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Full Length Research Paper

Alkaline-ethanol pulping of cotton stalks

Mehmet Akgül* and Ayhan Tozluoğlu

Duzce University, Faculty of Forestry, Konuralp Campus, 81620 Düzce, Turkey.

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In this study, the use of cotton stalks (*Gossypium hirsutum* L.) as a raw material for papermaking using soda ethanol (organasolv) with/without anthraquinone (AQ) were briefly examined. Yield, kappa number and viscosity were determined for resulting pulps and the hand sheets produced from pulps were tested for physical properties; tensile index, burst index, tear index and elrepho brightness. The obtained results showed that, pulp yield and viscosity of the soda pulp was increased by adding AQ, ethanol and with their combinations. On the other hand, the positive effects that various chemicals (AQ, ethanol, and their combinations) had on the pulp quality were also observed on the paper's physical and optical qualities, and these observed effects were thought of bearing considerable importance for paper manufacturers.

Key words*:* Soda, AQ, ethanol, cotton stalks.

INTRODUCTION

Today, nearly 10% of the total pulp production is made from non-wood plant fibers, including stalk, bast, leaf and seed fibers. In view of the enormous annual capacity of non-wood fiber material (mostly as agricultural waste) as a potential source for pulp production of 2.5 billions tons, the current nonwood pulp annual production of only 18 million tons is rather low (Atchison, 1996). Assuming an average pulp yield 50%, the utilization of non-fiber material as a source for pulp production, accounts only for 1.4%. On the other hand, the main obstacle of the use of this fiber supply is that, the annual plants have not been genetically improved with regard to their paper-making properties and the technologies for using them have not been optimized.

In 1998, the major raw material sources for non-wood pulp were straw, sugar cane bagasse and bamboo, with shares of 43, 16, and 8% of the total non-wood pulp capacity, respectively (Atchison, 1996). Technically, the non-wood pulps belong to the group of chemical pulps, and are predominantly produced according to the soda cooking process (Sixta, 2006). Lignocellulosic materials such as wood, bagasse, straw, reeds, and other plants and crops can be delignified effectively by a soda-type pulping with alkaline liquor containing small quantities of both ethylenediamine or like amino compound, and a cyclic keto compound, such as anthraquinone (Kubes et al., 1981).

Moreover, soda organosolv pulping is the other alternative method on soda pulping. There are several soda-organosolv pulping studies using non wood materials as rice straw (Pourjoozi et al., 2004; Rodríguez et al., 2008a; Rodríguez et al., 2008b), empty fruit bunches (EFB) (Mohamed Ibrahim et al., 2006; Rodríguez et al., 2008c), hemp (Gumuskaya et al., 2007; Tjeerdsma et al., 1994; Zomers et al., 1993), reed (Shatalov and Pereira, 2005; Puuronen et al., 1995), sugarcane bagasse (Moriya et al., 2005; Sanjuan and Gomez, 1991), wheat straw (Xu et al., 2006; Goel et al., 2000), cotton stalks (El-Sakhawy et al., 1995), cereal straw (Tschirner et al., 2002) and jute (Sahin, 2003). The main purpose of all modifications is to produce pulp with higher quality. Therefore, this study focuses on the potential use of cotton stalks for preparation of chemical pulps by soda organosolv with/without anthraquinone (AQ) methods.

MATERIALS AND METHODS

Experimental

The cotton stalks (*Gosspium hirsutum* L.) used in this study was from Adana and Kahramanmaras regions, in Turkey. Stalks were cleaned from leaves, roots, branches, calyxes and soil and then the stems were cut into pieces about 3 - 4 cm in length by hand. The

*Corresponding author. E-mail: mehmetakgul@duzce.edu.tr. Tel: 0380 542 1137, 0532 522 4459. Fax: 0380 542 1136.

Table 1. Pulping conditions and data on pulp characteristics.

