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Crystalline Structure Properties of Bleached and Unbleached Wheat Straw (*Triticum Aestivum* L.) Soda-Oxygen Pulp

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Abstract: In this study, the crystallinity index and crystallite size of wheat straw powder, soda-oxygen pulp and soda oxygen pulp bleached with hypochlorite (H) and hypochlorite and peroxide (HP) sequences were determined using an x-ray diffractometer method. The crystallinity indexes of these pulp samples were found to be 45.61%, 52.00%, 52.60% and 54.11%, respectively. The crystallite sizes of these pulp samples were also determined and were 6.4 nm, 3.4 nm, 4.3 nm and 4.6 nm, respectively. On the other hand, the crystallinity index and crystallite size of holocellulose, cellulose and alpha-cellulose in wheat straw were then found to be 65.00%, 55.20% and 46.40%, and 6.1 nm, 3.7 nm and 9.1 nm, respectively. Consequently, the crystallinity index and crystallite size in pulp increase with respect to the removal of the lignin and hemicelluloses in pulp. However, the results obtained are not consistent, because the chemical agents used in the removal of the lignin and hemicelluloses may cause hydrolysis and swelling of the cellulose with a contaminant reduction in crystallinity.

Key Words: Cellulose, crystallinity index, crystallite size, pulp, wheat straw, x-ray

Buğday Sapı (*Triticum Aestivum* L.) Soda-Oksijen Kağıt Hamurunun Kristal Yapı Özellikleri

Özet: Buğday sapı (*Triticum aestivum* L.) , soda-oksijen kağıt hamuru, hipoklorit (H) ve peroksitle (HP) kademeli ağartılmış kağıt hamurlarının kristallik dereceleri ve kristallit genişlikleri x-ışını difraktometre yöntemi kullanılarak belirlenmiştir. Bu örneklerin kristallik dereceleri sırasıyla %45.61, %52.00, %52.60 ve %54.11 olarak tespit edilmiştir. Bu örneklerin kristalit genişlikleri ise yine sırasıyla 6.4 nm, 3.4 nm, 4.3 nm ve 4.6 nm olarak bulunmuştur. Diğer yandan buğday sapı bünyesinde değişen oranlarda bulunan holoselülozun, selülozun ve alfa selülozun aynı özellikleri incelenmiş olup; kristallik dereceleri sırasıyla %65.00, %55.20 ve %46.40 olarak belirlenmiştir. Kristalit genişlikleri ise 6.1 nm, 3.7 nm, ve 9.1 nm olarak hesaplanmıştır. Sonuç olarak ; kağıt hamuru üretimi sürecinde buğday sapı yapısındaki lignin ve hemiselülozlar gibi amorf yapıdaki bileşenlerin uzaklaşmasına bağlı olarak kristallik derecelerinin arttığı görülmüştür. Ancak lignin ve hemiselülozların uzaklaştırılmasında kullanılan kimyasalların selülozun şişmesine ve hidrolizine neden olarak kristal yapı özelliklerini değiştirdiği yapılan çalışma sırasında ortaya konmuştur.

Anahtar Sözcükler: Selüloz, kristallik derecesi, kristalit genişliği, kağıt hamuru, buğday sapı, x-ışını

Introduction

The main chemical constituents of the cell wall in wood fibre are cellulose, hemicelluloses and lignin. Hemicelluloses and lignin are amorphous substances, whereas cellulose has crystalline and amorphous regions (Fengel and Wegener, 1984). The increasing of crystalline regions increases the rigidity of cellulose but decreases the elasticity of polymeric substances. In addition, the ratio of the crystalline region to the amorphous region in a cellulose structure affects the accessibility of cellulose molecules (Tripp, 1971).

The ratio of crystalline regions in the structure of cellulose to the amorphous region, crystalline length, lattice distortions in unit cell, and conformity of crystallinity of cellulose have been determined using different techniques such as x-ray diffraction, IR and NMR spectroscopy.

The crystallinity index of the hot-disintegrated thermomechanical pulp fibres and separated cell wall layers M+P+S1 and S2+S3 were found to be 33.19% and 38% respectively by using the x-ray diffraction method (Ahtee et al., 1988). Several researchers have investigated changes in the crystallinity index of cellulose during kraft and other alkaline pulping processes. In all cases, the proportion of crystalline cellulose was found to be higher in the pulp than in the starting wood, due to removal of the lignin and hemicelluloses during pulping. On the other hand, according to further experiments, decrystallisation of cellulose crystallites and crystallisation of amorphous glucan occurred concurrently during

pulping (Stewart and Foster, 1976). However, at kraft pulping yielding below 57%, the crystallinity index dropped due to the formation the of physically damaged cellulose (Evans et al., 1995).

