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THE EFFECT OF OXALIC ACID PRETREATMENT ON ALKALI PULPING PROCESS

Birol Üner
Süleyman Demirel University, Faculty of Forestry, Department of Forest Products Engineering
Isparta, Turkey

Mehmet Akgül
Necmettin Erbakan University Seydişehir Ahmet Cengiz, Engineering Faculty
Department of Material Engineering
Seydişehir, Konya, Turkey

M.Onurhan Gücüş
Istanbul University, Institute of Science
Istanbul, Turkey

Serkan Demir
Düzce University, Institute of Science
Düzce, Turkey

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ABSTRACT

The objective of this study was to determine prehydrolysis process on kraft and soda pulping process. Optimum cooking conditions were determined by different alkali concentration and cooking period. Oxalicacid was used to hydrolyzechip before cooking. Prehydrolysis proces increased the yield and viscosity of pulp. Incontrast, mechanical properties of paper were not changed significantly. Optical properties were decreased due to lignin content.

KEYWORDS: Prehydrolysis, oxalicacid, kraft, soda, pulp, paper.

INTRODUCTION

Traditional chemical pulping process usually carried out under strong alkaline or acidic cooking conditions. Cooking liquor has often contains environmentally polluting sulfur compounds in the composition (Kocurek 1989). As a result of that, the paper industry is usually

considered in hostile sector to the environment and is faced with legal pressure (Kordsachia et al. 1992). With today's technology, although the formation of the sulphur containing organic compound creates odor, problems were minimized diffusion to the atmosphere, bleached Kraft pulp is still polluting water with reject (Patt et al. 1992).

With regard to cooking conditions, many variables havean influence on the production of pulp. These parameters are the factors related to the wood material used (wood type, density and chemical composition, chip size, etc.), factors related to the cooking liquor and the factors depending on the implementation of the cooking process (Kırcı 2000). In addition to that, pulping process is also affected by the type and amount of chemicals used in the pretreatment process. In recent years, the pulp producers, in line with technological developments, aimed to less energy and chemical use, high efficiency and carry out their work by determining the quality fiber production (Black 2001). Therefore, the goal of pulp manufacturers to produce bleachable and strong fiber. In this context, extending the cooking period was utilized to remove more lignin from the pulp. However, chemicals has affected to cellulose besides hemicelluloses during extended cooking (Samuelson and Stolpe 1969). Cellulose chains suffer and begins to degrade due to chemical attack. Therefore, producers avoid long-term cooking.

Pretreatment is the most applied process in recent years (Mohieldin 2014, Solar et al. 2009, Salazar et al. 2012, Li et al. 2011). The basic approachof this process is to treat wood chips with chemicals or enzymes before cooking. As a result, the chipsare going to be softened and some contentsare going to leach out (Li et al. 2011). During the main cooking process, less chemicals and energy were utilized, better quality fiber were obtained.

Poplar wood is a fast growing hardwood species. It has lower density and porous structure. Consequently, pulping solvent can easily penetrate and remove lignin (Akgül and Kırcı 2009). Therefore, the objective of this project was to investigate the physical and optical properties of paper produced from poplar wood pretreated with oxalic acid. The optimal cooking conditions were determined by evaluating prehydrolyzed pulp properties.

MATERIAL AND METHODS

Material

Poplar wood (*Populus* x *euramericana* (I-214) in the age of 10-12 used in this study were obtained from Düzce-Sakarya-Kocaeli basin.

Chips preparation

The chipping process was performed byhand and dried in the laboratory. After that, the chips were sieved and appropriate chip size (25 x 20 x 2 mm) was achieved in the cooking process. Air dried chips were cleaned from dust and homogenized size was obtained.

Cooking process

The chips were cooked in a 15 L batch rotating digester (4 rpm) that was heated with electricity. Each cook was performed with 500 OD g of chips. Wood to liquor ratio was kept constant at 5/1. In order to determine optimum cooking conditions for pretreated soda and Kraft pulp, control cooking process was carried out. The cooking conditions were given in Tab. 1 and 2. After each cook, the mixture was cooled with water and rinsed with tap water for about an hour to remove alkali. The pulp were then disintegrated with laboratory pulp disintegrator for 10 min. After washing pulp stored in air tight polyethylene bags.

