Turkish Journal of Agriculture and Forestry

http://journals.tubitak.gov.tr/agriculture/

Research Article

Turk J Agric For
(2015) 39: 144-153
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doi:10.3906/tar-1403-41

Comparison of pulping and bleaching behaviors of some agricultural residues

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Received: 07.03.2014 • **Accepted:** 02.10.2014 • **Published Online:** 02.01.2015 • **Printed:** 30.01.2015

Abstract: The present study determines the characteristics of bleaching and beating of annual plants and agricultural waste, which constitute important raw material potential for the pulp and paper industry in Turkey. It also examines the effects of this process on several paper properties. Firstly, chemical contents are determined for each raw material and then evaluated for use in the pulp and paper industry. All raw materials studied are found to be suitable for use in the pulp and paper industry, according to the determined chemical content. Secondly, pulp with different properties is obtained and subsequently pretreated with the enzyme xylanase. It is then bleached using the elementary chlorine-free (ECF) method, utilizing the DEpD bleaching sequence, which is both easy to apply and highly effective. The bleaching behavior of each material is then determined. The highest ISO brightness value of 98.3% is obtained using soda-AQ pulps deriving from rye straw. This is followed by wheat straw (92.0%), reed (88.6%), corn stalks (87.6%), and rice straw (87.5%). Each unbleached pulp sample is beaten at a constant 3000 revolutions PFI (9000 rev. for hemp), and changes in freeness properties are determined. The hardest material to beat is hemp fibers, followed by reed, rye, corn, and cotton stalks. The best beatable pulps are rice straw, tobacco, wheat, sunflower, and barley stalks. Paper sheets from both unbleached and bleached pulps are tested.

Key words: Annual plants, enzyme, ECF bleaching, paper properties, soda-AQ pulping

1. Introduction

The use of agricultural residues as a source of cellulose in the paper industry is supported by many institutions, due in part to increasing environmental pressures (Camarero et al., 2004). The principal aim of these incentives is to minimize the environmental damage of the cellulose industry, in addition to reducing raw material pressure placed on forests (Pan et al., 1999). Another reason that renders the use of agricultural residues in the cellulose industry attractive is the limited forest resources of certain countries (Jimenez, 1999). When considering countries with an agriculture-dependent economy and limited forest sources, the use of agricultural residues and cultured or uncultured annual stalks for pulp manufacturing offer a significant solution to the raw materials problem (Okan et al., 2013). Being an agriculture-dependent country with limited forest resources, Turkey is still far from utilizing the current potential of agricultural residues in the cellulose industry. In total, 38,247 ha of agricultural fields are cultivated in Turkey. In this cultivated area, the potential number of stalks (including wheat, barley, corn, rye, cotton, and rice straw) usable in the cellulose industry over the last 3 years (2011–2013) is estimated at approximately 94,000 t. The worldwide tendency toward increased demand for paper and cardboard products persists; thus, a shortage will occur in the production of wood-derived cellulose, and inevitably the high growth potential of agricultural fibers will be used in order to overcome this limitation in the cellulose industry (Fillat et al., 2012).

Another important problem encountered in the paper industry concerns minimizing environmental pollution and developing technologies that create less pollution. After it was discovered that chlorine-containing components (for bleaching pulp with conventional methods) exist in the waste water of the bleaching process, and that these components react with lignin (a residue in the pulp) and are converted into environmentally hazardous chlorinated phenolic compounds and poisonous carcinogenic compounds (such as dioxin and furan groups), social pressures were exerted to limit the use of compounds containing chlorine, such as chlorine, chlorine dioxide, hypochloride, and chloride. All these facts led the pulp industry to develop new technologies that do not cause environmental problems in the production of bleached paper (Okan et al., 2013). However, the bleaching process

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of pulps (which are derived from annual plants) is difficult due to anatomic and chemical characteristics; therefore, modern totally chlorine-free bleaching procedures are not adequate to reach a high brightness level in this type of pulp (Camamero et al., 2004). For this purpose, when compared with other environmentally friendly technologies for bleaching pulps that are derived from annual plants, enzymatic procedures offer low-cost solutions by limiting the chlorine dioxide capacity (Stafford, 2000). Xylanase is a commercially available enzyme that is most often used for pretreatment of pulp bleaching. In a study where the bleaching stages were determined as DC(EOP)(DED) (D: chloride, C: chlorine, E: alkaline extraction, O: oxygen, P: peroxide), the total amount of chlorine could be reduced at a rate of 15%–23% with the use of the enzyme xylanase, without changing pulp quality in production plant conditions (Manji, 2006).

