Effect of Xylanase Pretreatment on the Kraft Pulping of Poplar

Mehmet Akgül,[a] Mehmet Onurhan Gücüş,[b,*] Birol Üner,[c] and Celil Atik [d]

This study aimed to determine the influence of prehydrolysis of wood chips on the kraft pulping of *Populus x euramericana*. Optimum cooking conditions were determined by evaluating different alkali concentrations and cooking periods. Xylanase was used to hydrolyze chips before cooking. Prehydrolysis process increased the yield and viscosity of pulp. Consequently, the mechanical properties of paper changed remarkably. In contrast, the optical properties of the unbleached kraft pulp declined due to lignin content.

Keywords: Enzyme treatment; Kraft pulp; Prehydrolysis; Xylanase

*Contact information: a: Karamanoglu Mehmetbey University, 70100 Karaman, Turkey; b: Department of Food Engineering, Karamanoglu Mehmetbey University, 70100 Karaman, Turkey; c: Department of Metallurgy and Materials Engineering, Karamanoglu Mehmetbey University, 70100 Karaman, Turkey; d: Department of Forest İndustry Engineering, İstanbul University, Beyazıt, 34452 Fatih İstanbul, Turkey; *Corresponding author: onurgucus@kmu.edu.tr*

INTRODUCTION

Traditional chemical pulping processes are typically carried out under strong alkaline or acidic cooking conditions. Besides, some chemical and enzymes can be added to process pulp improve yield and properties. Xylanase pretreatment has been the most applied process in recent laboratory research (Parthasarathy 1987; Quick 1999; Zhao *et al.* 2002; Solár *et al.* 2009; Li *et al.* 2011; Salazar *et al.* 2012; Mohieldin 2014; Hassan *et al.* 2018; Zhou *et al*. 2019). The basic approach of this process is to treat wood with chemicals or enzymes before cooking. As a result, the chips are softened, and some content is removed. During the main cooking process, lesser amounts of chemicals and less energy are utilized, and better fiber quality can be obtained.

Xylanase pretreatment has been used to enhance the conventional soda pulping of wheat straw and to evaluate the effect of xylanase pretreatment prior to soda pulping. Zhao *et al.* (2002) found that the pulp obtained from wheat straw pretreated with xylanase had a longer fiber length and a lower fine grain content than the control. The effect of xylanase pretreatment on rice straw unbleached pulp used to obtain nanofibers was examined, with soda and neutral sulfite pulping process used for isolation (Hassan *et al.* 2018). Slightly lower energy consumption (approximately 8%) was recorded for xylanase-treated soda pulp, whereas higher energy consumption (approximately 21%) was recorded for xylanase-treated neutral sulfite pulp relative to the untreated pulps. Xylanase treatment facilitated initial-stage fibrillation to separate fibrils via the removal of easily accessible xylan located mainly among cellulose fibrils of micrometer size but had no substantial effect on nanoscale fibrillation due to difficulties in the removal of xylan located between nanoscale fibrils. However, cellulose nanofibril samples from different xylanase treatments showed large decrease in the degree of polymerization (DP) (Zhou *et al.* 2019).

The use of alkaline and xylanase-assisted pretreatments have been studied. Following alkaline-xylanase treatment of the fibers (AXB-fibers), the required number of bleaching sequences to achieve an 83.3% whiteness index was decreased from 6 to 4. Twostage pretreatment, using a combination of alkaline and xylanase-assisted pretreatments, effectively reduced the number of bleaching sequences required, which reduced the amount of bleaching chemicals required and improved the whiteness of the fibers (Vanitjinda *et al.* 2019). When the pretreatment of xylanase enzyme to the mulberry branch fibers was applied, refining energy was reduced by 4%, and the fiber yield remained more than > 85%. Further, the fiber widths increased because of the improved swelling effect of the xylanase pretreatment. In some instances, the fine elements were reduced (Tao *et al.* 2019). Poplar wood is a fast-growing hardwood species. It has the lowest density and porous structure among the hardwood species. Consequently, pulping solution can easily penetrate and remove lignin from poplar wood (Akgül and Kırcı 2009). Therefore, this research aimed to investigate the physical and optical properties of paper produced from poplar wood pretreated with xylanase enzyme. The optimal cooking conditions were determined by evaluating prehydrolyzed pulp properties.