Pulp no.	A.A (%)	Max. temp. (ºC)	Time to max. temp (min.)	Time at max. temp. (min.)	AQ (%)	Ethanol (%)	Kappa, mL/g	Viscosity, g/cm^3	Brightness, % ISO	Yields % of o.d. wood	
										Screened	Rejects
1*	18	160	30	60	-	-	74.33	806	17.1	35.80	5.14
2**	18	160	30	60	0.15	-	59.63	872	22.5	37.98	1.01
3	18	160	30	60	-	20	59.60	881	20.4	38.56	1.00
4	18	160	30	60	-	30	59.20	898	22.3	39.18	0.85
5	18	160	30	60	-	40	52.67	922	25.6	40.65	0.81
6	18	160	30	60	-	50	49.29	948	24.0	40.81	0.68
7	18	160	30	60	0.15	20	51.55	905	23.8	40.12	0.89
8	18	160	30	60	0.15	30	46.68	965	24.1	41.03	0.83
9	18	160	30	60	0.15	40	44.35	1015	24.3	41.14	0.71
10	18	160	30	60	0.15	50	40.06	1032	23.3	41.16	0.64

*Optimum soda pulping of cotton stalks,** Optimum soda-AQ pulping of cotton stalks.

cotton stalks which were chopped to the length of 3 - 4 cm were milled in a Wiley mill, using a 0.4 mm screen. The milled samples were subjected to standard compositional analysis, according to Tappi standards. The chemical composition of cotton stalks were given in previous study (Akgul and Tozluoglu, 2009).

In this study, the experimental procedures were divided into two main categories. Soda-ethanol (organosolv) and soda-AQ-ethanol pulps were studied based on optimum soda and soda-AQ pulps which were determined and given in previous study (Akgul and Tozluoglu, 2009). Soda-ethanol cooks were prepared by adding 20, 30, 40, 50% ethanol (O.D. stalks) into optimum soda pulping and soda-AQ-ethanol cooks were obtained by adding 20, 30, 40, 50% ethanol (O.D. stalks) into optimum soda-AQ pulping, respectively. For each cooking, 600 g oven-dry cotton stalks, calculated as oven-dry, were cooked in a 15 L rotating digester. The liquor-to-straw ratio (L/kg) was 5:1, maximum temperature was 160°C and time to maximum temperature was 30 min for all cooking (Table 1). A total of 10 pulps were produced and the produced pulps were washed in cold water and screened using a laboratory flat screen with a slot width of 0.15 mm.The yield contents of the pulps and rejects were determined according to Tappi T 210 by gravimetric measurements in the laboratory environment. The Kappa number (Tappi T 236) and viscosity (SCAN cm 15:88) of the pulp samples were the averages of duplicate was analyzes.

Pulps were beaten in a stainless steel PFI mill with a matt surface according to the Tappi T 248 standard. Pulp samples were collected at three predetermined intervals of 0, 0.5 and 1 min in PFI mill. Freeness was measured using a Schopper Riegler device according to ISO Standard 5267-1 (Atic et al., 2005). Hand sheets of 60 g/m^2 O.D. grammage were produced in a Rapid Köthen machine for physical tests in accordance with relevant ISO standard 5269-2 method. Tensile properties, tearing resistance (Elmendorf method) and burst strength of hand sheets were measured according to ISO standards of 1924, 1974 and 2758, respectively. The brightness and opacity of the pulps were also determined according to appropriate ISO 2469 and 2471 standard methods, respectively (Grahama et al., 1999).

RESULTS AND DISCUSSION

A total of 10 pulps, including the optimum soda and soda-AQ pulps, were obtained adding AQ and ethanol into soda pulping (Table 1). Pulp yield was plotted against kappa number for soda-ethanol pulps in Figure 1 and for soda-AQ-ethanol pulps in Figure 2. Note that pulp yield increased and kappa number decreased when soda method was modified by ethanol and combination of AQ and ethanol. A higher pulp yield with soda-ethanol or soda-AQ-ethanol pulps, compared to the soda method, was due to the higher hemicellulose retention (Atik, 2002; Copur et al., 2007; Lowendahl and Samuelson, 1978; Nelson and Irvine, 1992; Mc Gee and April, 1982). In this study, between pulp yield and kappa number, a strong correlation (R^2 = 98% and R^2 = 97%) was observed with soda-ethanol and soda-AQ-ethanol pulps, respectively (Figures 1 and 2). This finding indicates that the relationship between pulp yield and kappa number observed previously by Kleppe (1970) and Copur et al. (2005) in single method and single source of raw material could apply on various pulping methods as well. The conclusion that can be drawn from this finding is that kappa number could be used to estimate the pulping yield for soda-ethanol and soda-AQ-ethanol methods.