The crystallinity index of cellulose in the compression wood, normal wood and opposite wood of Pinus densiflora were found to be 45-50%, 50% and 50-60%, respectively using the x-ray diffraction method (Tanaka and Koshijima, 1981). Awadel-Karim et al. (1999) carried out an x-ray diffraction analysis on the factors affecting the crystalline structure of cellulose during solvent purification treatment. Their x-ray results of the influence of acetone on cellulose indicated that the crystallinity index of solvent treated cotton cellulose showed a trend of a small gradual increase with the progressive increase of acetone concentration in the treatment, and the crystallite size of the cellulose was found to decrease with the increase of acetone content in the solvent composition.

Vozár (1998) used x-ray diffraction to determine the crystallinity index in holocellulose and cellulose in six hardwood species: aspen, lime tree, birch, beech, maple, and hornbeam. He found that the portion of crystalline phase of holocellulose in all the species is lower than cellulose in those species. In other study, the crystallinity index in cotton, mercerized cotton, pulp produced from wood, and regenerated cotton was found to be 73%, 51%, 60% and 35%, respectively (Eklund and Lindström, 1991).

In this study, changes in the crystalline structure of bleached and unbleached wheat straw pulps are investigated. In addition, the crystallinity index and crystallite size of holocellulose, cellulose and alpha-cellulose in wheat straw are determined using the x-ray diffractometer method.

Materials and Methods

Materials

Wheat straw, taken from the Konya region in Turkey, was used for pulping. Pulp was produced by the soda-oxygen pulping process. Wheat straw soda-oxygen pulp was bleached with hypochlorite (H) and, hypochlorite and hydrogen peroxide (HP) sequences. These conditions of pulping from wheat straw and bleaching of pulps obtained are as follows:

PULPING

Alkali charge:	16%
Temperature:	120 ºC
Time:	30 min
Liquor/raw mat.:	5/1
Oxygen pressure:	7 kg/cm^2

HYPOCHLORITE BLEACHING (H)

Concentration:	10%
Active chlorine:	1.5-2%
Time:	60 min
Temperature:	38 ºC
Effective chlorine:	226.94 g/l
Boric acid:	3.1 g/l
KCl:	3.7 g/l
NaOH:	0.8 g/l

PEROXIDE BLEACHING (P)

Concentration:	16%
Time:	60 min
Temperature:	70 ºC
H_2O_2 ratio:	25%
NaOH ratio:	3.0%
$MgSO_4$ ratio:	0.5%
$NaSO_3$ ratio:	3.0%

Methods

Chemical Analyses

The holocellulose and cellulose contents of wheat straw were determined according to Wise's chlorite and Kürschner-Hoffner nitric acid method, respectively. Standard methods of Tappi T 203 OS 71 and Tappi T 13 m-54 were used in the determination of the alpha-cellulose and lignin ratio of wheat straw. The viscosity and kappa number of pulp was then examined according to SCAN-CM 15:88 and SCAN C1:59 standard method, respectively.

Preparation of Samples for X-Ray Diffraction Analysis

In this study, special attention was given to preparation of the powder samples for x-ray intensity measurement. Pulp samples which were bleached and unbleached, and holocellulose, cellulose and alpha-cellulose samples obtained from wheat straw, were used for x-ray analysis. All the samples were ground in a Wiley mill and the powders obtained, were then screened passing thorough 40 mesh retained on 60 mesh. The procedure followed was that of Evans et al. (1995). The pressing of sample powders was carried out under axial force of about 5 tons to fill a circular hole with a diameter of 13 mm. In this way, the total intensity scattered by the samples should be approximately the same as the background intensity at high scattering angle.

X-ray Diffraction Method

The crystallinity index, crystallite size, and lattice distortions in unit cells were evaluated by they x-ray diffraction method. X-ray diffraction were recorded with a Rigaku 3D/Max series diffractometer provided with an automatic data processor. The radiation used was CuKα of wavelength 0.1542 nm. The x-ray unit was operated at 40 kV and 30 mA. The position of slits was chosen as 1°, 1° and 0.15°. Angular scanning was continued 3° to 50° at 10/min and data were collected using a 2-step scan mode with angular intervals of 0.05°.

