Turk J Agric For
32 (2008) 561-570

Comparison of Different Chemical Pulps from Wheat Straw and Bleaching with Xylanase Pre-Treated ECF Method

Saim ATEŞ[1], Celil ATİK[2], Yonghao NI[3], Esat GÜMÜŞKAYA[4]

[1]Kastamonu University, Faculty of Forestry, 37200 Kastamonu - TURKEY

[2]İstanbul University, Faculty of Forestry, 80895 Bahçeköy, İstanbul - TURKEY

[3]Limerick Pulp and Paper Centre, UNB, Fredericton, NB, E3B6C2, CANADA

[4]Karadeniz Technical University, Faculty of Forestry, 61080 Trabzon - TURKEY

Received: 29.04.2008

Abstract: Different pulping processes, kraft-anthraquinone (AQ), bio-kraft, soda-AQ, ALCELL, and FORMACELL were studied for wheat straw. Fungal pre-treatment with *Ceriporiopsis subvermispora*, white rot fungi, was applied to wheat straw before kraft-AQ pulping, the so-called bio-kraft process. Fiber properties, carbohydrate contents, FT-IR analyses, strength properties of resultant paper, and bleachability characteristics were included to determine the properties of these pulp samples. In addition, the effects of the xylanase pre-treatment on the subsequent Elemental Chlorine Free (ECF) bleaching process were investigated. The results indicated that kraft-AQ pulps from wheat straw exhibited better characteristics than the other pulp samples with lower kappa number, higher carbohydrate content, higher paper strength properties, and better bleachability. The highest kappa number, viscosity, and fiber coarseness were found for organosolv pulp samples; however, these pulps had the lowest carbohydrate contents and strength values and poor bleaching properties. It was concluded that the fungal pre-treatment of wheat straw with *C. subvermispora* had a positive effect on the bleachability and gave stronger pulp. There was no clear alteration in the crystallinity index of pulp samples based on the FT-IR results.

Key Words: Wheat straw, biopulping, enzyme prebleaching, organosolv pulping, FT-IR

Buğday Sapının Farklı Pişirme Yöntemleri ile Elde Edilen Kimyasal Hamurlarının Karşılaştırılması ve Enzim Ön İşlemli ECF Yöntemi ile Ağartılması

Özet: Buğday sapları pişirilmesi aşamasında kraft-anthraquinone (AQ), bio-kraft, soda-AQ, ALCELL, ve FORMACELL gibi farklı pişirme yöntemleri uygulanmıştır. Biokraft yöntemi kapsamında buğday sapları *Ceriporiopsis subvermispora*, beyaz çürüklük mantarı, ile kraft-AQ pişirme öncesinde ön işleme uğratılmıştır. Elde edilen farklı hamurlara ait lif özellikleri, karbonhidrat bileşimleri, FT-IR analizleri, direnç özellikleri, ve ağartma karakteristikleri belirlenmiştir. Bunlara ilave olarak, ksilanaz ön işleminin Elementer Klorsuz Ağartma (ECF) işlemi üzerine etkisi araştırılmıştır. Sonuç olarak, düşük kappa numarası, yüksek karbonhidrat bileşimi, en yüksek kâğıt direnç özellikleri ve en iyi ağartılabilirlik özelliği ile buğday sapları için kraft-AQ yöntemlerinin en iyi sonuçları verdiği görülmüştür. Organosolv hamur örneklerinin yüksek kappa numarası, viskozite ve lif kabalık değerlerinin yanında daha düşük karbonhidrat bileşimi ve direnç özellikleri ve daha zayıf ağartılabilirlik özelliklerine sahip oldukları gözlemlenmiştir. *C. subvermispora* ile ön işleme uğratılmış buğday saplarından üretilen kâğıt hamurlarının direnç özellikleri ve ağartma karakteristiklerinin olumlu yönde etkilendiği görülmüştür. FT-IR sonuçlarından da açıkça görüleceği üzere elde edilen hamurların kristalinite indekslerinde önemli bir değişim görülmemiştir.

Anahtar Sözcükler: Buğday sapı, biyolojik yöntem, enzim ön-ağartması, organosolv pişirme, FT-IR

* Correspondence to: saimates@kastamonu.edu.tr

Introduction

Since the 1970s, the world non-wood pulp production increased from 7% to 12% of the total pulp capacity and its annual growth rate is 2 to 3 times higher than that of wood pulp (Atchinson, 1998). Agricultural residues are important alternatives to wood as the raw material for the pulp and paper industry; in fact, they provide excellent specialty paper and constitute the only raw materials for the paper industry in some countries (Lam et al., 2001; Jimenez et al., 2006).

Similar to other countries, pulp and paper production and consumption rates in Turkey are increasing. However, forest resources are becoming more and more limited in Turkey and the paper industry of the country is in competition with other forest industries for the limited but precious resources. In paper and board production of Turkey, 34% of the raw material comes from wood, 40% from waste paper, 17% from import cellulose, and 9% from cereal straw (Özer, 2001). It was predicted that using more non-wood raw material for pulp production is inevitable. Wheat straw, abundantly available in Turkey, will become ever important as one of the raw materials for pulp and paper industry (Kangas and Baudin, 2003).