EXPERIMENTAL

Materials

The 10- to 12-year-old poplar wood (*Populus x euramericana* (I-214)) used in this study was obtained from the Düzce-Sakarya-Kocaeli basin (Forest Regional Directorates, Turkey).

Chips Preparation

The chipping process and drying were performed in the Duzce University Forest Products Engineering Laboratory. Then, the chips were sieved, and the appropriate chip size (25 mm × 20 mm × 2 mm) was selected for the cooking process. Air dried chips were cleaned, and a homogenized size was obtained.

Cooking Process

The chips were cooked in a 15-L batch-rotating digester (4rpm) that was heated with electricity. Each cook was performed with 500 g of chips. The wood to liquid ratio was kept constant at 5:1. To determine optimum cooking conditions for the pretreated kraft pulp, a controlled cooking process was carried out. The cooking conditions were given in Table 1. After each cook, the mixture was cooled with water and rinsed with tap water for approximately 1 h. to remove alkali. The pulp was then disintegrated with a laboratory pulp disintegrator for 10 min. After washing, the pulp was stored in airtight polyethylene bags. The dimensions of polyethylene bags were 15 * 30 cm. The results were compared to determine the optimum treatment condition.

Modified Kraft Pulp

Modified kraft pulp was prepared by adding 0.1% anthraquinone (AQ) and 4% polysulphide (PS) into the optimized cooking process.

Enzyme Pretreatment

The optimal conditions were found by testing various proportions according to the xylanase enzyme activity determined for the enzyme pretreatments. The optimal conditions were found where the amount of sugar removed from the chip at pH 8 and at the end of 1.5 h. The application conditions of enzyme 25 IU/g and 50 IU/g, pH values of 8 and 9, and cooking period of 60 min, 90 min, and 120 min were tested.

Table 1. The Control Kraft Cooking Process Used to Determine Optimum Conditions

Cooking Process	Cooking Parameters						
No.	AA* (%)	Sulfidity (%)	Max. Temp. (°C)	Max. Temp. Reaching Period (min)	Cooking Period (min)	AQ*(%)	PS*(%)
KK1	16	25	170	60	60	-	
KK2	16	25	170	60	90	-	
KK3	16	25	170	60	120	-	
KK4	18	25	170	60	60	-	
KK5	18	25	170	60	90	-	
KK6	18	25	170	60	120	-	
KK7	20	25	170	60	60	-	
KK8	20	25	170	60	90	-	
KK9	20	25	170	60	120	-	
KKOPT.	PKOPT.	25	170	60	PKOPT	0.1	
KKOPT.	PKOPT.	25	170	60	PKOPT	-	4

* AA: Active alkali; AQ: Anthraquinone; PS : Polysulphide

Pulpzyme HC enzyme with activity of 1000 IU/g was placed into a polyethylene bag that contained 100 g of wood chips oven dry (OD). The solvent to chip ratio was kept constant at 6:1. The polyethylene bags were placed in a preheated (60 °C) water bath. Reducing sugar analysis was performed on the solutions in the polyethylene bags according to the dinitrosalicylic acid (DNS) method (Miller 1959). After pretreatment, the chips were washed and prepared for the next step in the chemical cooking process.

Physical and Mechanical Properties

The kappa number, viscosity, and mechanical properties were measured for each pulp category. The standard procedures followed for tests were as follows: basis weight was determined according to ISO 536 (2012), density was determined according to ISO 534 (2011), moisture content was determined according to ISO 287 (2017), viscosity was determined according to SCANCM 15:88 (1998), kappa number was determined according to TS ISO 302 (2015), burst strength was determined according to TS EN ISO 2759(2014), tear strength was determined according to TS EN ISO 1974 (2012) thickness was determined according to TN ISO 534 (2012), tensile and elongation properties were determined according to TS EN ISO 1924-2 (2013), and opacity was determined according to TS ISO 2471 (2015).

RESULTS AND DISCUSSION

The kraft process is commonly utilized to obtain pulp. The optimum cooking conditions were identified as those of KK4 due to the high viscosity, high degrees of polymerization (DP), high screened yield, and low kappa number achieved. Pretreatment and chemical additions were carried out in the KK4 cooking process. Optimized conditions are shown in Table2. Polysulphide and AQ are the most common additives for improving pulp properties due to their selectivity. Adding PS and AQ into kraft pulping resulted in higher pulp viscosity, which indicated that the addition of these additives prevented cellulose degradation in pulping. The polysulphide pulping technique is used in kraft mills to increase pulp yield (Vaaler 2008). In general, the yield increase depends on the amount of sulphur added, pulping conditions, and the wood species. Multiple pre-treatment methods and techniques have been applied to increase the accessibility of the cellulose polymers.

