Effect of Two-step Thermal Treatments on Peroxide Bleachability of Thermomechanical Pulp

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In hydrogen peroxide bleaching of thermomechanical pulp (TMP), reaction temperature and time are the main factors that can improve the bleachability of pulp fibers. However, high temperatures can induce some problems such as cellulose degradation, yield loss, low fiber strength, and high environmental load. These negative effects of high temperature are mainly caused by radicals formed from the decomposition of hydrogen peroxide. To avoid the adverse effects of high temperature, we used two-step thermal treatments during hydrogen peroxide bleaching of TMP. The temperatures used in the two-step thermal treatments were 80 and 45 ˚C for a total bleaching time of 1 hour. In H_2O_2 bleaching of TMP, two-step thermal treatments were found to have had positive effects on the optical and physical properties of the pulp. The ISO brightness of the pulp bleached by two-step thermal treatments with hydrogen peroxide was identical to that of pulp bleached by conventional hydrogen peroxide bleaching. The post color number (PC number) of TMP was sharply increased after bleaching at 80 ˚C for 40 minutes. The post color number of TMP bleached by two-step thermal treatments is lower than that of TMP bleached by a one-step thermal treatment. The zero-span tensile index was also improved by two-step thermal treatments.

Keywords: Peroxide bleaching; Thermomechanical pulp; Brightness; Post color number; Two-step thermal treatment

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INTRODUCTION

Hydrogen peroxide is a clear and colorless liquid. It is sold commercially in 30% to 70% solution concentrations. It is well known that hydrogen peroxide brightens mechanical pulp and increases the brightness of bleached chemical pulp and secondary (recycled) fibers (Stevens and Hsieh 1997; Ni *et al.* 2001; Smook 2002).

Traditionally, hydrogen peroxide has been classified as a lignin-preserving bleaching reagent. It preferentially removes chromophoric structures present in residual lignin, but it is incapable of degrading the lignin network (Gratzl 1987). In an alkaline medium, hydrogen peroxide decomposes to create hydroperoxide ions, hydroxyl radicals, and superoxide anion radicals. The hydroperoxide ion is a strong nucleophile, whilst the other active oxygen species are electrophiles. The hydroperoxide ion cleaves quinones and conjugated carbonyl structures. Alpha and gamma aryl ether bonds represent major reactive sites for nucleophilic attack in hydrogen peroxide bleaching and beta aryl ether bonds represents minor reactive sites (Dence 1996).

To induce vigorous reaction of lignin structures with hydrogen peroxide, bleaching is usually carried out at high temperatures. However, there are some negative effects of high temperature on the pulp properties, such as yield loss, low fiber strength, high environmental load, and cellulose degradation. Lachenal (2005) reported that high amounts of quinone structures in pulp adversely affect the bleachability of the pulp. Furthermore, based on results of a study by Andrade and Colodette (2010), brightness reversion increases with reaction temperature in hydrogen peroxide bleaching. According to Argyropoulos and Rojas (2004), the cleavage of ether bonds is accompanied with formation of condensed structures in alkaline conditions at high temperature, and this condensation reaction causes the formation of hydroquinones, and consequently affects the brightness stability of pulp.

The brightness stability of TMP is particularly vulnerable to heat and light. Many researchers have reported that autoxidation reactions, in which reactive phenolic groups in lignin oxidize to produce quinones, have an important role in the thermal discoloration of mechanical pulp (Polcin and Rapson 1972; Gellerstedt and Pettersson 1980; Giust *et al*. 1991). Gellerstedt and Pettersson (1980) also reported that "the quinones can react further and form strongly colored condensed quinoid structures under alkaline conditions". Consequently, lignin-preserving bleaching forms new structures in the lignin, and bleached mechanical pulp has a higher propensity to discolor because of these new structures (Gellerstedt *et al*. 1983; Moldenius 1983; Mclellan *et al*. 1990).

In general, a pH range of 4.5 to 6 minimizes the heat-induced discoloration of mechanical pulp (Gellerstedt and Pettersson 1980; Gellerstedt *et al.* 1983; Lai *et al.* 1993; Narvestad *et al*. 2011; Poirier *et al.* 1996) According to Narvestad *et al.* (2013), kaolin clay can decrease the brightness of mechanical pulp, and iron in kaolin clay is a major factor in the decrease of brightness stability. Süss *et al.* (1998) have reported that increasing temperature in hydrogen peroxide bleaching accelerates the bleaching reactions; however, it does not cause the brightness of the pulp to reach the highest level possible and induces a much higher COD (Chemical Oxygen Demand) load. Furthermore, Yoon and Wang (1999) reported that increasing temperature does not affect the brightness during the first 40 min of bleaching but then the negative effect of high temperature, *i.e.*, reduction in brightness, is increased when the reaction time is more than 40 min.