The chemical pulping process is aimed to selectively extract lignin from lignocellulosic materials. The main drawbacks of conventional pulping processes are i) changed structures of the residual lignin so that the subsequent bleaching becomes more difficult, and ii) some negative environmental effects, such as sulfur-related compounds. During the last few decades many attempts have been made to use low-molecular weight alcohols and acids, such as ethanol, methanol, peroxyformic acid, formic acid, acetic acid, formaldehyde, ethanolamine, and ethylene–glycol for chemical pulping (Lora and Aziz, 1985; Muurinen, 2000). Therefore alternative pulping processes, such as biological and organosolv processes, have received much interest. Fungus or enzyme may also be used as a pre-treatment to improve the pulping process and/or pulp properties and to decrease environmental effects (Akhtar et al., 2000; Zhao et al., 2002). Many studies are available in the literature regarding the pulp yield, costs, environmental impact, and other aspects.

The objective of the present study was to compare different pulping methods for processing wheat straw for the purpose of producing paper-grade pulp. Fungal pre-treatment with *Ceriporiopsis subvermispora* before kraft-AQ pulping at low alkali concentration, and donated as bio-kraft process and xylanase enzyme treatment before the bleaching process, were also investigated. We also focused on characteristics and bleachability of pulp samples, FT-IR analyses and pulp strength properties obtained from the kraft-AQ at low and high alkali ratio, bio-kraft, soda-AQ, ALCELL, and FORMACELL.

Materials and Methods

Pulping

Wheat straw (*Triticum aestivum* L.*)*, the most abundant variety grown in Turkey, was used for kraft-AQ (both low active alkali ratio, denoted as L.a. kraft-AQ and high active alkali ratio, denoted as H.a. kraft-AQ), bio-kraft, soda-AQ, and organosolv (both ALCELL and FORMACELL) processes. Wheat straw was cut to 2-3 cm length in order to obtain good mixing in the reactor during the cooking process.

The cooking trials were conducted in a 15-l cylindrical rotary batch reactor wrapped in a heating jacket. The reactor was loaded with 500 g (o.d.) wheat straw for each trial and cooked with appropriate chemicals needed as shown in Table 1. The cooked material was filtered, washed, and defiberated in a refiner.

The optimum pulping conditions for wheat straw were selected based on previous studies (Kırcı and Akgül 1999; Lam et al., 2001; Tutus and Eroglu, 2001; Jahan et al., 2006). Two different kraft-AQ processes were conducted, a low active alkali ratio (L.a. kraft-AQ) at 10% active alkali charge and a high active alkali ratio (H.a. kraft-AQ) at 16% active alkali charge. To determine the effect of the fungal pre-treatment, *Ceriporiopsis subvermispora* CZ3 was applied to wheat straw before the L.a. Kraft-AQ pulping, denoted as “bio-kraft pulping”. Three replicates of all experiments were performed and an average reading was taken. The standard deviations were analyzed using MS Excel.

To remove the lignin precipitated on the fibers of the ALCELL pulp, further displacement washing was performed with 70% ethanol solution at 70 °C, 10% pulp consistency, a superficial velocity of 100 ml min^{-1}, and a dilution factor of 4.5 ml g^{-1}. The kappa number of the washed pulp thus obtained was 34.7.

Table 1. Pulping conditions.

Processes	A.Alkali charge (%)	Ethanol (%)	Formic acid (%)	Sulphidity (%)	AQ (%)	Liq.to straw ratio	Pulping time (min)	Pulping temp. (°C)
Kraft-AQ (L.a)[1]	10	-	-	20	0.1	6/1	40	160
Kraft-AQ (H.a)[2]	16	-	-	20	0.1	6/1	40	160
Bio-kraft*	10	-	-	20	0.1	6/1	40	160
Soda-AQ	16	-	-	-	0.1	6/1	60	160
ALCELL	-	50	-	-	-	8/1	150	165
FORMACELL	-	-	70	-	-	12/1	60	100

[1] Kraft-anthraquinone pulping with low active alkali ratio
[2] Kraft-anthraquinone pulping with high active alkali ratio
*Kraft-AQ pulping at low active alkali concentration (fungal pre-treatment applied to wheat straw)

Fungal pre-treatment

Ceriporiopsis subvermispora, a white-rot fungus, supplied by the Centre for Forest Mycology Research of the USDA Forest Products Laboratory in Madison WI, was used for pre-treatment. Liquid inocula were prepared in petri dishes as described by Atik and Imamoglu (2003). The spent medium in the dish containing the fungal biomass was then decanted; mycelium was washed with sterile distilled water and then blended aseptically in a warring blender. Liquid inoculum containing 0.1 mg ml^{-1} fragmented mycelium (dry wt.) was used for inoculation of the straws at a dosage of approximately 5 mg mycelium per 1 kg of wheat straw.

Prior to the experiment, the wheat straws were immersed in water. Corn Step Liquor (CSL) was used as a nutrient in order to lower inoculum demand (Akhtar et al., 1997). The CSL utilized in this study was supplied by a local starch producer, Pendik-Nişasta (İstanbul, TURKEY). The wet straws were steamed for 20 min for decontamination and cooled to room temperature before inoculation. Diluted sterile CSL were sprayed on straws (0.5% dry w w^{-1}) before inoculation. The inoculated straws were introduced to a sterilized aerated static bed bioreactor. The moisture content of the wheat straw was adjusted to approximately 50%. The straws were incubated at 27 ± 1 °C for 2 weeks with humidified air (0.05 l h^{-1}).

Bleaching

The same bleaching sequence, HQP (where H represents sodium hypochlorite, Q represents chelation agent, and P represents hydrogen peroxide), was applied to each pulp. To determine the effect of xylanase pre-treatment (X) on pulp bleachability, Pulpzyme HC (X1) from NovoNordisk was used before HQP bleaching stage and compared with control samples. The enzyme activity was determined by dinitrosalicyclic acid (DNS) method (Bailey, 1988). Diluted enzyme solution (30 ml) was incubated with 300 ml of 1% (w v^{-1}) birch wood xylan (Sigma) solution (100 mmol l^{-1} acetate buffer with 0.4% Tween 20, pH 5) at 40 °C for 20 min. One unit (U) of xylanase activity was defined as the amount of enzyme that catalyses the release of 1 µmol of xylose equivalent per minute. XHQP bleaching conditions are indicated in Table 2. For each bleaching stage, 30 g o.d. pulp sample

Table 2. Bleaching conditions.