In the present study, it is investigated whether the residual annual plants, which are cultivated across Turkey, can be feasibly used as raw material in the paper industry. The resulting pulps, which show different characteristics, are first exposed to prebleaching with the enzyme xylanase and then exposed to an easy-to-use and remarkably more efficient elementary chlorine-free bleaching (ECF) bleaching sequence, DEpD (D: chloride, Ep: alkaline-peroxide extraction). The bleaching characteristics of the resulting annual plant pulps are revealed. The beating degrees of raw material are also examined. The physical and optical properties of the trial papers made from those pulps are determined. Thus, each annual plant or agricultural waste material is evaluated in a production plant, either separately or together.

2. Materials and methods

2.1. Material

2.1.1. Raw Materials

Cultivated areas were studied for each raw material by taking into consideration the location and potential of study areas in Turkey. For this study, wheat, rye, and barley straw were supplied from Konya and cotton stalk was supplied from Adana. Tobacco and corn stalk were supplied from Samsun, sunflower stalk from Tekirdağ, rice straw from Çorum, reed from Afyonkarahisar, and hemp from Kastamonu. Initially, annual stalk samples were cleaned of leaves, root, soils, and other contaminants and then were cut into pieces of 4–5 cm using a cutter. Raw material experiments were then conducted on the whole stalk. For hemp, only phloem fibers were used.

2.2. Method

2.2.1 Analysis of raw material

Annual plant samples were ground and 60–80 mesh fractions were selected to determine chemical composition according to TAPPI standard TAPPI T 264 om-88. Samples were first placed in a Soxhlet extractor with alcohol-benzene extraction, according to T 204 cm-97, and then in an acetone extraction according to SCAN CM:49-03. Holocellulose content was determined by Wise's sodium chlorite method (Wise and Murphy, 1946) and cellulose content was determined according to Kurscher and Hoffner's nitric acid method (Rowell, 1984). In addition, alpha cellulose (T 203 cm-99), lignin (T 222 om-02), silica (T 207 cm-99), and ash (T 211 om-93) contents were determined. Determination of 1% sodium hydroxide and water (hot and cold) solubility of annual plants were carried out following the standard procedures described in T 212 om-98 and T 212 om-88, respectively.

2.2.2. Methods used for production and chemical analyses of pulp

Kappa number is described as the remaining lignin amount in pulp and expressed as a percentage of the total lignin content of the raw material. Easily bleachable pulp means that the kappa number is below 15 (Danielewicz and Šlusarska, 2006). In order to ensure that the kappa numbers of pulps were within the categories of easily and moderately bleachable pulps, previous studies were referenced (Jimenez et al., 1995; Lopez et al., 1996; Lopez et al., 2005; Rodriguez et al., 2008; Akgül and Tozluoğlu, 2009; Shakhes et al., 2011; Jahan and Rahman, 2012). The soda-anthraquinone (AQ) pulping method, the most suitable for agricultural residues (Eroğlu 1990), was chosen and applied to the cooking plan, as seen in Table 1.

Cooking trials were performed in a thermostatically controlled, rotary, laboratory-type reactor characterized by a capacity of 15 L, electrically heated, resistant to pressure of 25 kg/m^2, 4 rpm, with an automated temperature control table. The reactor was manually loaded and unloaded, and 600 g of completely dry cut stalks were used for all cooking procedures. Determinations of the kappa numbers and viscosities of pulp samples were carried out using the standard procedures described in T 236 om-99 and Scan-C 15:62, respectively.

Handsheets of 60 g/m^2 were formed, and several of their properties were evaluated in accordance with the TAPPI standard methods. The handsheets were conditioned in accordance with T 402 sp-98. The burst index of handsheets was measured by method T 403 om-97, the tensile indexes of handsheets were determined by method T 404 cm-92, and the tear index was determined by the standard procedure described in T 414 om-98. ISO brightness, yellowness, and opacity were calculated according to the ISO 2470-1, ASTM E313, and ISO 2470 standards, respectively, and the amount of bleaching yield was calculated using the dry solids content of the pulps.

Table 1. Cooking plan applied to the production of pulp, which is characterized as bleachable and derived from annual plants based on preliminary trials.