The effect of adding ethanol into optimum soda pulping, showed that the addition of 20, 30, 40 and 50% ethanol led to a yield increase of 7.71, 9.44, 13.5 and 14.0% and kappa number decrease of 24.7, 25.6, 41.1 and 50.8%, respectively. The results indicate that adding ethanol to the conventional soda process was effective for improving both delignification and the physical properties of cotton stalk pulps. It was found that, the delignification proceeded more rapidly and more selectively with ethanol-alkali than with alkali alone, giving higher yields at a given kappa number. Similar results were found by Sahin (2003) for jute soda organosolv pulps.

Moreover, addition of 20, 30, 40 and 50% ethanol into optimum soda-AQ pulp led to a yield increase12.1, 14.6, 14.9 and 15.0% and kappa number decrease of 44.2, 59.2, 67.6 and 85.6% compared to the soda pulping,

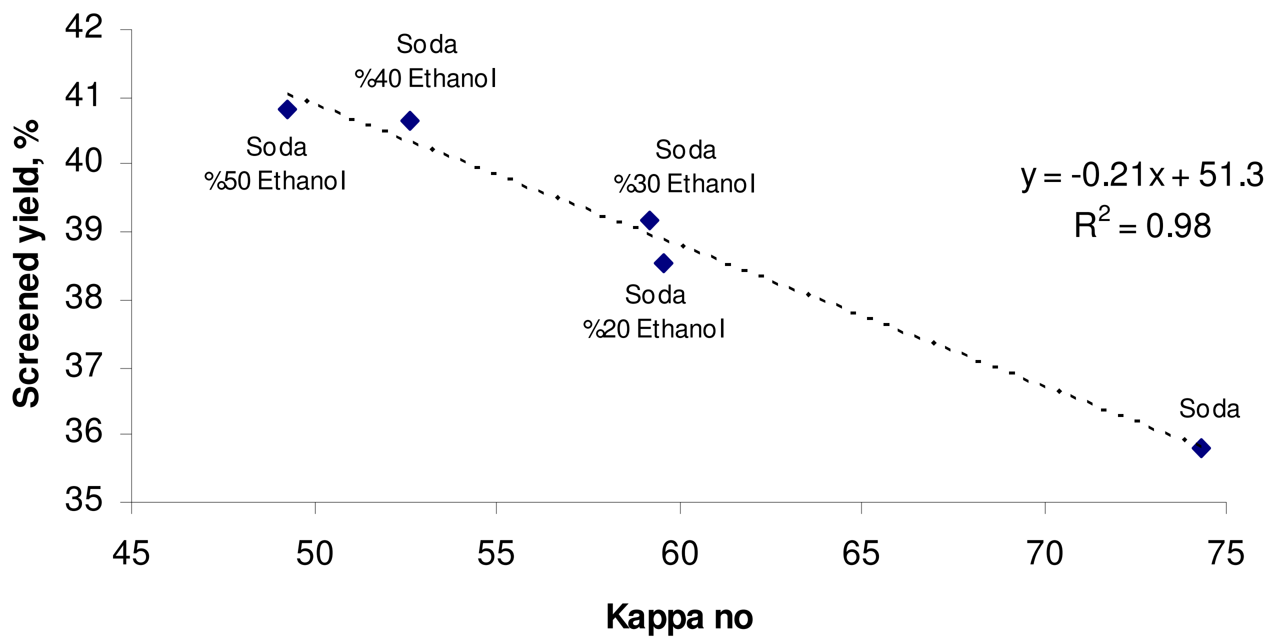

Figure 1. Screened yield vs. kappa number with pulping methods as parameter.

