table 7, it was determined that crystallinity and disorder parameter of α -cellulose content in hemp bast fibers increased with chemical treatments, compared to those of holocellulose content according to Ruland's method. Disorder parameter in Ruland's method is an important factor in crystallinity determination. Disorder parameter of α -cellulose was higher than that of holocellulose. Some workers concluded that decrystallization of cellulose and crystallization of amorphous glucan can occur concurrently during chemical treatments (Evans, Newman, Roick, Suckling, & Wallis, 1995). However, crystallinity of α -cellulose according to the Segal method decreased, compared to that of holocellulose. When the crystallite size of cellulose and holocellulose was found to be 4.9 and 4.1 nm, respectively,

Table 6
Solubility and lignin content of alkali sulfite pulp samples obtained from different cooking time

Cooking time (min)	Hot water solubility (%)	Acetone solubility (%)		NaOH %17 solubility (%)		Lignin (%)
	I. step	II. step	Start ^a	III. step	Start ^a	
60	1.87	4.87	5.71	13.30	18.44	3.42
90	1.87	3.70	5.51	12.25	16.53	2.89
120	1.36	3.26	5.67	12.08	16.47	2.76
150	1.23	2.99	4.19	11.39	15.97	2.68

^a Solubility was calculated according to beginning sample weight (g).

that of α -cellulose was determined as 7.3 nm. Increase in the crystallite size of α -cellulose resulted from swelling of the cellulose fiber with alkali treatment of holocellulose (Nishimura & Sarko, 1987a, 1987b).

In a previous study, it was determined that crystallinity and crystallite size of cellulose in hemp were 59% and 4.3 nm, respectively (Focher et al., 2001). Gümüşkaya et al. (2003) reported that the crystallinity and disorder parameter of cellulose in cotton linters without chemical treatments were found to be 57.9% and 2.2, respectively, according to Ruland's method. The crystallinity index of cotton linters, according to Segal method, was calculated as 52.4%. Crystallite size of cellulose in cotton linter was found as 6.1 nm. Gümüşkaya and Usta (2001) have also reported that the crystallinity and disorder parameter of cellulose in wheat straw, according to Ruland's method, were 55.67% and 2.47, respectively. Crystallite size of cellulose in wheat straw was calculated as 6.4 nm.

There is a general agreement that native cellulose is a composite of two distinct crystalline modifications, namely I_α and I_β , whose fractions vary depending on the origin of the cellulose sample. The I_α and I_β structures assigned to one-chain triclinic, and two-chain monoclinic cells, respectively. The two crystalline domains are known to coexist in a single microfibril, but their localization is still under discussion (Imai & Sugiyama, 1998; Wada & Okano, 2001). The I_β phase is considered to be more stable than the I_α phase, because I_α phase transforms into I_β after hydrothermal treatment. Most of the I_α phase could be converted into I_β under an atmosphere of helium. This suggests that the important factor is temperature and not the existence of water for the transformation between cellulosic polymers (Wada, 2001).

In this study, z -Discriminate function developed by Wada and Okano (2001) for distinction of crystalline

structure (monoclinic and triclinic) of cellulose in carbohydrate components of hemp bast fibers and pulp samples was used. z -Discriminate function was built up separating cellulose I_α and I_β by using d -spaces obtained from X-ray analyses by Wada, Sugiyama, and Okano (1993). D -spaces of carbohydrate components of hemp bast fibers and pulp samples obtained from X-ray analyses were used in z -Discriminate function. This procedure is as follows: $z = [1693 \times d_1 \text{ (nm)}] - [902 \times d_2 \text{ (nm)}] - 542$. Where $z > 0$ indicates the algal-bacterial type (I_α -rich) and $z < 0$ indicates the cotton-ramie type (I_β -dominant) (Wada & Okano, 2001; Wada, Sugiyama, & Okano, 2001).

As can be seen in Table 8, all crystalline structures for the carbohydrate components of hemp bast fibers were found to as monoclinic and this structure was not affected by chemical isolation.