Annual plant	NaOH, %	Temp., °C	Time, min	AQ (%)	Time to maximum temp (min.)
Wheat straw	16	160	40	0.1	60
Rice straw	16	160	40	0.1	60
Rye straw	16	160	40	0.1	60
Barley straw	16	160	40	0.1	60
Reed stalk	20	160	60	0.1	60
Corn stalk	16	160	60	0.1	60
Tobacco stalk	25	170	120	0.1	60
Cotton stalk	25	170	180	0.1	60
Sunflower stalk	20	170	180	0.1	60
Hemp	14	125	90	0.1	60

2.2.3 Pulp bleaching

2.2.3.1. Xylanase pretreatment (enzymatic procedure)

A commercially available enzyme called endo-xylanase was used for the preliminary biological process prior to the ECF bleaching sequence of pulps. Endo-xylanase was supplied from Sigma and its activity was determined according to the dinitrosalicylic acid method (Bailey, 1988). The diluted sample of enzyme (30 µL) was incubated in 300 µL of 1% (w/v) common beech wood-xylan solution at 40 °C for 20 min. Activity of 1 U of xylanase was calculated as the enzyme catalyzed by 1 mmol xylose per minute. Xylanase, 2 IU/g at a ratio of 7:1 (solution/stalk), was applied to each pulp sample, which was obtained following the production of paper pulp, and was applied for 2 h at pH 4.8 and 48 °C.

2.2.3.2. ECF bleaching procedure

This procedure aimed to determine the bleachability characteristics of raw materials by applying the DED bleaching sequence (D: chloride, Ep: alkaline-peroxide extraction) according to the easy-to-use and remarkably efficient conventional ECF bleaching method, following preliminary biological bleaching. The procedures of the bleaching sequence and application levels are given in detail in Table 2.

2.2.4 Refining process

According to the pretrial results, a reasonable PFI beating revolution of 3000 for annual plants and 9000 for hemp fibers was determined. Each sample of unbleached pulp was beaten to 3000 revolutions in the PFI beater under low load conditions, and beating characteristics were examined by Schopper Riegler degree (SR°) of the pulp. Because SR° values of hemp fibers were normally very low, those fibers were beaten for 9000 PFI revolutions.

2.2.5. Production of handsheets

Paper samples obtained from pulp with the Rapid–Köthen method and made from different types of agricultural residues were conditioned for 24 h in an air-conditioned

Table 2. Bleaching plan applied following preliminary biological bleaching.*

Bleaching stages	Bleaching conditions	
	Dosage	Time
D1	3% ClO_2	120
EP	1% NaOH 0.5% $MgSO_4$ 0.5% H_2O_2	180
D2	1.5% ClO_2	120

*: Temperature is 75 °C and concentration is 7%.

room according to ISO 287. Several optical and physical properties of each paper were then determined according to TAPPI standards.

3. Results and discussion

3.1. Chemical composition of raw material

The average composition of the raw materials is given in Table 3. Holocellulose is defined as the total content of carbohydrate materials. High holocellulose content, therefore, is considered desirable for the pulp and paper industry because it is correlated with higher pulp yield (Shakhes et al., 2011).

The holocellulose content of wheat straw, barley, corn, tobacco, cotton, and sunflower stalks was similar. Furthermore, there was nearly identical holocellulose content of rye, rice straw, and reed. The holocellulose content of hemp was found to be higher than other agricultural residues in this study. The holocellulose content in wheat straw, barley, corn, tobacco, cotton, and sunflower stalks is very close to that reported for wood species such as *Pinus pinaster*, *Fagus sylvatica* L., and *Pinus sylvestris* L. (Alonso, 1976; Inari et al., 2007). The holocellulose content in rye, rice straw, and reed was similar to that of other wood species such as poplar and spruce (Law et al., 2001; Bertaud and Holmbom, 2004). The holocellulose content of rye (*Secale cereale* L.), hemp (*Cannabis sativa* L.), sunflower *(Helianthus annuus* L.), tobacco (*Nicotiana tabacum* L.), barley (*Hordeum vulgare*), and corn stalks (*Zea mays* L.) was close to that reported in the literature (Lopez et al., 1996; Akgül and Tozluoğlu, 2009; Shakes et al., 2011). The lowest holocellulose contents were observed in wheat straw (*Triticum aestivum* L.) and cotton stalks (*Gossypium hirsutum* L.), while the highest holocellulose contents were observed in rice straw, compared to those found in the literature (Deniz et al., 2004; Rodriguez et al., 2008). The highest cellulose content was observed in hemp and the lowest cellulose content was observed in cotton stalks and sunflower stalks. Additionally, the cellulose content of these raw materials was nearly identical, with the exception of hemp. The amount of alpha cellulose, namely the fraction that is insoluble in 17.5% NaOH, was determined to be above 35%. According to Shakes et al. (2010), the presence of 35% alpha cellulose content has a satisfactory effect on paper strength properties. Furthermore, the pulp yield strongly correlated with both holocellulose and alpha cellulose content. When examining Table 3, it can be seen that the alpha cellulose content of wheat straw, barley, rye, corn, and sunflower stalks is significantly different compared to rice straw and reed. The alpha cellulose content of hemp was 72.29%, higher than the other agricultural residue samples.