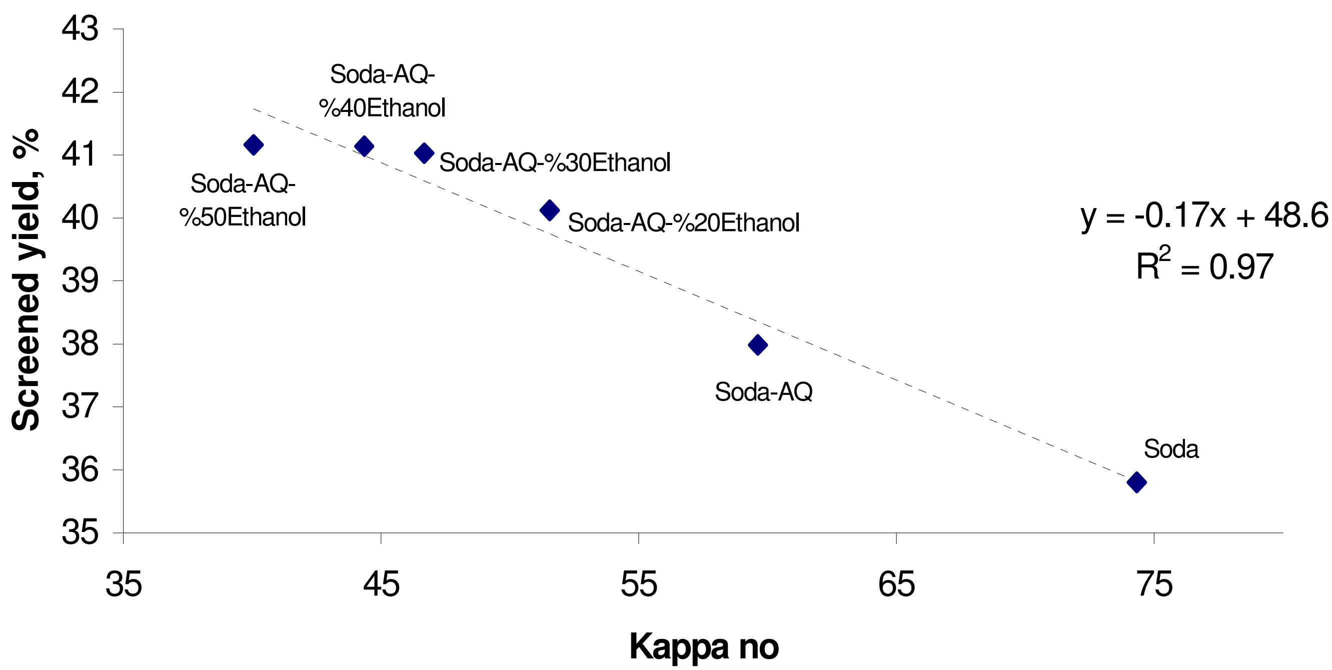

Figure 2. Screened yield vs. kappa number with pulping methods as parameter.

respectively (Table 1). Therefore, it can be concluded that pulps with lower kappa numbers could be achieved when AQ and ethanol are added together to the soda pulping. This shows that, addition of AQ and ethanol in soda pulp can be used to reach a certain kappa number in a shorter cooking time, resulting in advantages of shorter process and reduced energy consumption.

In terms of the amount of screening rejects, compared to the soda pulp, soda-ethanol and soda-AQ-ethanol pulps resulted in lower rejects. They observed a significant reduction in pulp rejects when 0.15% AQ and 50% ethanol were used in soda pulping. The potential effect of