	X	H	Q	P
Stock concentr, % o.d.	10	5	5	10
Temperature, °C	40	40	60	80
Reaction time, h	2	2	1	2
pH initial	5.00	-	-	-
Enzyme IU g^{-1}	1.0			
NaClO, % o.d.		7		
EDTA, % o.d.			1.0	
H_2O_2, % o.d.				2
NaOH, % o.d.				1
$MgSO_4$, % o.d.				0.3

X: xylanase, H: hypochlorite, Q: chelation agent (EDTA),
P: hydrogen peroxide

was taken. All bleaching stages were performed in plastic ziplock bags in a water bath with intermittent kneading. Prior to use and after each bleaching step, pulps were thoroughly washed.

Pulp characterization

The yields and rejects of the pulps were determined according to TAPPI T 210 cm-93. The fiber characteristics were measured using a Fiber Quality Analyzer (FQA). Kappa number and viscosity of the pulp samples were determined according to TAPPI T 236 cm-85 and TAPPI T 230 om-94, respectively. After making handsheets of about 60 g m^{-2} in a Rapid Kothen Sheet Machine, the strength properties of handsheets made from each pulp sample were determined in accordance with the following standards: breaking length and stretch (TAPPI T 404 cm-92), burst index (TAPPI T 403-om-91), and tear index (TAPPI T 414-om-88).

Pulp samples obtained from the 6 different pulping processes were also subjected to FT-IR spectroscopy measurement. The dried samples (1 mg / 300 mg KBr) were embedded in potassium bromide (KBr) pellets and analyzed using a Nicolet 20SX FT-IR spectrophotometer. They were recorded in the absorption mode in the range of 4.000–400 cm^{-1} with an accumulation of 64 scans and resolution of 4 cm^{-1}. These spectra were normalized at 2.900 cm^{-1} (C–H stretching vibration).

Results

Screened yield, reject, viscosity, and kappa number of pulp samples are presented in Table 3. The L.a. kraft-AQ process had the highest yield of 48.2%, followed by the ALCELL, bio-kraft, H.a. kraft-AQ, FORMACELL, and soda-AQ processes. Under the same pulping conditions, the bio-kraft process had a higher yield than the L.a. kraft-AQ process.

The viscosity of pulps from the H.a. kraft-AQ and FORMACELL processes were similar. The pulp viscosity from the bio-kraft process was 2.2 points higher than that from the L.a. kraft-AQ process. Although viscosity and screened yield of the soda pulp are lower by about 4% and 4.1 points, respectively, kappa number is higher by 0.7 points than the H.a. kraft-AQ pulp under conditions similar to soda-AQ process (Table 3). The pulp viscosity from the ALCELL process was the lowest (14.4 cp) in all the samples studied.

The FQA results on the fiber characteristics of the 6 pulp samples are presented in Table 4. The pulps derived from the FORMACEL, ALCELL, and L.a. kraft processes have relatively the highest coarseness, 0.132, 0.125, and 0.111 mg mm^{-1}, respectively. Biokraft fibers have the lowest coarseness, kink index, and shorter fiber length compared to L.a. kraft AQ pulp cooked under the same conditions.

Results of sugar analyses of wheat straw pulps obtained from different pulping processes are presented in Table 5. There was no significant difference between carbohydrate contents of L.a. kraft-AQ and bio-kraft pulps. The fungal pre-treatment had a negligible effect on the sugar composition of the resulting pulps. It is evident from Table 5 that there is no significant difference between the sugar amounts of the soda and kraft pulps, too. The 2 organosolv processes, ALCELL and FORMACELL, due to the acidic nature of the processes, had much lower xylose and no arabinose content in the pulps.

Table 3. Results from 6 different pulping processes.

Pulping methods	Screened Yield (%)	Screen Reject (%)	Viscosity (cp)	Kappa Number
L.a. Kraft-AQ	48.2 ± 2.6	3.6 ± 0.6	29.4 ± 0.2	32.7 ± 1.2
H.a. Kraft-AQ	44.5 ± 2.1	0.2 ± 0.1	26.0 ± 0.1	9.7 ± 0.4
Soda-AQ	40.5 ± 1.9	0.5 ± 0.3	21.9 ± 0.1	10.4 ± 0.5
ALCELL	46.2 ± 2.0	1.2 ± 0.5	14.4 ± 0.3	34.7 ± 1.1
Bio-kraft	45.5 ± 2.3	1.5 ± 0.2	31.6 ± 0.1	16.0 ± 0.3
FORMACELL	42.9 ± 3.5	1.4 ± 0.3	25.9 ± 0.1	39.1 ± 1.3

Table 4. Fiber properties of pulp samples determined from FQA.

Pulping methods	Coarseness (mg mm^{-1})	Fiber length (mm)	Curl index	Kink index (%)	Fines (%)
L.a. Kraft-AQ	0.111	0.503 ± 0.11	0.058	1.04	34.54
H.a. Kraft-AQ	0.096	0.439 ± 0.07	0.062	1.13	40.66
Soda-AQ	0.097	0.421 ± 0.06	0.120	1.85	40.79
ALCELL	0.125	0.497 ± 0.08	0.090	1.64	37.56
Bio-kraft	0.091	0.463 ± 0.05	0.051	0.90	36.84
FORMACELL	0.132	0.464 ± 0.10	0.074	1.58	39.88

Table 5. Various sugar contents of the wheat straw pulps.