Oxalic acid pretreatment

Oxalic acid prehydrolysis was carried out with dilute solutions (0.5 – 1 % and 1.5 v/v solutions) for 10 min at 130°C. 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 from each pulp category. The standard procedures followed for tests are listed below. Basis weight: ISO 536 (TS 3122, 1998), density: ISO 534 (TS EN ISO 534, 2006), moisture content: ISO 287 (TS 11093-3, 2001), viscosity: SCAN CM 15:88, kappa: TS ISO 302, burst strength: ISO 3123 (TS EN 2759, 2004), tear strength: TS 4423 EN 21974, thickness: ISO 534 (TS EN ISO 534, 2006), tensile, elongation: ISO 1924-2 (TS 3121-2, 2004), opacity: TS ISO 2471.

Tab.1: The control kraft cooking process to determine optimum conditions.

Cooking	Cooking parameters				
	AA (%)	Sulfidity (%)	Max. temp. (°C)	Max.temp. reachingperiod (min.)	Cooking period (min.)
KK1	18	25	170	60	60
KK2	18	25	170	60	90
KK3	18	25	170	60	120
KK4	20	25	170	60	60
KK5	20	25	170	60	90
KK6	20	25	170	60	120

Tab. 2: The control Soda cooking process to determine optimum conditions.

Cooking	Cooking parameters				
	AA (%)	Sulfidity (%)	Max. temp. (°C)	Max.temp. reaching period (min.)	Cooking period (min.)
KS1	18	-	170	60	60
KS2	18	-	170	60	90
KS3	18	-	170	60	120
KS4	20	-	170	60	60
KS5	20	-	170	60	90
KS6	20	-	170	60	120

RESULTS AND DISCUSSION

The oxalic acid were used in the pre-hydrolysis stagein different amounts, 1.5 % oxalic acid concentration ratio was found to be the most effective amount comparing carbohydrate loss and yield. Therefore, 1.5 % oxalic acid concentration was used in pilot cook of soda and kraft pulp. After consideration of total pulp yield, screened yield, kappa number and viscosity,

the best cooking condition was determined as KS4 for soda and KK4 for Kraft pulping process. As a result of these cooks, optimum yield and viscosity were obtained.Under these conditions, prehydrolysed cook pulp properties were given in Tab. 3. The prehydrolysis treatment with 1.5 % oxalic acid concentration influenced wood chips. As a result, very small difference has been determined among the yield of different cooking process. However, prehydrolysis treatment has made a significant contribution on the pulp viscosity and the DP. Sieved material was obtained below 1 % with the pre-hydrolysis process. Soft Poplar wood helped the chemicals penetrate in and homogeneously dispersed, partial hydrolysis of lignin and hemicelluloses facilitated the release of carbohydrates. Consequently, higher pulp yield was obtained and the less sieved material remained on the screen. Pulp yield was increased around 0.32 to 2.32 %. However, more hemicelluloses was lost in oxalic acid application.

Tab. 3: Determining the soda and kraft optimal cooking conditions and the results of prehydrolysis process.

Cooking	Screened Yield (%)	Screened (%)	Total Yield Verim(%)	Kappa No	Viscosity ($cm^3.g^{-1}$)	DP	Holo-cellulose (%)	Lignin (%)	Alcohol-BenzeneSol. (%)	Hot water Sol. (%)
KK1	45.18	2.14	47.32	27.11	1122	1707	94.75	4.07	0.21	1.77
KK2	45.57	1.12	46.69	25.52	1025	1545	95.24	3.83	0.76	1.62
KK3	44.77	0.73	45.50	23.71	980	1470	96.34	3.56	0.28	1.45
KK4	**46.13**	**0.83**	**46.96**	**22.26**	**888**	**1318**	**96.41**	**3.34**	**0.96**	**1.67**
KK5	44.26	0.74	45.00	21.69	865	1281	97.07	3.25	0.83	1.47
KK6	43.15	0.54	43.69	20.68	834	1230	97.27	3.11	0.11	1.35
KK4-OA	**45.03**	**0.04**	**45.07**	**13.20**	**1275**	**1966**	**97.32**	**1.97**	**0.69**	**0.9**
KS1	37.22	1.38	50.60	2.,8	1214	1862	94.52	3.12	0.31	2.25
KS2	42.64	6.96	49.60	19.35	1204	1844	93.79	2.90	0.98	1.73
KS3	45.58	2.86	48.44	21.77	1234	1896	92.54	3.73	1.51	1.73
KS4	**48.78**	**011**	**48.90**	**15.03**	**1175**	**1770**	**94.79**	**2.25**	**0.97**	**2.53**
KS5	46.68	0.04	46.72	14.43	881	1306	95.05	2.16	0.92	2.45
KS6	45.23	004	45.27	16.31	736	1071	94.47	2.45	1.10	1.25
KS4-OA	**49.10**	**0.12**	**49.22**	**19.83**	**1410**	**2197**	**94.88**	**3.17**	**1.29**	**0.6**