Therefore, the present study was initiated to improve the bleaching efficiency achievable by hydrogen peroxide bleaching of TMP by using a two-step thermal treatment. The most effective bleaching method was identified as the two-step thermal treatment, which mitigated to the greatest extent the adverse effects of high temperature.

EXPERIMENTAL

Materials

The bleaching trials were carried out with an industrial pine TMP containing lignin supplied by a Korean mill. Standard methods were used to measure the ISO brightness (KS M ISO 2470), klason lignin content (KS M 7045), and CIELAB (KS M ISO 5631). The basic characteristics of the TMP are presented in Table 1. The Canadian standard freeness of TMP is 200 mL C.S.F.

Reagent grade hydrogen peroxide (35% solution) was purchased from Junsei. Sodium hydroxide (powder) and sodium silicate (water glass, solution) with a weight ratio between SiO_2 and Na_2O of 2.5 were supplied by Daejung Chemicals & Metals. EDTA (Ethylenediamine-tetraacetic acid, solution) was purchased from Fluka.

Table 1. Basic Characteristics of TMP

	ISO brightness, %	*L**	*a**	*b**	Klason lignin content, %
TMP	51.12	85.56	-0.52	15.49	28.4

Methods

Hydrogen peroxide bleaching

Two-step thermal treatments were used to evaluate the dependence of the bleachability of TMP on bleaching temperature and time. The bleaching temperatures were 80 and 45 °C in the P stage (hydrogen peroxide bleaching stage). All samples were washed after bleaching with 400 mL of hot water for 1 h. The bleaching conditions of TMP are shown in Table 2, and the bleaching sequence is shown in Table 3. All the components of the bleaching liquor were premixed and put in plastic bag with pulp slurry at the first stage. The plastic bag was immersed in a water bath and the pulp at 80 °C brought to 45 °C with 10 sec. delay by using two of water bath. The initial and final pH were 11.0 to 11.5 and 10.4 to 10.7. All of bleaching conditions were repeated five times.

Table 2. Bleaching Conditions of TMP

Pulp conc., %	H_2O_2 conc., % on o. d. pulp	NaOH conc., % on o. d. pulp	Na_2SiO_3 conc., % on o. d. pulp	EDTA conc., % on o. d. pulp	Temperature, °C	Reaction time, min
15	4.5	1.8	0.29	0.3	45	10 to 60
					80	

Table 3. Bleaching Sequences of TMP

Symbol	1st P stage		2nd P stage	
	Temperature, °C	Time, min	Temperature, °C	Time, min
P_{10}	80	10	45	-
$P_{10}P_{50}$		10		50
P_{20}		20		-
$P_{20}P_{40}$		20		40
P_{30}		30		-
$P_{30}P_{30}$		30		30
P_{40}		40		-
$P_{40}P_{20}$		40		20
P_{60}		60		-
Control of temperature in 1st and 2nd P stage	50~90	30	-	-
	80	30	20 to 60	30

Measurement of residual hydrogen peroxide

1 mL of bleaching effluent was prepared in a 100 mL beaker with 49 mL of distilled water and mixed thoroughly. A 25 mL aliquot was then pipetted into a 100 mL beaker containing 20 mL of 0.01 N sulfuric acid. The resulting solution was titrated with 0.01 N potassium permanganate to the first permanent pink color. Residual hydrogen peroxide was calculated using *Eq. 1* and tabled as the ratio of residual hydrogen peroxide to initial input.

$$\text{Residual } H_2O_2, \% = \frac{V \times f \times 0.00017005}{W \times \frac{25}{50}} \times 100 \quad (1)$$

Optical properties of TMP

The ISO brightness of TMP was determined according to the KS M ISO 2470 standards, using Elrepho (L&W). To evaluate the color reversion, the post color number (PC number) was determined according to the TAPPI useful method 200. TAPPI UM 200 describes ageing at 105 °C for 4 h in a dry oven. The PC number uses the ratio of absorption coefficient to scattering coefficient by the following equation (Eq. 2):

$$\text{PC No.} = 100 \times \left(\frac{k}{s_{after\ ageing}} - \frac{k}{s_{before\ ageing}}\right) \quad (2)$$

Analysis of fiber characteristics

The reaction of lignocelluloses with hydrogen peroxide forms carbonyl and carboxyl groups (Wojciak *et al*. 2010). Bulk carboxylic acid group content was measured by TAPPI T-237 (Katz *et al.* 1984). The zero-span tensile index of TMP was determined according to the KS M ISO 15361 standards, using TS-100 (Pulmac).