Pulping methods	Arabinose (%)	Glucose (%)	Xylose (%)
L.a. Kraft-AQ	2.09	66.31	21.52
H.a. Kraft-AQ	1.71	71.51	22.71
Soda-AQ	1.74	69.82	20.57
ALCELL	u.d.	64.56	12.09
Bio-kraft	2.17	67.75	20.90
FORMACELL	u.d.	63.33	5.56

u.d.: undedectable

The strength properties of the 6 different pulp samples are presented in Table 6. The organosolv pulps (ALCELL and FORMACELL processes) had the lowest strength properties, while the H.a. kraft-AQ pulp had the highest strength properties, namely: 89.15 Nm g^{-1} for the tensile index, 7.74 Mn m g^{-1} tear index, and 3.32 kPa m g^{-1} for the burst index. Slightly lower strength properties for the L.a. kraft-AQ pulp compared to H.a. kraft pulp were expected on account of a lower alkali charge. The fungal pre-treatment of the straw with *C. subvermispora* in the bio-kraft process slightly increased the tensile and tear indexes, but increased the burst index more (from 2.49 kPa m g^{-1} to 3.19 kPa m g^{-1}).

FT-IR spectra of wheat straw and the 6 pulp samples are displayed in Figure 1. The crystallinity index (CrI) of cellulose was evaluated as the intensity ratio between the intensity of certain bands in IR spectra was sensitive to cellulose crystallinity. The crystallinity index in A_{1371}/A_{2900} was higher in the L.a. kraft-AQ pulp samples than the other pulping process, as presented in Table 7. For the other 5 pulp samples, there was no significant difference in the crystallinity index.

H.a. kraft-AQ and soda-AQ unbleached pulps have the highest ISO brightness values (Figures 2 and 3). After the xylanase stage, no significant changes were observed with the brightness properties of the pulps (Figure 3). The affect of enzymatic treatment was observed after H stage where the ISO brightness values of xylanase pre-treated pulps increased from 66.27 ± 0.2 to 73.43 ± 0.1, from 70.97 ± 0.2 to 77.28 ± 0.2, from 71.70 ± 0.3 to 75.84 ± 0.1, from 52.03 ± 0.4 to 53.62 ± 0.2, from 37.12 ± 0.3 to 37.66 ± 0.2, from 18.78 ± 0.3 to 19.03 ± 0.2 ISO points for the bio-kraft, H.a. kraft-AQ, soda-AQ, L.a. kraft-AQ, FORMACELL, and ALCELL pulps, respectively. Organosolv pulps were found to be hard to bleach. The ISO brightness development of ALCELL and FORMACELL pulps were only 13.4 and 18.8 points, respectively, after the XHQP bleaching sequence.

Table 6. Strength properties of paper sheets from unbleached wheat straw chemical pulp using 6 different pulping processes.

Pulping	CSF	Bulk ($cm\ g^{-1}$)	Tensile Index ($N.m\ g^{-1}$)	Tear Index ($mN.m\ g^{-1}$)	Burst Index ($kPa.m\ g^{-1}$)
L.a. Kraft-AQ	550 ± 15	1.62 ± 0.05	82.10 ± 3.1	7.19 ± 0.7	2.49 ± 0.2
H.a. Kraft-AQ	450 ± 10	1.71 ± 0.06	89.15 ± 3.0	7.74 ± 0.5	3.32 ± 0.4
Soda-AQ	515 ± 15	1.76 ± 0.08	64.10 ± 2.9	7.37 ± 0,6	2.54 ± 0.2
ALCELL	540 ± 13	1.82 ± 0.08	53.19 ± 3.8	5.97 ± 1.0	2.06 ± 0.5
Bio-kraft	495 ± 10	1.76 ± 0.07	82.89 ± 2.5	7.34 ± 0,5	3.19 ± 0.4
FORMACELL	585 ± 18	1.90 ± 0.10	30.32 ± 4.1	5.04 ± 0.8	1.28 ± 0.2