Table 3. Chemical compositions of used agricultural residues.

	Wheat straw	Barley straw	Rye straw	Rice straw	Reed stalk	Corn stalk	Tobacco stalk	Cotton stalk	Sunflower stalk	Hemp
Components (%)										
Holocellulose	69.84	66.01	76.95	79.39	78.85	69.92	64.29	62.79	66.85	86.08
Cellulose	50.70	49.30	51.65	55.30	56.65	55.70	50.95	47.30	47.80	80.70
α-Cellulose	42.07	38.70	44.55	53.67	52.56	46.78	36.40	29.74	44.20	75.29
Lignin	22.33	19.47	17.25	23.77	22.79	18.16	15.15	23.79	14.43	6.42
Silica	7.33	6.88	2.07	15.67	1.23	2.98	0.94	0.34	0.44	1.24
Ash	11.63	10.97	4.01	15.44	4.17	7.75	14.44	4.99	7.99	3.62
Solubilities (%)										
Acetone	5.37	5.39	4.51	3.02	2.98	8.10	5.58	3.84	4.86	1.62
Alcohol-benzene	9.33	8.71	7.44	2.21	3.26	8.57	8.06	8.36	7.48	1.59
1% NaOH	53.67	56.25	44.35	45.63	36.81	46.43	50.57	48.88	50.05	20.04
Hot water	14.71	16.25	15.72	13.81	9.80	16.82	21.56	17.91	24.26	5.85
Cold water	11.33	11.01	11.95	9.66	7.61	14.64	17.15	15.05	21.08	5.29

The desirable lignin content level is below 30% because lignin is considered to be an undesirable polymer, and its removal during pulping and bleaching requires a high amount of energy and chemicals (Shakes et al., 2011). The lignin content of hemp was fairly low compared to other agricultural residues samples in this study, but no significant difference in lignin content was found in most other agricultural residues studied.

Overall, high silica and ash content were found in agricultural samples. Compared to wood, this type of raw material commonly has silica and ash contents, which can cause problems in the manufacturing process. Ash content in trace elements also causes lower bleaching efficiency (Dutt et al., 2009).

The alcohol-benzene and acetone solubility of hemp and rice straw is lower than that of other agricultural samples in this study. In the other 8 agricultural samples, alcohol-benzene and acetone solubility contents were found to be very similar.

According to Table 3, the NaOH and hot and cold water solubilities of hemp were found to be fairly lower than in the other agricultural residue samples. Barley, sunflower, tobacco, and wheat straw contain a significantly higher content of soluble compounds in both hot and cold water and also 1% NaOH. Generally, the presence of extractives in wood increased the pulping effluent load and consumption of pulping reagents and reduced the pulp yield (Azizi et al., 2010). For instance, as seen in Table 4, total yield of rye and rice straw was higher than in wheat straw and barley stalk, although all cooking methods were the same. The reason is that wheat straw and barley stalk contain a considerably higher content of soluble compounds in 1% NaOH and hot and cold water compared to rye and rice straw.

3.2. Pulp properties obtained from annual plants with soda-AQ cooking method

Screened yield, kappa numbers, and viscosity values of bleachable (kappa number ≤ 15) pulps derived from annual plants using the soda-AQ method are given in Table 4.

It is obvious that cooking conditions vary when the cooking plan of each annual plant is examined. This fact is an important criterion for the availability of relevant raw materials. It is well known that higher lignin content in the pulp means more bleaching chemicals and more energy for its removal. Table 4 shows that wheat, barley, rye, and rice straw are easily cooked raw materials, while corn stalk is moderately hard to cook. Tobacco, cotton, and sunflower stalks are hard-to-cook raw materials. The term ‘hard cooking conditions’, when used for a given pulping process in bleaching, refers to the amount of lignin remaining in the unbleached pulp. Therefore, cooking conditions have a remarkable effect on kappa numbers and viscosity. Figure 1 shows that among pulps cooked under the same conditions, the lowest kappa values were obtained with rye (10.0), corn (10.14), reed (10.88), rice (11.2), wheat (12.60), and barley straw (12.7). When the viscosity value, indicating the depolymerization degree of cellulose, is examined, it is observed that easily cooked pulps have similar viscosities. However, harder cooking conditions were applied to obtain economically bleachable pulps from tobacco, cotton, and sunflower stalks, which are among the hard-to-cook pulps. In conclusion, this approach showed that the viscosities of those pulps were low (5.79 cP, 6.07 cP, and 7.49 cP, respectively).