When the disorder parameters (k) of carbohydrate components of hemp bast fibers were lower than other raw material used in the pulp and paper industry, it was found that the crystallinity was higher. According to these results, it could be said that the crystalline structure of carbohydrate components in hemp bast fibers was more pure and stable than those of wood species and annual plants used in the pulp and paper industries.

The increased demand for optimized fiber utilization in chemical pulping operations requires an in-depth understanding of the fiber material down to the ultrastructural level. The relationship between structural parameters such as cellulose crystallinity and the physical properties of pulp fibers is one aspect that has not been fully explored (Akerholm, Hinterstoisner, & Salmen, 2004).

It was determined that crystallinity of cellulose in alkali sulfite pulp samples according to Ruland's method increased in rising cooking temperature, as shown in Table 9. The crystallinity index of cellulose in pulp samples determined by Segal method increased until 180 °C and decreased at 200 °C. The crystallite size of cellulose in

Table 8
Crystalline structure properties of carbohydrate components of hemp bast fibers

Sample	d_1	d_2	z	Crystalline structure	β (°)
Raw material	0.60207	0.53844	−15.37	I_β	83.22
Holocellulose	0.59608	0.54336	−29.95	I_β	83.37
Cellulose	0.59211	0.52730	−22.18	I_β	84.70
α -Cellulose	0.59409	0.53202	−23.09	I_β	83.67

Table 7
Crystallinity and crystallite size of carbohydrate components of hemp bast fibers

Carbohydrate components	Crystallinity (%)		Crystalline index (%)	d -space (nm) (002)	Crystallite size (nm) (002)
	X_{cr}	k			
Raw material	39.6	0.3	76.97	0.39398	4.1
Holocellulose	47.6	0.5	89.19	0.39226	4.9
Cellulose	51.0	0.8	85.66	0.39746	4.5
α -Cellulose	53.6	1.3	83.24	0.40921	7.3

Table 9
Crystallinity and crystallite size of raw material and pulp samples

Cooking temperature (°C)	Crystallinity (%)		Crystalline index (%)	d-space (nm) (002)	Crystallite size (nm) (002)
	X_{cr}	k			
140	47.7	0.6	82.96	0.39141	5.4
160	51.9	0.8	84.75	0.39383	5.3
180	53.4	0.6	89.26	0.39056	7.1
200	54.6	0.6	80.22	0.40280	7.6

alkali sulfite pulp samples increased with cooking temperature from 5.4 to 7.6 nm. It was determined that cellulose I_β (monoclinic) was converted to cellulose I_α (triclinic) at 200 °C by using the z -discriminate function. The changes in crystalline structure of cellulose in alkali sulfite pulp samples are given in Table 10.

Several workers have investigated the changes in cellulose crystallinity during Kraft and other alkaline pulping processes (Hattula, 1986; Sashilov, Evstigneev, Shalimova, & Zacharov, 1986; Stewart & Foster, 1976). In all cases, the proportion of crystalline cellulose was higher in pulp than in the raw material, due to removal of the lignin and hemicelluloses during pulping (Evans et al., 1995).

Some authors have noted that cellulose undergoes changes in crystallinity upon chemical or physical treatments, particularly heating. It was reported that cotton linters underwent moderate increases in crystallinity upon mere exposure to humid atmospheres. It was demonstrated that a suspension of cellulose in water and subsequent drying resulted in variable increases in relative crystallinity index that were more dramatic at lower initial relative crystallinity index values. It was reported that, in aqueous media at relatively high temperatures (130–190 °C), extensive recrystallization was observed for both cello dextrans (to form cellulose II lattices) and high DP celluloses (to form cellulose IV). More recently, some workers have also reported that amorphous cellulose subjected to hydrothermal treatment at temperatures above 100 °C

showed decreased DP and moderate recrystallization to cellulose IV. Several workers have also noted increases in crystallinity of lignocellulosic biomass materials upon treatment with alkali, steam, and acid chlorite (Weimer et al., 1995).