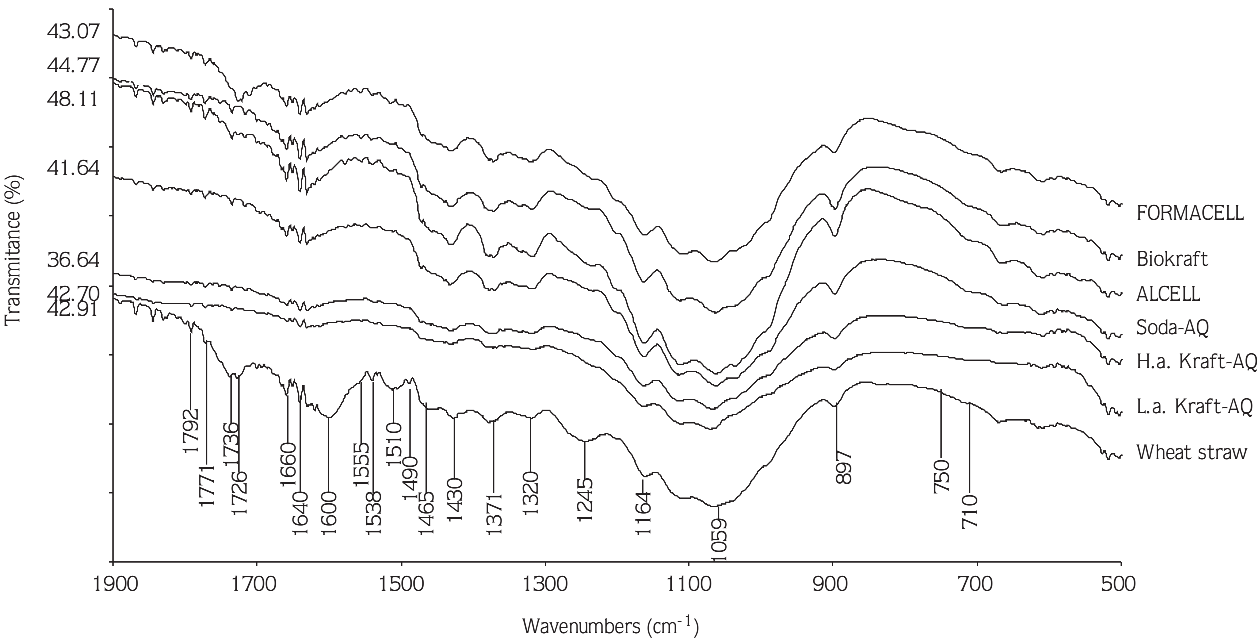

Figure 1. FTIR spectra of the wheat straw pulps.

Table 7. The crystallinity indexes of wheat straw pulps.

	Wheat straw	L.a. Kraft-AQ	H.a. Kraft-AQ	Soda-AQ	ALCELL	Bio-kraft	FORMACELL
A1430/A897	1.05	0.90	0.98	0.97	1.05	1.00	1.01
A1371/A2900	1.43	1.59	1.37	1.56	1.58	1.47	1.55
A1371/A670	0.99	0.93	1.00	0.93	0.96	0.93	0.94
A1371/A690	1.01	0.94	1.01	0.96	1.02	0.97	0.99

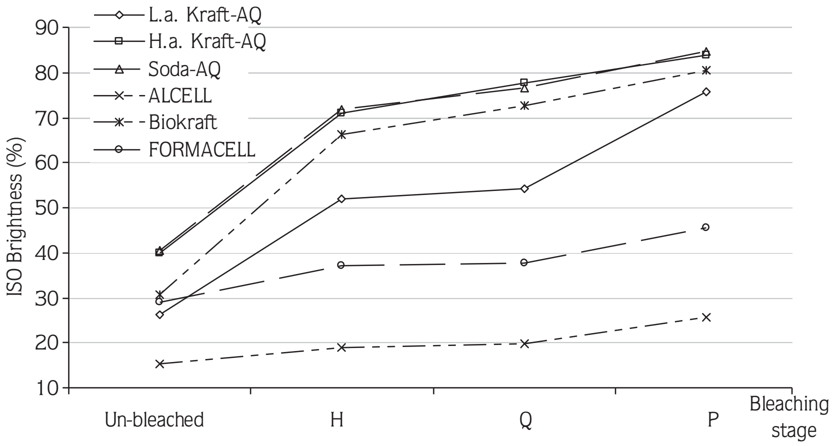

Figure 2. Brightness development during HQP bleaching sequence.

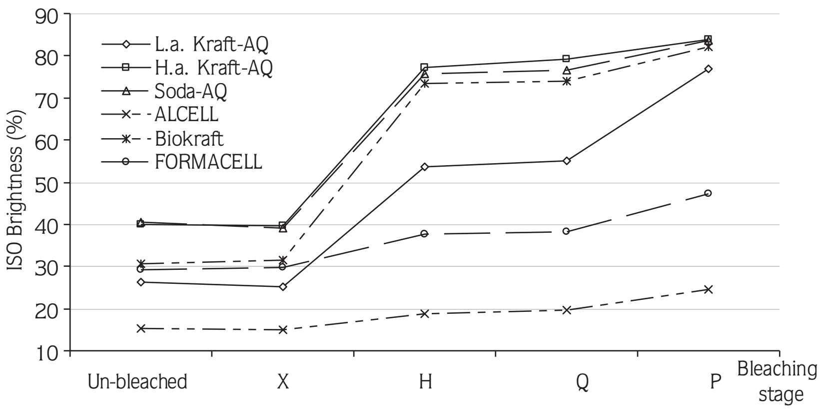

Figure 3. Brightness development during XHQP bleaching sequence.

Discussion

Pre-treatment of wheat straw with *C. subvermispora* was found effective in decreasing the kappa number by 50% (kappa number from 32.7 to 16.0). Similar results were found by Scott et al. (1995). Due to the decreased kappa number from the fungal pre-treatment, the use of lower amount of chemicals would be expected in the bleaching process. The difference between the bio-kraft and the L.a. kraft-AQ in screened yields is due both to more delignification and to more carbohydrate dissolution (Scott et al., 1998). A low pulp yield and high kappa number from the FORMACELL process were earlier reported by Jahan et al. (2006) who investigated pulping of rice straw with formic acid.

Christov et al. (1998) stated that the viscosities of the fungal pre-treated pulp were higher than the corresponding controls. Similarly, our results corrected this statement in Table 3. However, high alkali charge and formic acid can cause cellulose degradation, resulting in similar viscosity loss (Lam et al., 2001; Deniz et al., 2004). Since lignin dissolution is more rapid in the H.a. kraft-AQ process than the soda-AQ process, the pulping time was short for the H.a. kraft-AQ process, resulting in a higher yield and a higher pulp viscosity. A simultaneous decrease in viscosity and kappa number was observed for kraft pulps, which is compatible with an earlier finding (Deniz et al., 2004). Compared with L.a kraft-AQ pulp, decrease in viscosity of the soda-AQ and H.a. kraft-AQ pulps can be explained with alkaline pulping for an extended period, which increases the fraction of amorphous regions and correlates consistently with lower viscosity. Lower alkali charge in kraft pulping resulted in slightly higher viscosity for pulps when they were cooked to the same conditions. This could be explained with higher chain breakage on polysaccharides due to the alkali cleavage of the glycosidic bonds for pulps with lower kappa number (Kocurek, 1989).