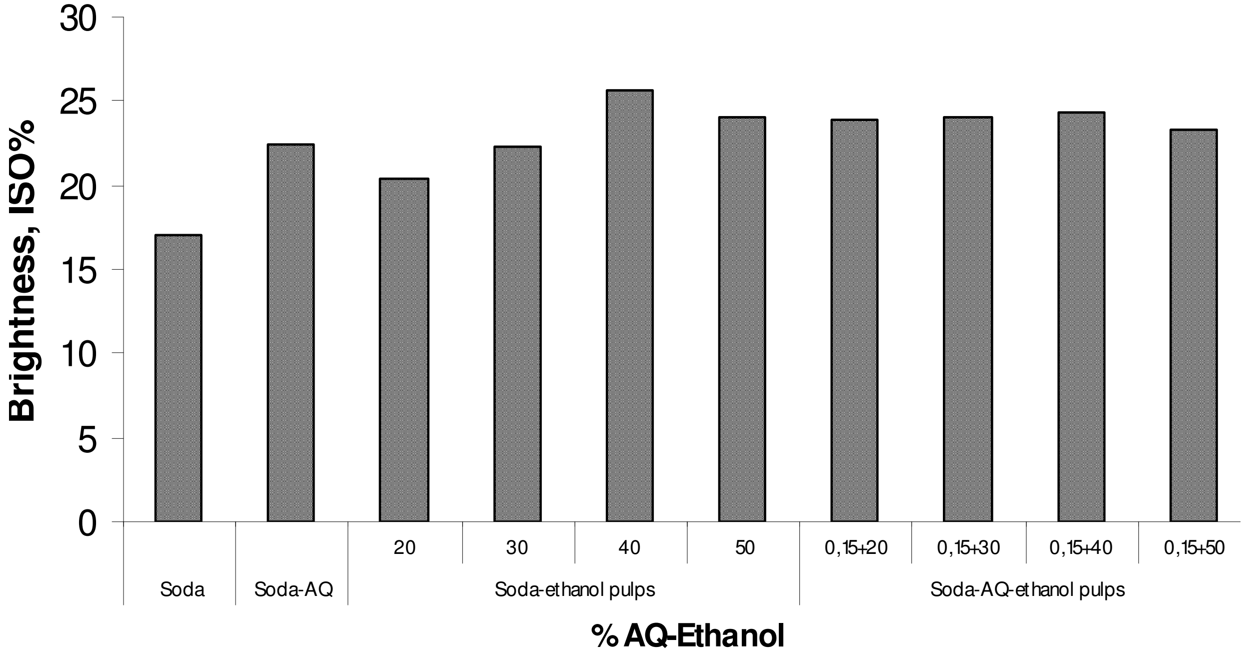

Figure 3. Effect of ethanol on soda and soda-AQ pulp's brightness.

screening rejects on pulp yield is two-fold. If rejects are returned to the process for re-cooking, it may result in slightly lower pulp yield; if rejects are refined and added to the screened pulp, the yield of the pulp remains the same but kappa number of the pulp increases. On the other hand, compared to the soda pulp, soda-ethanol and soda-AQ-ethanol pulps resulted in higher viscosity.

Adding ethanol into optimum soda pulping, the results showed that the addition of 20, 30, 40 and 50% ethanol led to a viscosity increase of 9.30, 11.4, 14.4 and 17.6%, respectively. However, adding ethanol into optimum soda-AQ pulping, the results showed that the addition of 20, 30, 40 and 50% ethanol led to a viscosity increase of 12.3, 19.7, 25.9 and 28.0% are compared to the soda pulping, respectively. It can be concluded that pulps with higher viscosity could be achieved when AQ and ethanol are added together to the soda pulping.

The Elrepho brightness of unbleached hand sheets was measured and tabulated in Table 1. Hand sheets from soda-AQ-ethanol pulps gave higher brightness than the other pulping methods in general. Addition of 40% ethanol in soda pulping gave the highest brightness (Figure 3). In terms of pulp strength properties, adding ethanol or the combination of AQ and ethanol had a significant effect on the ease of pulp refining, compared to the soda pulping (Table 2). A significant ease on pulp refining was observed when 0.15% AQ and 40% ethanol were added into soda cook. The ease in beat ability of ethanol added pulps may mean some energy savings in refining. A faster rate of refining associated with ethanol with/without AQ could be attributed to differences in the relative amounts of holocellulose and lignin contents and higher hemicellulose content enhancing swelling and flexibility.

Refining had a positive effect on tensile and burst strength for all pulps, and when pulps were refined to 0.5 and 1 (min.) in PFI mill, the tensile index of the pulps increased as shown in Table 2 and Figure 3. Higher tensile and burst indices brought about by refining could be explained with the refining effects of external and internal fibrillations. When the unrefined (0 min.) optimum soda and soda-ethanol pulps were compared, the obtained data indicated 10.8, 13.3, 30.7 and 0.01% increase in tensile indices (Figure 4) in soda-ethanol pulps, respectively. Also, the burst indices of unrefined (0 min.) soda ethanol pulps were higher than soda pulp except pulp of soda-20% ethanol. On the other hand, adding ethanol into optimum soda-AQ pulp resulted in more increase in the strength properties; an increase of 32.5, 53.6, 51.2 and 44.0% in tensile indices (Figure 4) and 7.80, 37.7, 20.8 and 9.09% in burst indices (Figure 5) were observed for pulps of soda-AQ-20, 30, 40 and 50% ethanol compared to the soda pulp, respectively. The soda-ethanol pulp produced using 40% ethanol had the highest tensile and burst indices.

In terms of tear index, adding 20% ethanol into soda pulp exhibited the highest tear index (1 min. PFI) compared to other soda-ethanol pulps (Figure 6). For soda-AQ-ethanol pulps, soda- 0.15% AQ- 30% ethanol pulps gave the highest tear index (1 min. PFI). The lowest tear index in all pulps observed with soda-0.15% AQ-30% ethanol pulp (0 min. PFI) comprising highest hemicellulose

Table 2. Pulp PFI data and paper physical properties.