It was found that the crystallinity of cellulose in alkali sulfite pulp samples measured according to Ruland's method increased with cooking temperature, as shown in Table 11. However, crystallinity of cellulose in alkali sulfite pulp samples measured according to Segal method increased up to 120 min (cooking time). After that, it decreased at 150 min (cooking time). Crystallite size of cellulose in alkali sulfite pulp samples was found to be as 7.1 nm at 90 min (cooking time). It was determined that I_β (monoclinic) in crystalline structure of cellulose in alkali sulfite pulp samples was dominant at all cooking times, as shown in Table 12.

Awadel-Karim et al. (1999) reported that the time factor was shown to have a lesser affect on the crystallinity index after the initial solvent purification treatment when other parameters were kept constant (i.e., temperature, solvent composition, liquor to solid ratio, and acidity). The slight increase in crystallinity index and considerable decrease in crystallite size were found with increasing reaction time.

3.3. FT-IR measurements

FT-IR spectroscopy has been extensively used in cellulose research, since it presents a relatively easy method of

Table 10
Crystalline structure properties of pulp samples

Cooking temperature (°C)	d_1	d_2	z	Crystalline structure	β (°)
140	0.60212	0.55348	−29.03	I_β	85.37
160	0.60083	0.55177	−29.48	I_β	83.69
180	0.59608	0.54838	−34.48	I_β	85.54
200	0.62104	0.52575	28.19	$I_\alpha + I_\beta$	83.67

Table 12
Crystalline structure properties of raw material and pulp samples

Cooking time (min)	d_1	d_2	z	Crystalline structure	β (°)
60	0.60830	0.54171	−7.77	I_β	83.39
90	0.59608	0.54838	−34.48	I_β	85.54
120	0.59608	0.54502	−31.45	I_β	84.86
150	0.59608	0.53361	−21.16	I_β	83.67

Table 11
Crystallinity and crystallite size of raw material and pulp samples

Cooking time (min)	Crystallinity(%)		Crystalline index (%)	d-space (nm) (002)	Crystallite size (nm) (002)
	X_{cr}	k			
60	42.4	1.0	86.07	0.39226	5.6
90	53.4	0.6	88.76	0.39056	7.1
120	39.7	1.4	87.75	0.38971	5.4
150	45.9	1.5	84.25	0.39141	5.8

obtaining direct information on chemical changes that occur during various chemical treatments (Sun, Sun, Zhao, & Sun, 2004). IR spectroscopy has been also employed to determine the degree of crystallinity and crystalline modification of cellulose obtained from various origins (Evans et al., 1995).

The IR ratio A_{1370}/A_{670} was used by Richter, Krause, and Schempp (1991) to determine relative crystallinity index. It also was used to study the conversion of cellulose I into cellulose II during chemical treatments (Akerholm et al., 2004).

In this study, A_{1370}/A_{670} ratios were found to be 8.8 for holocellulose, 8.1 for cellulose, and 7.6 for α -cellulose. According to these results, it can be said that IR crystallinity index decreased by applying alkali treatment to holocellulose content of hemp bast fibers for α -cellulose isolation. Oh, Yoo, Shin, and Seo (2005) reported that the absorbance ratio of the bands at ~ 1430 and 900 cm^{-1} (A_{1430}/A_{900}), regarded as the crystallinity index, decreased with increasing NaOH concentration.

As can be seen in Fig. 1, IR crystallinity of cellulose in alkali sulfite pulp samples increased until 180°C , but it decreased at 200°C . IR crystallinity of cellulose in alkali sulfite pulp samples increased by extending cooking time from 60 to 90 min, clearly. It did not change between 90 and 150 min, evidently.

We investigated how the crystalline allomorphs of cellulose in alkaline sulfite pulp samples changed depend on cooking temperature and time by using FT-IR spectroscopy. I_α and I_β may have a different H-bonding pattern since their FT-IR spectra are not identical in the OH stretching region (Wada et al., 1993). Several workers reported that bands at 750 and 710 cm^{-1} were assigned to I_α and I_β phases, respectively (Hinterstoisser & Salmen, 1999; Sassi, Tekely, & Chanzy, 2000; Wada & Okano, 2001).