Environmental load of effluents

To analyze the lipophilic extractives, bleaching effluents were extracted three times by separatory funnel with a mixture of hexane:acetone(2:1) (Orsa and Holmbom 1994). Solvents were evaporated by rotavator R-124(BUCHI), and dried extractives were weighed and redissolved in chloroform. Gas chromatograph analyses of the extractives were performed in a Hewlett-Packard HP 5890 equipped with a flame ionization detection system using a fused silica capillary column (CP SIL 5CB, Varian; 30 m × 0.25 mm i.d., 0.25 μ film thickness). The injection port and detector temperature were 300 °C, and the carrier gas was helium. The oven temperature was programmed from 100 °C (1 min) to 325 °C (3 min) at 15 °C/min. Pyridine was used as an internal standard. A DR/2500 spectrophotometer, based on soluble COR-Cr measurement, was used to analyze SCOD value of bleaching effluents.

RESULTS AND DISCUSSION

Analysis of Residual Hydrogen Peroxide Contents

Measurement of the amount of residual hydrogen peroxide is necessary in order to be able to use hydrogen peroxide efficiently. Figure 1 shows the impact of one- and two-step thermal treatments on the amount of residual hydrogen peroxide. It can be seen that the decomposition of hydrogen peroxide mainly occurred during the first 30 min of bleaching. The amount of residual hydrogen peroxide after the two-step thermal treatments was nearly identical with that of the one-step thermal treatment. It may be seen that the reaction time of the 1st P stage, which was conducted at a high temperature (80 °C), affected the decomposition of hydrogen peroxide. Consequently one may conclude that the decomposition of hydrogen peroxide strongly depends on reaction temperature and 30 min is enough to ionize hydrogen peroxide.

Optical Properties of TMP

Brightness is a quality that is important in white papers. Brightness is the reflectivity to light in the blue portion of the spectrum of naturally colored pulps, and of the paper and board made from such pulp. The brightness tends to improve with bleaching. Figures 2(a) and 2(b) show the variation in the ISO brightness of TMP with reaction temperature in the 1st and 2nd P stages of two-step thermal treatments.

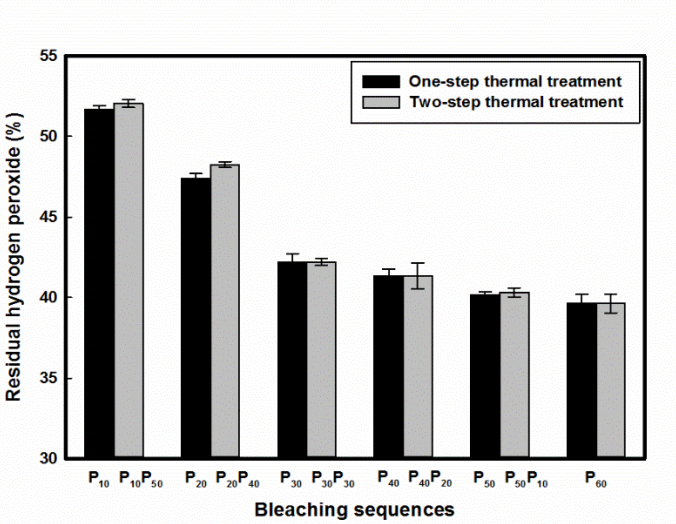

Fig. 1. The impact of bleaching sequences on the amount of residual hydrogen peroxide