Pulp	PFI, min.	SR, mL	Tensile index, Nm/g	Tear index, mNm^2/g	Burst index, $kPam^2/g$
	0	30	16.6	3.84	0.77
Soda (%18AA)	0.5	54	24.4	4.88	1.35
	1	59	24.6	5.76	1.38
	0	48	26.6	4.89	1.37
Soda-%0.15 AQ	0.5	61	28.5	5.54	1.53
	1	70	28.6	6.34	1.76
	0	38	18.4	4.16	0.74
Soda-%20 Ethanol	0.5	69	27.8	5.42	1.33
	1	82	28.6	6.84	1.47
	0	41	18.8	3.74	0.85
Soda-%30 Ethanol	0.5	62	28.1	5.54	1.38
	1	74	31.3	5.61	1.68
	0	49	21.7	4.69	1.03
Soda-%40 Ethanol	0.5	72	29.1	5.76	1.97
	1	79	35.6	5.76	2.16
	0	48	16.7	3.34	0.80
Soda-%50 Ethanol	0.5	70	23.2	4.21	1.11
	1	74	29.8	3.78	1.16
Soda-%0.15 AQ-%20 Ethanol	0	50	22.0	3.79	0.83
	0.5	70	27.0	5.08	1.31
	1	71	28.0	5.21	1.44
Soda-%0.15 AQ-%30 Ethanol	0	46	25.5	4.58	1.06
	0.5	73	34.1	5.63	1.58
	1	78	35.2	5.85	1.61
Soda-%0.15 AQ-%40 Ethanol	0	48	25.1	3.14	0.93
	0.5	73	33.4	4.14	1.40
	1	89	34.1	5.49	1.46
Soda-%0.15 AQ-%50 Ethanol	0	49	23.9	4.49	0.84
	0.5	72	30.4	4.83	1.39
	1	80	32.3	4.80	1.46

and lowest lignin contents.

Conclusions

Adding ethanol into soda pulping resulted in an increase in pulp yield and reduction in both kappa number and screening rejects. The benefits of AQ and ethanol addition into soda pulping were a significant increase in pulp yield and reduction in kappa number and screening rejects. Positive effects of AQ and ethanol in pulping were brought about by their prevention of cellulose degradation, which resulted in pulps with higher viscosity. Addition of 40% ethanol in soda pulping gave the highest brightness and tensile and burst strength.

The results shown that although, the paper behaviours strongly affected by the addition of solely AQ chemicals, the effect of ethanol had further enhancement by AQ

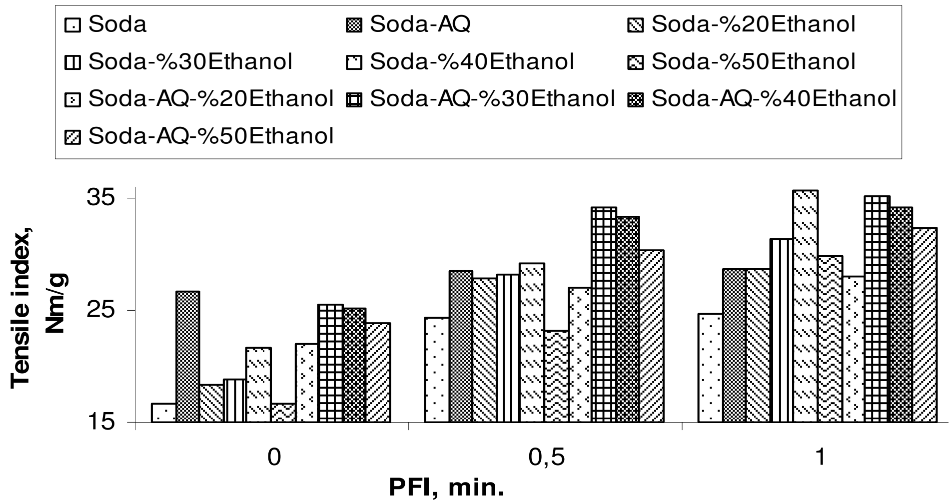

Figure 4. Effect of ethanol on soda and soda-AQ pulp's tensile index.