Determination of the Crystallinity Index

The crystallinity indexes of our samples were determined by Ruland's method. This method was developed to take into account diffuse scattering due to thermal vibrations and lattice imperfections in the crystalline part of a substance. The crystalline properties in cellulose were calculated by the equation below (Balta-Calleja and Vonk, 1989).

$$X_{cr} = X_{cr}^{1} \times K$$

$$X_{cr} = \frac{\int_0^\infty s_2 I_c(s) ds}{\int_0^\infty s^2 I(s) ds} \times \frac{\int_0^\infty s^2 \bar{f}^2 ds}{\int_0^\infty s^2 \bar{f}^2 D ds}$$

where Xcr is the crystallinity index, $s = 2\sin\theta/\lambda$, θ, q the angle between the atomic plane and both incident and reflected beams, λ the wavelength of x-rays, Ic(s) and I(s) the coherent scattering intensities at s in the crystalline and total region, respectively, $\bar{f}^2$ the mean squared amplitude of the atomic scattering factor ($\bar{f}^2 = \Sigma N_i f_i^2 / \Sigma N_i$), Ni and the number of atoms of type i and the atomic scattering factor, respectively, and D the disorder function (Ruland, 1960).

D is expressed as follows:

$$D = \exp(-ks^2)$$

$$k = k_r + k_1 + k_2$$

where k express the disorder parameter, k_r the thermal motion, and k_1 and k_2 the lattice imperfections of the first and second kinds (Vonk, 1973). While the crystalline region in the samples was separated from the total diffractogram region, birch xylan was used as an amorphous standard.

Determination of Crystallite Size

The average size of crystallite was calculated from the Scherrer equation. The Scherrer equation is a method based on the width of the diffraction patterns occurring in the x-ray reflected crystalline region. In this study, the size of crystallites were determined by using the diffraction pattern obtained from (002) of pulp samples.

$$L_{(hkl)} = \frac{k\lambda}{B_{(hkl)} \cos\theta}$$

where $L_{(002)}$ is the size of crystallite , k is the Scherrer constant (0.84), λ is x-ray wavelength, and $B_{(hkl)}$ is the full width half maximum (FWHM) of the reflection hkl measured in 2θ and is the corresponding Bragg angle (Ahtee et al.,1988).

Results and Discussion

The Crystalline Structure of Chemical Components in Wheat Straw

The results of the chemical analyses of wheat straw and the crystallinity index and crystallite size of chemical components are given in Table 1.

As can be seen in Table 1 and Figure 1, the crystallinity index was found to be higher in holocellulose than in cellulose and alpha cellulose. It can be explained that the lignin was removed from carbohydrates in the straw by using chemicals while holocellulose in the straw was obtained according to the Wise's chlorite method.

Table 1. Some properties of the crystalline structure of wheat straw chemical components.

Chemical content	Sample no	Chemical ratio		Crystallinity index,%			Crystallite size$_{(002)}$		d-space$_{(002)}$	
		%	SD	X_{cr}	S.D.	k	nm	SD	nm	SD
Straw powder	1	-	-	45.57	0.11	1.73	6.4	0.09	4.13	0.02
Holocellulose	2	72.48	0.02	65.23	0.09	0.4	6.1	0.06	4.40	0.01
Cellulose	3	46.81	0.01	55.67	0.29	2.47	3.7	0.12	4.13	0.03
Alpha-cellulose	4	38.12	0.04	45.30	0.17	1.87	9.1	0.05	4.11	0.03
Lignin	-	18.63	0.05	-	-	-	-	-	-	-

SD: Standard Deviation

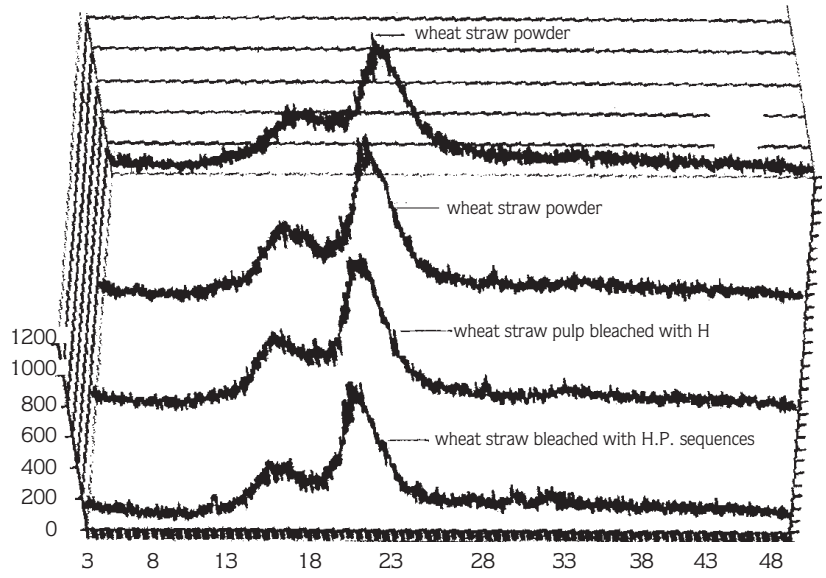

Figure 1. Comparison of diffraction patterns of wheat straw and carbohydrate component.