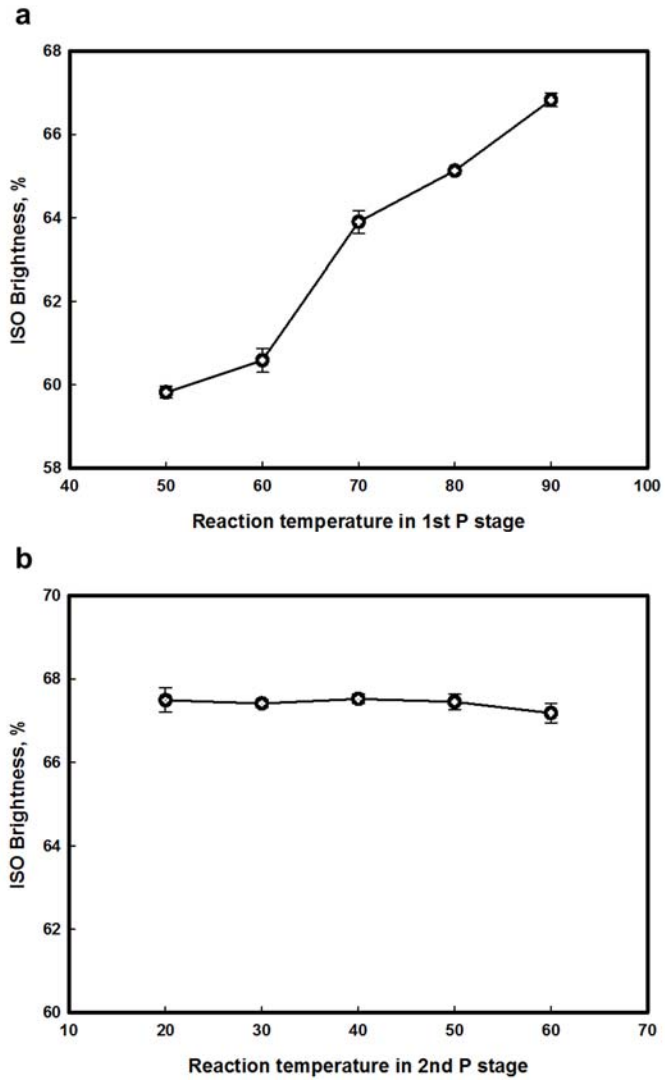

Fig. 2. The effects of reaction temperature in the 1st P stage and the 2nd P stage on the ISO brightness of TMP (Reaction time of 1st P stage: 30 min, reaction time of 2nd P stage after bleaching at 80 °C for 30 min: 30 min)

As shown in Fig. 2, the ISO brightness gradually rose with increasing reaction temperature in the 1st P stage but was unaffected by reaction temperature in the 2nd P stage. The ISO brightness of bleached pulp at 80 °C in the 1st P stage was 65.2% in Fig 2(a). After that, ISO brightness increased to about 67.5% in the 2nd P stage regardless of the reaction temperature. It is assumed that the first 30 min is enough to ionize hydrogen peroxide and the bleaching reaction between reactive species and pulp components can occur at low temperature during the last 30 min. In the 1st P stage, the increase in ISO brightness depended on the reaction temperature, whereas the reaction temperature in the 2nd P stage only very slightly affected the increase in the ISO brightness of TMP during the last 30 min.

As can be seen in Fig. 3, the ISO brightness of TMP gradually increased with reaction time in the 1st P stage, but there was hardly any change in the ISO brightness of TMP in the two-step thermal treatments except for $P_{10}P_{50}$. P_{60} was bleached at 80 °C for 60 min; however, the ISO brightness of P_{60} was similar to that of $P_{30}P_{30}$ bleached at 45 °C during the last 30 min. And the ISO brightness of $P_{30}P_{30}$ was higher than P_{30} bleached at 80 °C for 30 min. It is likely that sufficient time is required for the reaction between reactive species and pulp components and its reaction can occur at low temperature during the last 30 min.