In a study conducted with tobacco stalks, it was found that for soda-AQ pulps that were treated with 20% active alkaline solution at 170 °C for 90 min of cooking and 0.1%

Table 4. Yield and chemical properties of pulps made from annual plants with soda-AQ method.

Name of sample	NaOH, %	AQ, %	Temp., °C	Time, min	Screen yield,%	Reject, %	Total yield,%	Kappa no.	Visc., cP
Wheat straw	16	0.1	160	40	37.1	0.8	37.9	12.6	24.62
Barley straw	16	0.1	160	40	32.6	1.4	34.0	12.7	24.92
Rye straw	16	0.1	160	40	43.5	0.4	43.9	10.0	28.88
Rice straw	16	0.1	160	40	41.2	1.4	42.6	11.2	26.75
Reed	20	0.1	160	60	42.3	0.2	42.5	10.8	37.48
Corn stalk	16	0.1	160	60	42.4	1.3	43.7	10.4	32.01
Tobacco stalk	25	0.1	170	120	22.9	2.4	25.3	13.4	5.79
Cotton stalk	25	0.1	170	180	17.8	1.4	19.2	17.6	6.07
Sunflower stalk	20	0.1	170	180	31.1	0.5	31.6	13.7	7.49
Hemp	14	0.1	125	90	64.2	0.0	64.2	14.8	65.87

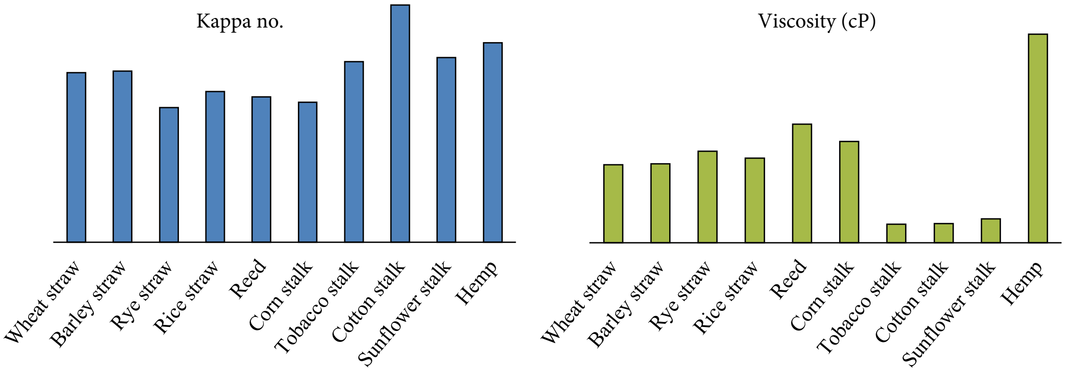

Figure 1. Kappa numbers and viscosity values of annual plant and agricultural waste soda-AQ pulps.

AQ conditions, the kappa number was 28.7 and viscosity was 46.0 cP, and it was not possible to bleach those pulps in an economic manner (Ateş et al., 2010). In another study conducted for producing economically bleachable paper pulp, it was found that for tobacco stalks manufactured in conditions of 25% active alkali ratio, 165 °C pulping temperature, 180 min pulping time, and the addition of 0.2% AQ, the kappa number was 20 (Shakhes et al., 2012). Based on cooking studies conducted on cotton stalks under various conditions, the kappa number was 33.1 and the viscosity was 31.0 cP in the following conditions: 18% active alkali ratio, 0.075% AQ, solution-to-stalk ratio of 4:1, and 165 °C (Ali et al., 2001). In a study conducted for obtaining bleachable pulps from sunflower stalks under different cooking conditions, the kappa number of pulps obtained from stalks was 25 under conditions of 16% active alkali, 170 °C, and the addition of 0.13% AQ soda (Khristova et al., 1998). In another study conducted for the production of bleachable soda-AQ pulp from corn stalks with or without preliminary hydrolysis, corn stalks were treated with cooking procedures in different alkaline conditions (150 °C, stalk/solution ratio of 6:1, AQ rate of 0.1%, and cooking time of 60 min). Based on those cooking conditions, the kappa number was 27.4 when 14% alkaline was applied, 24.8 when 16% alkaline was applied, and 21 when 18% alkaline was applied (Jahan and Rahman, 2012).