In this study, crystalline allomorphs was found as I_β (monoclinic) in carbohydrate components of hemp bast fibers. It was found that cooking time did not affect crystalline allomorphs at 180°C (cooking time). As can be seen in Fig. 2, cooking temperature at 200°C affected crystalline allomorphs and monoclinic structure was converted to triclinic structure. Monoclinic structure did not change at 140 , 160 , and 180°C .

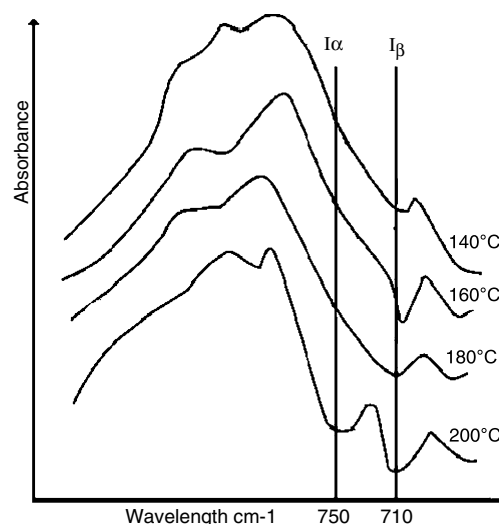


Fig. 2. FT-IR spectra of alkali sulfite pulp samples obtained from different cooking temperatures.

Roundeau-Mouro et al. (2003) reported that the percentage of I_β allomorph was estimated by $\%I_\beta = A_{710}/(A_{710} + A_{750})$ with A_{710} and A_{750} being the integrated absorbance at about 710 and 750 cm^{-1} . According to this formula, I_α / I_β was calculated as $62/38$ in alkaline sulfite pulp samples obtained by processing at 200°C .

4. Conclusion

It was concluded that hemp (*C. sativa* L.) bast fibers had high crystalline cellulose. Crystalline structure of cellulose in hemp bast fibers was very strong and stable. Crystallinity of cellulose in hemp bast fibers increased on chemical treatments for isolation of carbohydrate components and alkaline sulfite pulping process, but the crystalline allomorphs did not change. Monoclinic structure was converted to triclinic structure in alkaline sulfite pulp samples obtained from cooking temperature at 200°C . Crystallinity of cellulose in alkali sulfite pulp samples obtained from 140 up to 180°C increased, but it decreased at 200°C . When cooking time was extended in pulping, crystallinity of cellulose in alkali sulfite pulp samples obtained from 60 up to 120 min increased and then it decreased at 150 min.

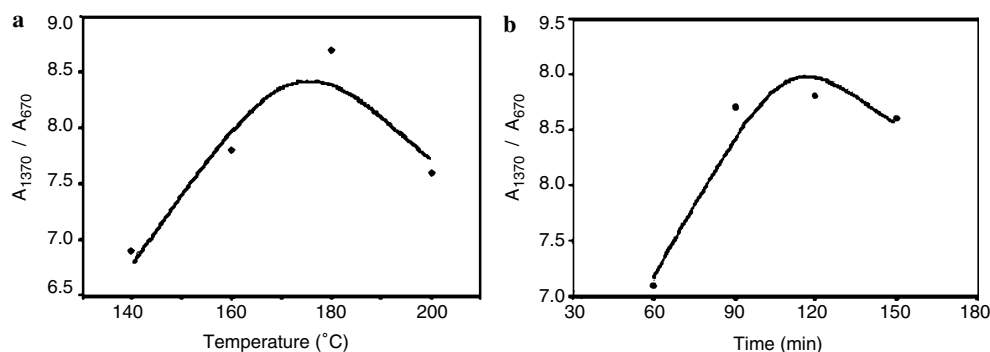


Fig. 1. Dependence of IR crystallinity of cellulose during alkali sulfite pulping on cooking temperature (a) and time (b).

It was concluded that cooking temperature during alkaline sulfite pulping process had more effect on carbohydrate components and crystalline structure of pulp samples than cooking time.

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