Generally speaking, there is a good correlation between the fiber coarseness and pulp yield. Namely, high yield pulps give the higher coarse fibers, except the bio-kraft pulp, which can be explained by the structural changes of wheat straw due to the bio-treatment. Such a pre-treatment improved the penetration of the pulping chemicals to the raw material, therefore, enhancing the delignification reactions (Oriaran et al. 1990). Due to the high alkali ratio and carbohydrate degradation, the soda-AQ and H.a. kraft-AQ processes resulted in higher fine contents in comparison with other processes (Table 4). It is noticed that the FORMACELL process also led to relatively high fine content. This can be explained by the formation of acetates in carbohydrates and lignin structures (Gullichsen and Fogelholm, 2000), as well as the acid hydrolysis.

Increasing the alkali charge from the L.a. kraft-AQ to the H.a. kraft-AQ process led to a decrease in the arabinose content and some increase in the glucose and xylose contents (Table 5). Xylan and cellulose were depolymerized by peeling and alkaline hydrolysis of glycosidic bonds, which were assumed to take place during the consecutive stages in the pulping process as the result of simultaneous reactions, as proposed by De Groot et al. (1994). Since acid hydrolysis is not selective, some hydrolysis of wood hemicelluloses also occurs during cooking. Xylan was particularly affected. Some reacts further to produce furfural. Cellulose stands cooking better. Pulp yield is lower than that for the corresponding kraft pulp (Gullichsen and Fogelholm, 2000).

The FORMACELL pulp had the lowest strength properties in this study (Table 6). This phenomenon was explained by Lam et al. (2001) that the hydrogen bondings between amorphous cellulose chains and water are destroyed during cooking. Also Lam et al. (2001) stated that increasing the formic acid charge during cooking caused 2 main effects on pulp properties: i) a sharp reduction in pentosanes content; ii) a gradual increase in viscosity. Saake et al. (1995) and Seisto and Popius-Levin (1997) showed that reducing pentosanes content was the main cause for the decreased strength properties in such a process.

Our results showed that the increased carboxyl and hydroxyl groups in pulp were given as one of the reasons for the increased strength of the bio-kraft pulp (Table 6). Other possible reasons included the formation of fungal exudates that would increase the fiber-to-fiber bonding capacity (Pellinen et al., 1989; Setliff, 1990). In addition, the internal fibrillation due to fungal pre-treatment may also have a positive effect on the strength properties. Imamoglu and Atik (2007) indicated that the bio-treatment promoted the internal fibrillation of pulp fibers, and thus delamination of the fiber wall, both of which increased the swelling degree, flexibility, and conformability of pulp fibers. Furthermore it is known that tensile strength correlates well with swellability (Imamoglu and Atik, 2007). The lowest curl and kink indexes (Table 4) and high tensile strength properties (Table 6) indicate the increased swellability of bio-kraft pulp. Because of the positive effect of the sulphide on the strength properties of the kraft pulps, H.a. kraft-AQ process gave stronger papers than the soda-AQ process (Kocurek, 1989)

As it can be seen in Figure 1, the absorbance peaks at 1430 cm^{-1} and 897 cm^{-1} were assigned to CH_2 bending mode and deformation of anomeric CH_2, respectively (Kataoka and Kondo, 1998). The rations of the absorbency at A_{1430}/A_{897} and A_{1371}/A_{2900} were used to measure the relative cellulose crystallinity (Hassan et al., 2000). Meanwhile, the ratios at A_{1371}/A_{690} and A_{1371}/A_{670} can be used as an indicator for the transformation of cellulose I and cellulose II during alkaline treatment (Hassan et al., 2000; Akerholm et al., 2004). This method actually uses the ratio of the combined areas of the peaks at 1370, 1335, and 1315 cm^{-1}, which represented the CH bending with a peak at 670 cm^{-1} (C-OH out of plane bending mode) (Evans et al., 1995).

It was designated that the entire lignin-associated absorbance (1600, 1510, 1490, and 1420 cm^{-1}) band decreased by the cooking procedures. The band at 1640 cm^{-1} corresponds to the bending mode of the absorbed water. Sun et al (2004) stated before that the sharp peak at around 903 cm^{-1}, which represents the C_1 group frequency or ring frequency, is characteristic of β-glycosidic linkages between the glucose units. The changes of the carbonyl absorption region at 1726 and 1660 cm^{-1} might enable the evaluation of the effects of organic acid during the organosolv processes (Xua et al., 2006). Obviously, a remarkable increase of carboxyl absorption observed in spectrum of the FORMACELL pulp at 1726 cm^{-1} revealed that a noticeable oxidation of the lignin structure did occur during the pulping process. Bazaranova et al. (2002) stated that the bands at 1712 cm^{-1} are indicative of the valent C = O linkages of carboxymethyl groups conjugated with phenol hydroxyls. Esterification of the phenol and alcohol of the propane chain occurred during the FORMACELL process (Jahan et al., 2007).