3.3. Some physical properties of papers obtained from bleached and unbleached pulps

SR°, viscosity, grammage, and some physical and optical properties of paper obtained at an equal PFI beating stage of pulp papers, which were derived from annual plants with the soda-AQ method, are given in Table 5.

A comparison of pulps obtained from annual plants and agricultural residues, using the soda-AQ method with regard to pulp freeness, is given in Figure 2. When Figure 2 is examined, the hardest material to beat is hemp fibers, followed by reed, rye, corn, and cotton stalks. The best beatable pulps are rice straw, tobacco, wheat, sunflower, and barley stalks. Therefore, pulps obtained from this group can be beaten together.

As regards Table 5, it is also observed that unbleached pulps can be more difficult to beat than bleached pulps. The underlying reason is that the amount of xylan is low in pulps that have received enzymatic pretreatment (Fillat, 2012). In other words, bleaching causes fibers to become more individual and therefore cause more difficulty in beating. In studies investigating the effect of xylanase on beating pulp, other investigators have found similar results (Wong et al., 1997; Roncero et al., 2003; Valls et al., 2010).

The changes observed in the breaking length, burst, and tearing resistance of the handsheets obtained from pulp after bleaching was performed are demonstrated in Figure 3. As Figure 3 indicates, resistance values were adversely influenced after the pulps obtained from hemp, cotton stalks, and reed fibers were bleached. A mean reduction of 3.8 units was observed in the tearing index of hemp phloem, which is directly proportional to the length of the fiber. This was followed by reed with a reduction of 2.08 units and cotton stalks with a reduction of 0.71 units. Moreover, hemp, cotton, and tobacco stalks have higher rankings in terms of lignin residue in the paper pulp, and it is possible to speculate that when the lignin is removed from the stalks, the physical properties are adversely affected.

An increase was observed in the resistance properties of paper pulps made from wheat straw, barley, rye, and rice straw (among cereal stalks) as well as corn, tobacco, and sunflower stalks when the pulp was bleached. Breaking length, burst, and tearing resistances increased at rates of 15.12%, 34.5%, and 18.0%, respectively, as a consequence of the ECF bleaching method with pretreatment of xylanase (X+DEpD), particularly for the pulps obtained from rice straw.

Degradation occurs when bleaching is done under alkaline conditions. This leads to a significant reduction in viscosity (Camarero et al., 2004). The physical properties

Table 5. SR°, viscosity, and some physical properties of pulps in constant beating stages.

Raw materials	PFI (rpm)	SR°	Viscosity (cP)	Grammage (g/m^2)	Density (kg/m^3)	Bulkiness (g/cm^3)	Tear index (mNm^2/g)	Burst index (kPam^2/g)	Breaking length (km)	Tensile index (Nm/g)
Unbleached										
Barley straw	3000	56.5	24.92	64.65	711.75	1.40	3.72	3.81	6.77	66.34
Hemp	9000	37.0	65.87	77.42	645.16	1.55	26.61	2.59	3.11	30.51
Sunflower stalk	3000	56.5	7.49	71.24	689.39	1.45	3.49	1.99	4.24	41.61
Rye straw	3000	35.3	28.88	72.45	679.18	1.47	6.47	3.38	6.03	59.14
Reed	3000	21.0	37.48	73.92	537.63	1.86	9.09	2.06	4.18	40.97
Tobacco stalk	3000	61.0	5.79	75.27	711.20	1.41	3.32	2.25	4.36	42.74
Wheat straw	3000	57.5	24.62	67.20	896.06	1.12	3.58	4.84	7.95	78.00
Corn stalk	3000	41.5	32.01	68.68	735.89	1.36	5.36	3.16	5.92	58.01
Rice straw	3000	65.5	26.75	69.76	611.02	1.64	4.89	3.42	6.02	59.00
Cotton stalk	3000	45.0	6.07	75.40	591.40	1.69	4.75	2.11	3.79	37.13
X + DEpD Bleached										
Barley straw	3000	43.5	22.22	68.95	759.10	1.32	4.02	4.47	6.74	66.08
Hemp	9000	11	32.49	58.06	483.87	2.07	22.81	1.60	2.13	20.84
Sunflower stalk	3000	41.5	7.15	70.56	682.88	1.46	3.55	2.08	4.56	44.73
Rye straw	3000	24.0	29.40	74.60	699.34	1.43	6.87	3.71	6.37	62.49
Reed	3000	15.0	16.13	73.79	536.66	1.86	7.01	1.34	3.02	29.60
Tobacco stalk	3000	45.0	5.76	67.61	638.81	1.57	3.05	2.32	4.84	47.47
Wheat straw	3000	45.0	25.00	69.35	924.73	1.08	4.28	4.93	8.16	80.00
Corn stalk	3000	30.0	29.66	71.10	761.81	1.31	5.42	3.50	6.19	60.66
Rice straw	3000	53.5	29.85	62.90	550.98	1.81	5.77	4.60	6.93	67.97
Cotton stalk	3000	26.5	5.85	92.34	724.23	1.38	4.04	1.69	3.22	31.61