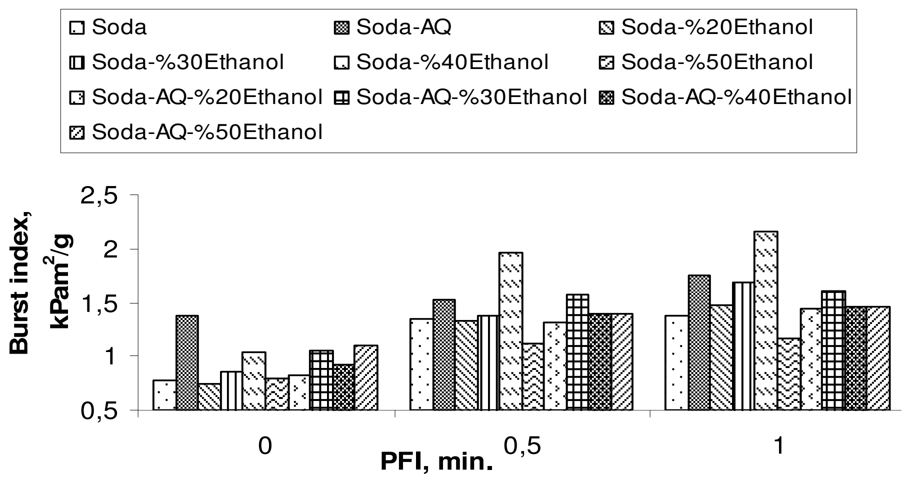

Figure 5. Effect of ethanol on soda and soda-AQ pulp's burst index.

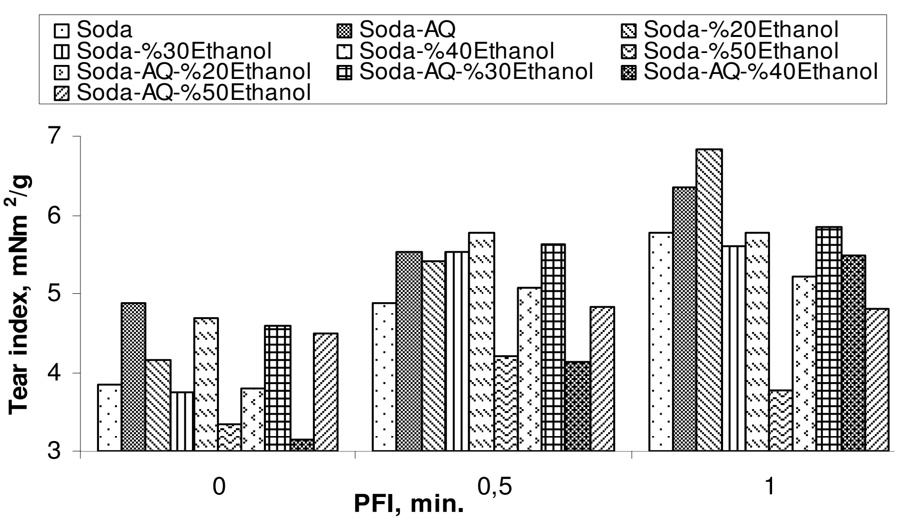

Figure 6. Effect of ethanol on soda and soda-AQ pulp's tear index.

addition. It can be said that it will be interesting to search the effect of ethanol and AQ mixtures on the paper behaviours.

REFERENCES

Akgul M, Tozluoglu A (2009). A comparison of soda and soda-AQ pulps from cotton stalks. Afri. J. Biotechnol. 8(22): 6127-6133.

Atchison JE (1996). Twenty-five years of global progress in nonwood plant fiber repulping. Tappi J., 79: 87–95.

Atic C, Immamoglu S, Valchev I (2005). Determination of spesific beating energy-applied on certain pulps in a valley beater. J. Univ. Chem. Technol. Metallurgy 40 (3): 199-204.

Atik C (2002). Soda-AQ pulping of okra stalks. Cell. Chem. Technol., 3-4: 353-356.

Copur Y, Makkonen H, Amidon TE (2005). The prediction of pulp yield using selected fiber properties. Holzforchung, 59: 477-480.

Copur Y, Tozluoglu A, Karademir A (2007). Pulping of licorice: An alternative raw material to produce pulp. Cell. Chem. Technol., 41(2-3): 155-159.

El-Sakhawy M, Lonnberg B, Ibrahim AA, Fahmy Y (1995). Organosolv Pulping 2: Ethanol pulping of cotton stalks. Cellulose Chem. Technol., 29(3): 315-329.

Goel A, Jewell M, Tschirner U, Ramaswamy S (2000). Comparison of refining response of soda AQ and organosolv wheat straw pulps with traditional wood pulps. Tappi Pulping/Process and Product Quality Conference, pp. 1071-1081.

Grahama GA, Stoyanov AP, Ueda M, Yahiaoui A (1999). Sugar-cellulose composites II: The properties of paper containing monosaccharides. Tappi J., 82(4): 196-202.