Table 2. Optimized Cooking Conditions

Cooking Process	Screened Yield (%)	Rejects (%)	Total Yield (%)	Kappa No.	Viscosity (cm^3/g)	DP	Holocellulose (%)	Lignin (%)	Alcohol-Benzene Sol. (%)	Hot Water Sol. (%)
KK4	46.13	0.83	46.96	22.26	888	1318	96.41	3.34	0.96	1.67
KK10	48.72	0.12	48.84	17.8	925	1379	96.78	2.67	0.88	1.75
KK11	47.82	0.21	48.03	19.99	935	1396	96.44	3	0.33	1.87

Note: KK_{OPT} = KK4; K10 = KK4 + AQ; K11 = KK4 + PS
KK4 = Kraft optimum; AQ = Anthraquinone; PS = Polisulphur; KSLNZ = Xylanase

Pre-treated pulp production systems have become important in recent years due to environmental concerns, energy usage, and efforts to increase the efficiency of the pulping process (Martin *et al.* 2000). Pretreatments aim to make the fibrous raw materials more suitable for the pulping and papermaking process. Table 3 shows that lignin content was similar for each cooking process. However, the DP of cellulose and viscosity were higher when xylanase pretreatment was applied. Lignin amounts decreased or remained the same in kraft, modified kraft, and kraft with pre-treatment. In contrast, the DP of cellulose increased. Oxidative pretreatment strengthens carbohydrates against degradation and activates during the pulping process to remove lignin. Chemical consumption was reduced, and the final brightness was improved with the application of this enzyme. During the pulping process, xylan deposits onto fibers and protects them against alkali. Xylanase enzyme reacts with xylan in wood and breaks lignin-carbohydrate bonds. Therefore, lignin was easily reached and extracted using a solvent (Tarasov *et al.* 2018). During this process, some hemicelluloses were also removed from the pulp and the holocellulose content was reduced. Pretreatment of the chips with enzyme reduced the screened yield. In contrast, the total yield, viscosity, and DP increased. Enzyme treatments cause physical loosening of fiber walls due to the partial depolymerization of the hemicellulose chain. In addition, xylan precipitation onto cellulose fibers prevents lignin removal. Pretreatment reduces the xylan content and overcomes this protection, which aids lignin removal and changes the chemistry of the resulting fiber.

Pretreatment improved the physical and mechanical properties. Xylanase may have changed the crystalline region of fiber and improved fibrillation, which enhanced fiber-to-fiber bonding, increased breaking length, and increased the tensile index (Table 4). In contrast, Batalha *et al.* (2011) found different results when kraft pulp was treated with xylanase. In their study, fiber was treated after the kraft pulping process, and xylanase treatment reduced the tensile index. Fibrillation may improve inter-fiber bonding properties, and treatment may change the chemistry of fiber, cause carboxylic acid formation, and increase hydrogen bonding ability (Liu *et al.* 2012).

Table 3. Pulp Properties

Cooking Process	Screened Yield (%)	Rejects (%)	Total Yield (%)	Kappa No.	Viscosity (cm^3/g)	DP	Holocellulose (%)	Lignin (%)	Alcohol-Benzene Sol. (%)	Hot Water Sol. (%)
KK4	46.13	0.83	46.96	22.26	888	1318	96.41	3.34	0.96	1.67
KK4-AQ	48.72	0.12	48.84	17.80	925	1379	96.78	2.67	0.88	1.75
KK4-PS	47.82	0.21	48.03	19.99	935	1396	96.44	3.00	0.33	1.87
KK4-KSLNZ	45.64	4.47	50.11	24.48	1525	2396	94.18	3.64	2.54	1.2
KK4-KSLNZ-AQ	47.96	0.08	48.04	14.38	1350	2094	94.92	2.15	1.08	1.2
KK4-KSLNZ-PS	39.5	17.2	56.7	28	1953	3149	95.48	4.2	2.62	1.1

Table 4. Pulp and Paper Properties (Mechanical and Optical)