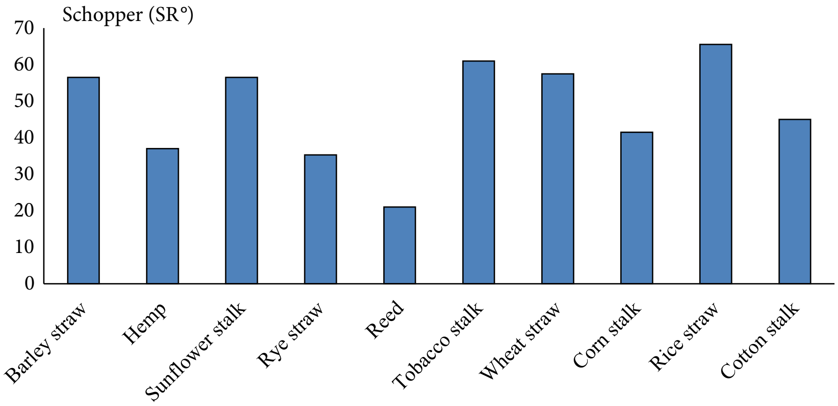

Figure 2. PFI beating behaviors of annual plant and agricultural waste soda-AQ pulps.

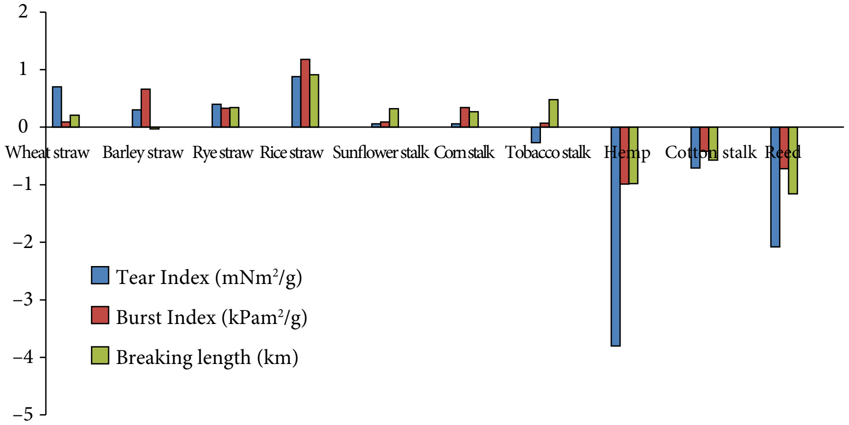

Figure 3. Change in the physical properties of annual plant pulps depending on the bleaching.

of the pulp are related not only to the amount of cellulose, but also to the ratio of hemicellulose. High amounts of cellulose usually give strong pulps, and a low ratio of cellulose to hemicellulose reduces the resistance of paper (Brannvall, 2004). Briefly, the reactions of different annual plants to a bleaching sequence applied under the same conditions are derived from the change of their effects on chemical compounds and fiber morphologies.

3.4. Optical properties of papers as a result of ECF bleaching

The brightness values of handsheets bleached in accordance with the XDEpD X (xylanase) + D (chlorine dioxide) + Ep (alkaline peroxide) + D (chlorine dioxide) sequence are given in Table 6.

Soda-AQ pulps produced from different annual plants under different cooking conditions (optimum, should the resultant kappa number be the same) were pretreated with the enzyme xylanase, followed by bleaching with a DEpD bleaching sequence. Changes in brightness values of the pulps after the bleaching procedure was fully complete are given in Figure 4 and Table 6. It is shown there that no remarkable change is observed in brightness properties. However, the effects of pretreatment with the enzyme can clearly be seen at the end of the next bleaching stage. In other words, the results of this enzymatic procedure have small but remarkable effects on brightness. An examination of the literature shows that this is similar to a study conducted on the effects of pretreatment with xylanase on the brightness of paper pulp (Stafford et al., 2000; Ateş et al., 2008).