Since the nitric acid used in the determination of cellulose content in straw removes the less ordered carbohydates as hemicellulose and lignin from other carbohydrates, the crystallinity index in cellulose was finally higher than in wheat straw powder. However, the crystallinity index in cellulose was lower than that in holocellulose due to the nitric acid used in the determination of cellulose content, showing a remarkable effect on swelling and the hydrolysis of the cellulose.

Rozmarin et al. (1977) studied the effect of acid hydrolysis on the crystalline structure of cellulose. They found that with increased acid concentration, the crystallinity index decreased rapidly. In addition, the crystallinity index of alpha cellulose decreases because NaOH penetrates and swells the cellulose fibres. As can be seen in Table 1 and Figure 1, the highest and lowest crystallite size were found in (9.1nm) alpha cellulose and in (3.7 nm) cellulose, respectively.

The Chemical Properties and Crystalline Structure of Bleached and Unbleached Soda-Oxygen Wheat Straw Pulp

The chemical properties and crystalline structure of bleached and unbleached soda-oxygen wheat straw pulp are presented in Table 2.

As presented in Table 2 and Figure 2, while the viscosity of unbleached pulp was 603 cm^3/g, the viscosity of pulp bleached with HP sequences was 563 cm^3/g. Consequently, DP and Kappa numbers and lignin contents of pulps decrease with the increasing bleaching

Table 2. Chemical properties and crystalline structure of wheat straw soda-oxygen pulp.

Pulp samples	Sample no	Viscosity		DP	Kappa no		Lignin		Crystallinity index			Crystallite Size		d-space	
		(cm^3/g)	SD		Value	SD	%	SD	Xcr%	SD	k	nm	SD	nm	SD
Unbleached pulp	1	603	0.05	859	23.43	0.04	3.52	0.03	52.00	0.01	2.6	3.4	0.06	4.09	0.02
Pulp bleached H	2	562	0.03	795	20.86	0.02	3.13	0.04	52.61	0.02	2.4	4.3	0.07	3.98	0.02
Pulp bleached HP	3	561	0.04	794	15.95	0.05	2.40	0.01	54.10	0.04	3.2	4.6	0.11	3.93	0.01

SD: Standard Deviation

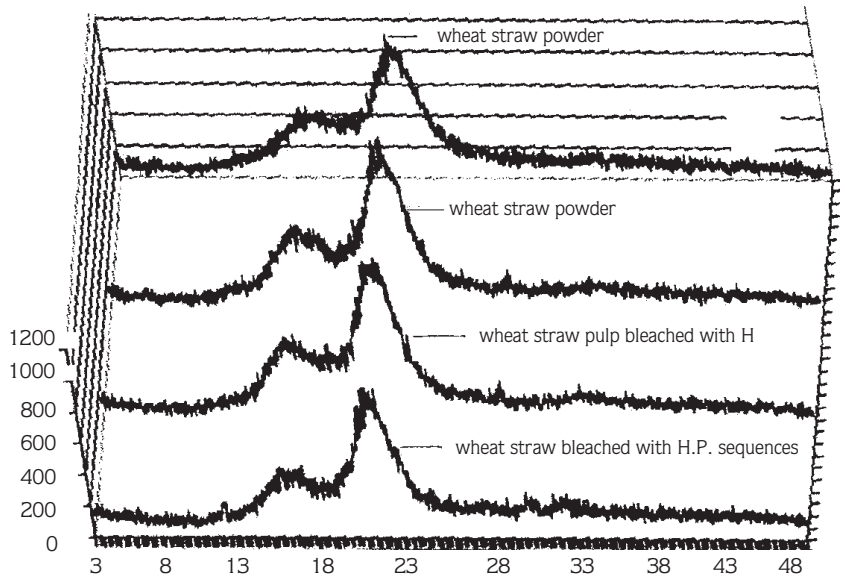

Figure 2. Comparison of diffraction patterns of bleached and unbleached pulps.

sequences. On the other hand, the crystallinity index and crystallite size of wheat straw powders were 45.5% and 6.4 nm, respectively. These data in soda-oxygen wheat straw pulp were 52.00% and 3.4 nm. The crystallinity index and crystallite size in the same pulps with bleached H were 52.61% and 4.3 nm respectively. However, these rates in the pulps bleached with HP sequences were 54.10% and 4.3 nm.

The crystalline size was found to be higher in wheat straw powders than in soda-oxygen pulps (Figure 2). However, the crystallinity index was found to be lower in wheat straw powders than in soda-oxygen pulps. It is possible to that the reason for the increase in the crystallinity index is the removal of lignin in samples with cooking and bleaching.

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