Paper properties were given in Tab. 4 for oxalic acid hydrolyzed pulp. Strength properties of paper were slightly reduced in the prehydrolysed pulp (Tab. 4). One of the factors that directly affect the breaking length was fibers individual strength properties and the fiber to fiber bonding. In addition to that, breaking length was directly affected by the number of fibers to fiber bonding (Eroğlu and Usta 2004). Moreover; applied pulping methods, chemical type and the amounts, temperature and time may lead to significant strength gains or losses by affecting the structure of the fibers. Oxalic acid pretreatment cause to leach out some of hemicelluloses and forms new carboxylic acid ends which leads to better swelling ability of the fiber. Swollen fiber becomes more comformable to each other and gives similar or better properties (Samuelsen and Stolpe 1969; Allison, 1985; Parthasarathy 1987; Quick 1999; Wathen 2006).

Tab. 4: The physical properties of the paper obtained from the pre-treated poplar wood chips.

Cooking	Pretreatment condition OA (%)	Thickness (µm)	Gramaj (%)	Tensile index ($Nm.g^{-1}$)	Elongation (%)	Burst index ($kPa.m^2.g^{-1}$)	Tear index ($mN.m^2.g^{-1}$)	Breaking length (km)	Brightness %
KK4		1.09	99.19	89.66	2.05	4.91	6.87	9.143	29.72
KK4-OA	1,5	1.15	87.70	80.26	1.64	5.02	6.34	8.185	25.51
KS4		0.75	67.65	10.31	1.45	6.10	6.643	10.423	30.82
KS4-O4	1,5	0.76	69.35	101.07	1.45	5.99	5.941	10.103	27.57
Cooking	**Pretreatment condition OA (%)**	**Thickness (µm)**	**Gramaj (%)**	**Tensile index ($Nm.g^{-1}$)**	**Elongation (%)**	**Burst index ($kPa.m^2.g^{-1}$)**	**Tear index ($mN.m^2.g^{-1}$)**	**Breaking length (km)**	**Brightness %**
KK4		1.09	99.19	89.66	2.05	4.91	6.87	9.143	29.72
KK4-OA	1,5	1.15	87.70	80.26	1.64	5.02	6.34	8.185	25.51
KS4		0.75	67.65	101.31	1.45	6.10	6.643	10.423	30.82

One of the most important optical properties of the paper is the brightness. The brightness is the percentage of diffuse reflected light from a thick layer of paper. The prehydrolysis of poplar chips affected the paper brightness and reduced. This could be due to the carbonyl group and carboxylic acid formation in the pulp (Silva et al. 2011).

CONCLUSIONS

The use of easy to cultivate poplar wood in the cooking process emancipate this technology to dependent of forest. The properties of the pulp produced by this OA pretreatment process are quite different from those obtained via soda and Kraft process. The pretreatment process improves the DP and the viscosity of pulp while retaining desirable mechanical and optical properties. The oxalic acid pretreatment process provides valuable pulp properties at higher yields. Screen loss decreases with the oxalic acid pretreatment.

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Birol Üner*
Süleyman Demirel University
Faculty of Forestry
Department of Forest Products Engineering
Dogu Kampusu 32260 Isparta
Turkey
Corresponding author: biroluner@sdu.edu.tr

Mehmet Akgül
Necmettin Erbakan University Seydişehir Ahmet Cengiz
Engineering Faculty
Department of Material Engineering
Seydişehir
Konya
Turkey

M.Onurhan Gücüş
Istanbul University
Institute of Science
İstanbul
Turkey

Serkan Demir
Düzce University, Institute of Science
Düzce, Turkey