When Table 6 is examined, it is obvious that brightness increases as bleaching advances. ISO brightness values for fully bleached annual plant pulps are given in Figure 4. Accordingly, the highest ISO brightness value of 98.3% was

Table 6. Brightness properties of annual plant soda-AQ pulps following XDEpD bleaching.

Raw material	Control	X stage	X + D1 stage	X + D1 + Ep stage	X + D1 + Ep + D2 stage
Wheat straw	34.5	36.70	62.34	76.06	92.0
Barley straw	39.0	42.06	62.05	74.17	86.0
Rye straw	47.8	48.62	72.51	85.09	98.3
Corn stalk	44.0	43.41	60.74	70.12	87.6
Sunflower stalk	28.3	25.72	34.85	55.79	71.9
Rice straw	40.7	40.27	54.40	66.18	87.5
Tobacco stalk	31.2	30.85	44.43	56.81	68.4
Cotton stalk	19.3	17.02	35.35	42.71	61.0
Hemp	44.4	38.55	56.83	78.41	80.1
Reed	38.3	37.78	53.46	75.75	88.6

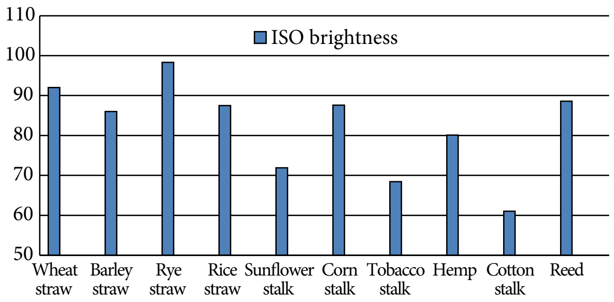

Figure 4. ISO brightness properties of fully bleached annual plant pulps.

obtained from soda-AQ pulps derived from rye straw. This was followed by wheat straw (92.0%), reed (88.6%), corn (87.6%), and rice straw (87.5%). The weakest reaction to the XDEpD bleaching sequence was obtained from cotton, tobacco, and sunflower stalks, and the corresponding ISO brightness values were 61.0%, 68.4%, and 71.9%, respectively.

In a study conducted on wheat straw that underwent a DEpD bleaching sequence with xylanase pretreatment, it was found that brightness increased as long as the bleaching stages advanced. ISO brightness of fully bleached wheat straw pulp was approximately 85%. It was reported in the same study that the XDEpD bleaching sequence is the best alternative to the DEpD bleaching sequence in terms of brightness and optical properties (Jimenez et al., 1995). Similar brightness values were determined in another bleaching study that involved the enzymatic pretreatment of paper pulps obtained from wheat straw pulps using the Biokraft method (Ates et al., 2008).

3.5. Conclusions

As a consequence of different cooking procedures for obtaining bleachable pulps from each of the primary agricultural residues, this paper determined that tobacco, cotton, and sunflower stalks are not appropriate for obtaining bleachable pulp. When agricultural residues were examined with regards to beatability using the ECF bleaching method with xylanase pretreatment, it was found that bleached pulps were usually more difficult to beat than unbleached pulps. It is understood that among all raw materials used, rice straw was the best type with regard to beatability. However, it can be speculated that reed, hemp, and cotton stalks are not suitable for ECF bleaching with enzymatic pretreatment. Generally, no positive change was observed in the physical properties of agricultural residues after bleaching was completed. However, it was found that the ECF bleaching method with enzymatic pretreatment, similar to the beating process, was not a suitable method for reed, hemp, and cotton stalks due to the reduction in physical properties after bleaching was completed. When the brightness value was examined after the ECF method with enzymatic pretreatment was complete, an increase was observed for all types of pulps. However, considering bleaching efficiency, the best reaction to the XDEpD bleaching sequence was given by cotton (216%), wheat (167%), sunflower (154%), and reed (131%), while the weakest reaction to bleaching (as indicated by comparison to baseline unbleached brightness) was given by hemp, corn, and rye pulps, as indicated by a corresponding increase at a rate of 80%, 99%, and 160%, respectively.

In conclusion, it was found that the type of agricultural residues appropriate for xylanase pretreatment using ECF bleaching were rice, barley, wheat straw, and corn (in descending order) and unfavorable types were cotton, hemp, and reed.

Acknowledgment

The authors are grateful to the Scientific and Technological Research Council of Turkey (TÜBİTAK; Project No.: 108 O 594) for financial support of this work.

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