Cooking	Pretreatment Conditions			Schopper Riegler degrees	Tensile Index	Elongation (%)	Burst Index ($kPa.m^2/g$)	Tear Index ($mN.m^2/g$)	Breaking Length (km)	Brightness (%)	Opacity (%)	Whiteness (%)
	AQ (%)	PS(%)	Xylanase									
KK4	-	-	-	44.7	89.66	2.05	4.91	6.87	9.143	29.72	91.54	34.45
KK4-AQ	0.1	-	-	42	80.05	1.62	4.44	6.42	8.169	27.37	89.23	30.34
KK4-PS	-	4	-	40	107.76	2.28	6.21	8.24	10.838	19.55	90.65	28.54
KK4-KSLNZ	-	-	50	57	114.93	1.79	7.23	4.66	12.645	18.54	95.65	31.56
KK4-KSLNZ-AQ	0.1	-	50	49	118.04	1.84	6.49	4.74	12.037	20.67	95.23	29.65
KK4-KSLNZ-PS	-	-	50	52	120.02	1.99	7.65	4.89	12.965	19.43	94.65	27.54

The xylanase treatment caused higher porosity and fibrillation of pulp fibers, and the fibers became more flexible and released more fibrils. The hydrolysis of xylan and the removal of surface lignin eased the pulping process and resulted in better fiber characteristics. However, the lignin amount in pulp varies. This could have caused increased opacity, reduced brightness, and decreased whiteness (Table 4).

Paper optical properties can be expressed as brightness, opacity, and whiteness. These properties varied with the light absorption and reflectivity. Brightness is a feature associated with the ability to reflect light centered at 457 nm wavelength. Enzyme-treated pulp had the lowest brightness. This may have been due to rendered lignin cellulose linkages causing precipitation onto fibers, which could have prevented the penetration of chemicals. Consequently, increased opacity and the reduced removal of chemicals decrease the brightness. This is related to lignin carbohydrate complex. Lignin and cellulose are maybe linked each other in contrast to lignin hemicellulose cellulose complex.

CONCLUSIONS

The aim of the oxidative pretreatment was to protect the carbohydrates against degradation and oxidation and activate to the pulp for the delignification process. The pretreatment process resulted in higher yield and improved pulp quality. The pretreatment process employed in this study is an efficient method to remove lignin. Therefore, it can provide energy savings to factories that produce pulp and high-quality fibers and improve strength properties.

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REFERENCES CITED

Akgül, M. A., and Kırcı, H. (2009). "An environmentally friendly organosolv (ethanol-water) pulping of poplar wood," *Journal of Environmental Biology* 30(5), 735-740.

Batalha, L. R., Da Silva, J., Jardim, C., Oliveira, R., and Colodette J. (2011). "Effect of ultrasound and xylanase treatment on the physical-mechanical properties of bleached eucalyptus kraft pulp," *Natural Resources* 2(2), 125-129. DOI: 10.4236/nr.2011.2201

Hassan, M., Berglund, L., Hassan, E., Abou-Zeid, R., and Oksman, K. (2018). "Effect of xylanase pretreatment of rice straw unbleached soda and neutral sulfite pulps on isolation of nano fibers and their properties," *Cellulose* 25, 2939-2953. DOI: 10.1007/s10570-018-1779-2

ISO 287 (2017). "Paper and board – Determination of moisture content of a lot—Oven-drying method," International Organization for Standardization, Geneva, Switzerland.

ISO 534 (2011). "Paper and board – Determination of thickness, density and specific volume," International Organization for Standardization, Geneva, Switzerland.

ISO 536 (2012). "Paper and board – Determination of grammage," International Organization for Standardization, Geneva, Switzerland.

Li, X., Cai, Z., Horn, E., and Winandy, J. E. (2011). “Effect of oxalic acid pretreatment of wood chips on manufacturing medium-density fiberboard,” *Holzforschung* 65(5), 737-741. DOI: 10.1515/HF.2011.060

Liu, N., Qin, M., Gao, Y., Li, Z., Fu, Y., and Xu, Q. (2012). “Pulp properties and fiber characteristics of xylanase-treated aspen APMP,” *BioResources* 7(3), 3367-3377. DOI: 10.15376/biores.7.3.3367-3377

Martin, N., Angliani, N., Einstein, D., Khrushch, M., Worrell, E., and Price, L. (2000). *Opportunities to Improve Energy Efficiency and Reduce Greenhouse Gas Emissions in the U.S. Pulp and Paper Industry*, Berkeley, CA: Lawrence Berkeley National Laboratory, (LBNL 46141) DOI: 10.2172/767608

Miller, G. L. (1959). “Use of dinitrosalicylic acid reagent for determination of reducing sugar,” *Analytical Chemistry* 31, 426-428. DOI:10.1021/ac60147a030

Mohieldin, S. D. (2014). “Pretreatment approaches in non-wood plants for pulp and paper production: A review,” *Journal of Forest Products and Industries* 3(2), 84-88.