According to Sugiyama et al. (1991) and Gümüşkaya et al. (2007), bands at 710 and 750 cm^{-1} were assigned to I_α (triclinic) and I_β (monoclinic) phases in cellulose, respectively. Figure 1 showed that the absorption band at 750 cm^{-1} was not detectable. Based on the above results we concluded that cellulose in wheat straw had low crystallinity (Table 7) and I_β polymorphic crystal structure (710 cm^{-1}) in cellulose was dominant (Liu et al., 2005).

The acidic conditions in the ALCELL and FORMACELL had a negative effect on xylan redeposition (Wong and Mansfield, 1999), therefore a higher coarseness and lower xylan content of the organosolv pulps in Tables 4 and 5 confirm these results. However, the application of xylanase stage before bleaching had the highest positive effect on the final brightness for the bio-kraft pulp and the L.a. kraft-AQ pulp, from 80.52 ± 0.1 to 82.16 ± 0.2 and from 75.71 ± 0.2 to 77.03 ± 0.1 ISO brightness, respectively (Figure 3). The improved brightness on the chemical pulps due to fungal pre-treatment was reported by Mohiuddin et al. (2006) and Bajpai et al. (2004). This confirmed that biopulps need lower amount of chemicals during pulp bleaching. Effect of the sulphidity during pulping on the bleachability of the pulps was not found significant.

Conclusions

In this study, 2 organosolv processes, ALCELL and FORMACELL, and 4 alkaline pulping processes, soda–AQ, low alkali kraft-AQ, high alkali kraft-AQ, and bio-kraft, were compared on straw cooking. The results showed that the alkaline processes provided better pulp and paper properties. There was no clear alteration in the crystallinity index of pulp samples based on the FT-IR results.

Fungal pre-treatment of wheat straw using *C. subvermispora* prior to kraft pulping had a positive effect on strength properties and bleaching characteristics of the resulting pulp. The L.a. kraft-AQ wheat straw pulp was obtained with better characteristics compared to the other pulps; it has lower kappa number, better paper strength, and better bleachability than the others. On the other hand, the organosolv processes, both ALCELL and FORMACELL, led to higher kappa number and lower viscosity, carbohydrate content, strength properties and bleachability. The brightness gain obtained from the xylanase pre-treatment of the H.a. kraft-AQ, soda-AQ, and ALCELL pulps were not significant, while there were some improvements in the L.a. kraft-AQ, bio-kraft, and FORMACELL pulp samples.

The pulp produced from alkaline processes can be used in the production of bleachable quality paper. Especially for L.a. kraft-AQ and bio-kraft processes, xylanase pre-treatment can make important contributions to boost the bleaching.

Acknowledgements

This work was supported by The Scientific and Technological Research Council of Turkey.

References

Akerholm, M., B. Hinterstoisser and L. Salmena. 2004. Characterization of the crystalline structure of cellulose using static and dynamic FT-IR spectroscopy. Carbohyd. Res. 339: 569-578.

Akhtar, M., M.J. Lentz, R.A. Blanchette and T.K. Kirk. 1997. Corn steep liquor lowers the amount of inoculum for biopulping. Tappi J. 80: 161-164.

Akhtar, M., G.M. Scott, R.E. Swaney and D.F. Shipley. 2000. Biomechanical pulping: a mill-scale evaluation. Resour. Conserv. and Recy. 28: 241-252.

Atchinson JE. 1998. Update on global use of non-wood plant fibers and some prospects for their greater use in the United States. In: Proceedings of the North American Nonwood Fiber Symposium, Atlanta, pp. 1-3.

Atik, C. and S. Imamoglu. 2003. Influence of Corn Steep Liquor in Nutrient Medium over Productivity of Biopulping Fungus Ceriporiopsis subvermispora. Anadolu University J. Science and Technology. 4: 89-92.

Bailey, M.J. 1988. A note on the use of dinitrosalicylic acid for determining the products of enzymatic reactions. Appl. Microbiol. and Biot. 29: 494-496.

Bajpai, P., S.P. Mishra, O.P. Mishra, S. Kumar, P.K. Bajpai and S. Singh. 2004. Biochemical pulping of wheat straw, Tappi J. 3: 3-6.

Bazaranova, N.G., E.V. Karpova, I.B. Katrakov, V.I. Markin, I.V. Mikushina, Y.A. Olhov and S.V. Hudenko. 2002. Metodi issledovania drevesini proizvosnih. Altayski Gosudarstveni Universitet, Barnaul.

Christov, L. P., M. Akhtar and B. A. Prior. 1998. The potential of biosulfite pulping in dissolving pulp production, Enzyme and Microb. Tech. 23: 70-74.

De Groot. B., J.E.G. Van Dam, R.P. Van Der Zwan and K. Riet. 1994. Simplified kinetic modelling of alkaline delignification of hemp woody core. Holzforschung. 48: 207-214.

Deniz, İ., H. Kirci and S. Ates. 2004. Optimization of Wheat Straw (*Tiriticum du*rum) Kraft Pulping, Ind. Crop. and Prod. 19: 237-243.

Evans, R., R.H. Newman, U. Roick, I.D. Suckling and A.F.A. Wallis. 1995. Changes in cellulose crystallinity during kraft pulping. Comparison of infrared, x-ray diffraction and solid state NMR results. Holzforschung. 49: 498-504.

Gullichsen, J. and C.J. Fogelholm. 2000. Chemical pulping. published in cooperation with the Finnish Paper Engineers' Association and TAPPI, Finland.

Gümüşkaya, E., M. Usta and M. Balaban. 2007. Carbohydrate components and crystalline structure of organosolv hemp *Cannabis sativa* L. bast fibers. Bioresearch Technol. 98: 491-497.