Gumuskaya E, Usta M, Balaban M (2007). Carbohydrate components and crystalline structure of organosolv hemp (*Cannabis sativa* L.) bast fibers pulp. Bioresour. Technol., 98(3): 491-497.

Kleppe PJ (1970). Kraft pulping. Tappi J., pp. 35-47.

Kubes GJ, Macleod JM, Fleming BI, Bolker HI (1981). Pulping with an alkaline liquor containing a cyclic keto compound and an amino compound. United States Patent 4248663.

Lowendahl L, Samuelson O (1978). Carbohydrate stabilization during soda pulping with addition of anthraquinone. Tappi J., 61(2): 19-21.

Mc Gee JK, April GC (1982). Chemicals from Renewable Resources: Hemicellulose Behavior During Organosolv Delignification of Southern Yellow Pine, Chem. Eng. Commu., 19: 49-56.

Mohamed IMN, Nor NMY, Azian H, (2006). Comparison Studies Between Soda Lignin and Soda-anthraquinone Lignin in Terms of Physico-chemical Properties and Structural Features. J. Appl. Sci., 6(2): 292-296.

Moriya RY, Goncalves AR, Faria FP (2005). Enzymatic bleaching of organosolv sugarcane bagasse pulps with recombinant xylanase of the fungus *Humicola grisea* and with commercial Cartazyme HS xylanase. Applied Biochemistry and Biotechnology - Part A Enzyme Eng. Biotechnol., 121-124: 195-203.

Nelson PJ, Irvine GM (1992). Tearing resistance in soda-AQ and kraft pulps. Tappi J., 75(1): 163-166.

Pourjoozi M, Mohammadi-Rovshandeh J, Navaee-Ardeh S (2004). Bleachability of rice straw organosolv pulps. Iranian Polymer J., 13(4): 275-280.

Puuronen M, Muurinen E, Sohlo J (1995). Organosolv pulping of reeds, 8th International Symposium on Wood and Pulping Chemistry, Helsinki, Finland: Proceedings,2: Poster Presentations, pp. 467-472.

Rodríguez A, Moral A, Serrano L, Labidi J, Jiménez L (2008a). Rice straw pulp obtained by using various methods. Bioresour. Technol., 99(8): 2881-2886.

Rodríguez A, Serrano L, Moral A, Jiménez L (2008b). Pulping of rice straw with high-boiling point organosolv solvents. Biochem. Engine. J., 42(3): 243-247.

Rodríguez A, Serrano L, Moral A, Pérez A, Jiménez L (2008c). Use of high-boiling point organic solvents for pulping oil palm empty fruit bunches. Bioresour. Technol., 99(6): 1743-1749.

Sahin HT (2003). Base-catalyzed organosolv pulping of jute. Journal of Chemical Technol. Biotechnol., 78(12): 1267 – 1273.

Sanjuan DR, Gomez DF (1991). Pulpeo organosolv modificado con bagazo de cana (Modified Organosolv Pulping with Sugarcane Bagasse), 24o Congresso Anual de Celulose e Papel (24th Pulp and Paper Annual Meeting) pp. 123-136.

Shatalov AA, Pereira H (2005). Arundo donax L. reed: New perspectives for pulping and bleaching. Part 4. Peroxide bleaching of organosolv pulps. Bioresour. Technol., 96(8): 865-872.

Sixta H (2006). Chemical pulping Part I, Wiley-VCH Verlag GmbH&Co. KGaA, Weinheim, ISBN: 3-527-30999-3.

Tjeerdsma BB, Zomers FHA, Wilkinson EC, Sierra-Alvarez R (1994). Modeling organosolv pulping of hemp [*Cannabis sativa*]. Holzforschung, 48(5): 415-422.

Tschirner U, Ramaswamy S, Goel A (2002). Effect of cereal straw fiber addition to papermaking furnish, Annual Meeting - Technical Section. Canadian Pulp and Paper Association, Preprints. A301-A304.

Xu F, Liu CF, Geng ZC, Sun JX, Sun RC, Hei BH, Lin L, Wu SB, Je J (2006). Characterisation of degraded organosolv hemicelluloses from wheat straw. Polymer Degradation Stability, 91(8): 1880-1886.

Zomers FHA, Gosselink RJA, Tjeerdsma BF (1993). Organosolv pulping and test paper characterization of fiber hemp. Pulping Conf. (Atlanta) Proc., 2: 475-484.