Parthasarathy, V. R. (1987). *Oxidation of Loblolypine (Pinusteada L.) with Alkaline Hydrogen Peroxide Prior to Soda AQ Pulping*, Ph.D. Dissertation, North Carolina State University, Raleigh, NC, USA.

Quick, S. A. (1999). *Modification of the Soda/AQ Pulping Process as an Alternative to the Kraft Process for the Production of Softwood Pulp*, Master’s Thesis, North Carolina State University, Raleigh, NC, USA.

Salazar, C., Mendonça, R.T., Baeza, J., and Freer, J. (2012). “Kraft pulping and ECF bleaching of *Eucalyptus globulus* pretreated by the white-rot fungus *Ceriporiopsis subvermispora*,” *Acta Scientiarum Technology* 34(3), 277-281. DOI: 10.4025/actascitechnol.v34i3.12410

SCAN CM 15:88 (1998). “Viscosity in cupri-ethylenediamin (CED) solution,” Scandinavian Pulp, Paper and Board Testing Committee, Stockholm, Sweden.

Solár, R., Geffertova, J., Mamoň, M., Geffert, A., and Košíková, B. (2009). “Influence of alkaline and alkaline/oxidation pre-treatments of hornbeam wood on the properties of kraft pulp,” *Cellulose Chemistry and Technology* 43(4-6), 163-177.

Tao, W., Guo, L., Meng, A., Wang, L., Ren, H., and Zhai, H. (2019). “Effects of xylanase pretreatment on the quality of refiner mechanical mulberry branch fibers,” *Advances in Polymer Technology* 2019, article ID 6252013. DOI: 10.1155/2019/6252013

Tarasov, D., Leitch, M., and Fatehi, P. (2018). “Flow through autohydrolysis of spruce wood chips and lignin carbohydrate complex formation,” *Cellulose* 25(2):1377–93. DOI: 10.1007/s10570-017-1643-9

TS ISO 302 (2015). “This standard specifies a method for the determination of the kappa number of pulp,” Turkish Standards Institution, Ankara, Turkey.

TS EN ISO 534 (2012). “Paper and board – Determination of thickness, density and specific volume,” Turkish Standards Institution, Ankara, Turkey.

TS EN ISO 1924-2 (2013). “Paper and board – Determination of tensile properties – Part 2: Constant rate of elongation method (20 mm/min),” Turkish Standards Institution, Ankara, Turkey.

TS EN ISO 1974 (2012). “Paper – Determination of tearing resistance – Elmendorf method,” Turkish Standards Institution, Ankara, Turkey.

TS EN ISO 2471 (2015). “This international standard specifies a method for the determination of the opacity (paper backing) of paper by diffuse reflectance,” Turkish Standards Institution, Ankara, Turkey.

TS EN ISO 2759 (2014). "This standard specifies a method for measuring the bursting strength of board submitted to increasing hydraulic pressure," Turkish Standards Institution, Ankara, Turkey.

Vaaler, D. A. G. (2008). *Yield-increasing Additives in Kraft Pulping: Effect on Carbohydrate Retention, Composition and Handsheet Properties*, Ph.D. Dissertation, Norwegian University of Science and Technology, Trondheim, Norway.

Vanitjinda, G., Nimchua, T., and Sukyai, P. (2019). "Effect of xylanase-assisted pretreatment on the properties of cellulose and regenerated cellulose films from sugarcane bagasse," *International Journal of Biological Macromolecules* 122, 503-516. DOI: 10.1016/j.ijbiomac.2018.10.191

Zhao, J., Li, X., Qu, Y., and Gao, P. (2002). "Xylanase pretreatment leads to enhanced soda pulping of wheat straw," *Enzyme and Microbial Technology* 30(6), 734-740. DOI: 10.1016/S0141-0229(02)00050-9

Zhou, H., John, F. S., and Zhu, J. Y. (2019). "Xylanase pretreatment of wood fibers for producing cellulose nanofibrils: A comparison of different enzyme preparations," *Cellulose* 26(1), 543-555. DOI: 10.1007/s10570-019-02250-1

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