Hassan, M.L., R.M. Rowell, N.A. Fadl, S.F. Yacoub and A.W. Christiansen. 2000. Thermoplasticization of bagasse. I. Preparation and characterization of esterified bagasse fibers. J. of Appl. Polym. Sci. 76: 561-574.

Imamoglu, S. and C. Atik. 2007. Effects of biological pre-treatment of pine chips on the beating performance of kraft pulp. Prog. Nat. Sci. 17: 102-106.

Jahan, M.S. Z.Z. Lee and Y. Jin. 2006. Organic acid pulping of rice straw. I: Cooking. Turk. J. Agric. For. 30: 231-239.

Jahan, M.S., D.A.N. Chowdhury and M.K. Islam. 2007. Atmospheric formic acid pulping and TCF bleaching of dhaincha *Sesbania aculeata*;, kash *Saccharum spontaneum*; and banana stem *Musa cavendish*. Ind. Crop. and Prod. 26: 324-331.

Jimenez, L. V. Angulo, E. Ramos, M.J. De la Torre, J.L. Ferrer. 2006. Comparison of various pulping processes for producing pulp from vine shoots. Ind. Crop. and Prod. 23: 122-130.

Kangas K. and, A. Baudin. 2003. Modeling and projections of forest products demand, supply and trade in Europe. Geneva Timber and Forest Discussion Paper, UNECE/FAO, Geneva.

Kataoka, Y. and T. Kondo. 1998. FT-IR microscopic analysis of changing cellulose crystalline structure during wood cell wall formation. Macromolecules. 31: 760-764.

Kırcı, H. and M. Akgül. 1999. Autocatalyzed ethanol-water pulping of wheat *Triticum aestivum* L.; straw, Turk. J. Agric. For. 232: 1283-1290.

Kocurek, M.A. 1989. Alkaline Pulping. Tappi Press, Atlanta, USA.

Lam, H.Q. Y.L. Bigot, M. Imas and G. Avignon. 2001. Formic acid pulping of rice straw. Ind. Crop. and Prod. 14: 65-71.

Liu, R., H. Yu and Y. Huang. 2005. Structure and morphology of cellulose in wheat straw. Cellulose. 12: 25-34.

Lora, J.H. and S. Aziz. 1985. Organic acid pulping: A versatile approach to wood refining. Tappi J. 68: 94-97.

Mohiuddin, G., M. Rashid, M. Rahman, S.A. Hasib and A. Razzaque. 2006. Biopulping of whole jute plant in soda-antraquinone AQ; and kraft processes. Tappi J. 4: 23-27.

Muurinen, E. 2000. Organosolv pulping. A review and distillation study related to peroxiacid pulping. Doctoral thesis. University of Oulu, Finland.

Oriaran, T.P., P. Labosky and P.R. Blankenhorn. 1990. Kraft pulp and papermaking properties of *Phanerochaete chrysosporium* degraded aspen. Tappi J. 73: 147-152.

Özer, T. 2001. Türkiye Selüloz ve Kağıt Endüstrisinin 1999 yılı Genel Durumu. Seka Dergisi. 68: 8-11.

Pellinen, J., J. Abulhasan, and H.M. Chang. 1989. Biological delignification of pulp by *Phanerochaete chrysosporium*. J. Biotechnol. 10: 161-170.

Saake, B., R. Lehnen, S. Lummitsch and H.H. Nimz. 1995. Production of dissolving and paper grade pulps by the Formacell process. In: 8th International Symposium on Wood and Pulping Chemistry, Book: 2, Helsinki, Finland, pp. 237-242.

Scott, G.M., M. Akhtar, M.J. Lentz and R.E. Swaney. 1998. Engineering, Scale-up and economic aspects of fungal pre-treatment of wood chips. In: Environmental Friendly Technologies for the Pulp and Paper Industry (Eds.:Young RA and Akhtar M.). John Willey and Sons Inc., New York, pp. 341.

Scott, G.M., M. Lentz, M. Akhtar, M. Sykes, S. Abubakr and M. Lentz. 1995. Fungal delignification and biomechanical pulping of wood Proceedings 1995 Int. Environmental Conf. Book 2. Tappi Press, Atlanta, pp. 1155-1161.

Seisto, A. and K. Poppius-Levlin. 1997. Fiber characteristics and paper properties of formic acid / peroxyformic acid birch pulps. Nord. Pulp Pap. Res. J. 12: 237–243.

Setliff, E.C. 1990. Biomechanical pulping with white-rot fungi, Tappi J. August 1990, 141-148.

Sugiyama, J., J. Persson and H. Chanzy. 1991. Combined infrared and electron diffraction study of the polymorphism of native celluloses. Macromolecules. 24: 2461-2468.

Sun, X.F., R.C. Sun, J. Tomkinson and M.S. Baird. 2004. Degradation of wheat straw lignin and hemicellulosic polymers by a totally chlorine-free method. Polym. Degrad. and Stabil. 83: 47-57.

Tutus, A and H. Eroglu. 2001. A practical solution to silica problem in wheat straw pulping Part I. Appita J. 56: 111-115.

Wong, K.K.Y. and S.D. Mansfield. 1999. Enzymatic processing for pulp and paper manufacture-a review. Appita J. 52: 409-418.

Xua, F., J.X. Sun, R.C. Sun, P. Fowler and M.S. Baird. 2006. Comparative study of organosolv lignins from wheat straw. Ind. Crop. and Prod. 23: 180-193.

Zhao, J., X. Li, Y. Qu and P. Gao. 2002. Xylanase pre-treatment leads to enhanced soda pulping of wheat straw. Enzyme and Microb. Tech. 30: 734-740.