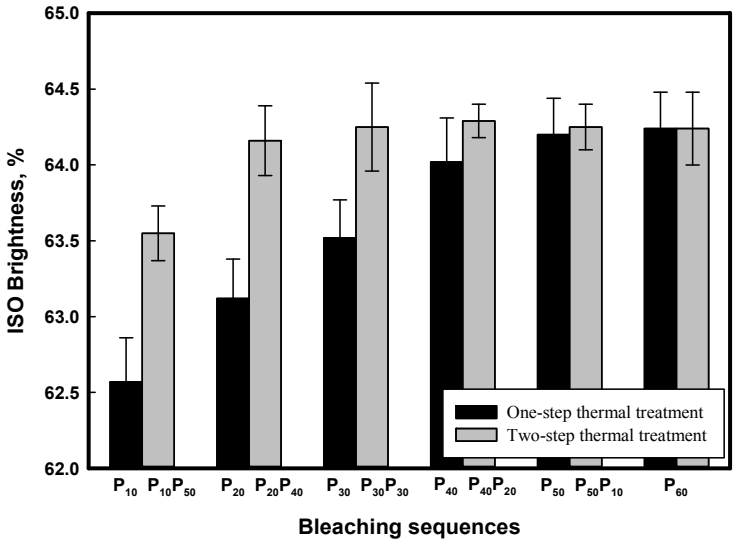

Fig. 3. The impact of bleaching sequences on the ISO brightness of TMP

As can be seen in Fig. 4(a), the PC number of TMP increased sharply between the P_{30} and P_{40} samples, but there was no further change in the PC number of TMP after 40 min. Figure 4(b) shows the PC number of TMP treated by two-step thermal treatments. The PC number of $P_{30}P_{30}$ was 8.3, which was higher than the PC number of P_{30}, but was lower than that of P_{60}, which was bleached for the same time. Consequently, it may be seen that lower temperatures in the later phase of bleaching induced some positive effects such as improvement in brightness stability whilst preserving an identical ISO brightness. Gellerstedt (2007) reported that high moisture contents dramatically decrease the brightness stability. Compared with P_{60}, $P_{30}P_{30}$ had more lipophilic extractives by low temperature in the later phase of bleaching (Fig. 7), and it is assumed that lipophilic extractives affect the moisture contents of bleached TMP.

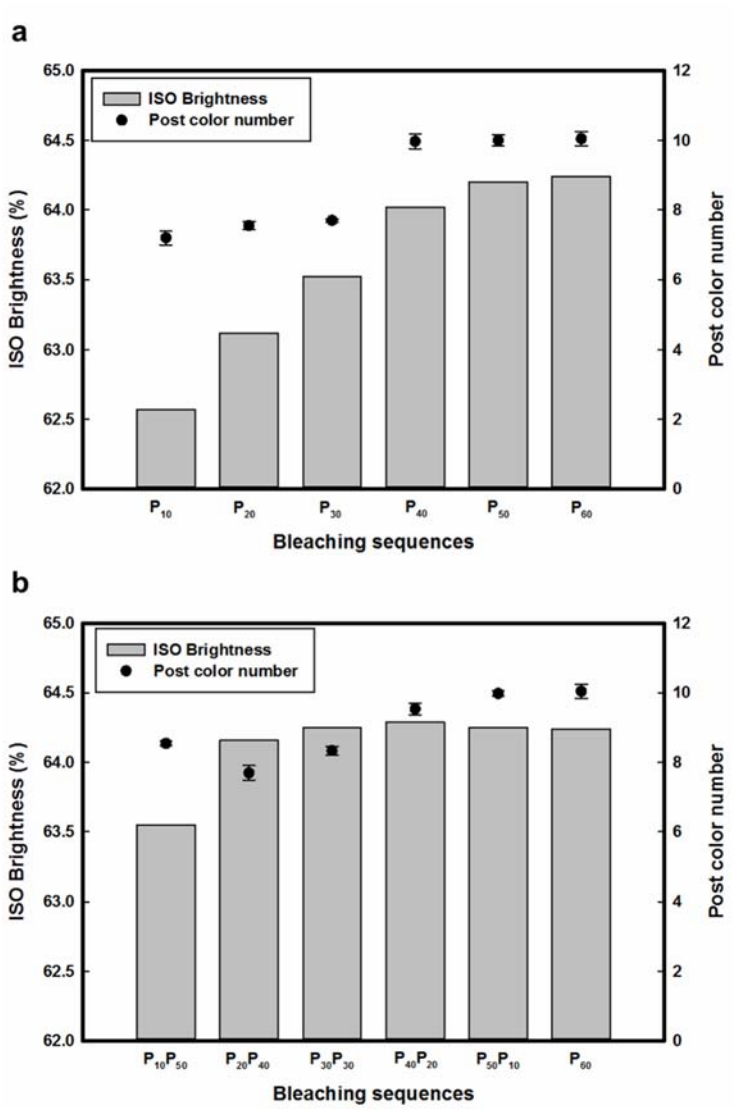

Fig. 4. The impact of one- and two-step thermal treatments on the PC number of TMP

Analysis of Carboxyl Groups in TMP

Alkaline peroxide bleaching could increase the total number of carboxyl groups, surface charge, and dissolved anionic substances, but the excess degradation by superfluous hydroxide and peroxide could result in the decrease in the number of carboxyl groups in fibers because of the production and dissolution of low-molar-mass substances. The total amount of carboxyl groups from polysaccharides in fibers remains constant, and any increase in their number should result from the carboxyl groups newly formed by the lignin oxidation during peroxide bleaching. (Fu *et al.* 2013)

As can be seen in Fig. 5, two distinct sections can be distinguished in the rate of carboxylic acid group formation: an initial rapid increase for the first 30 min, followed by no increase in the rate. Asgari and Argyropoulos (1998) found a similar result. The carboxyl groups of TMP bleached by two-step thermal treatments are similar to those bleached by one-step thermal treatments. Consequently, it is concluded that the carboxyl group formation mainly occurs during the first 30 min of bleaching and depends strongly on the reaction temperature.

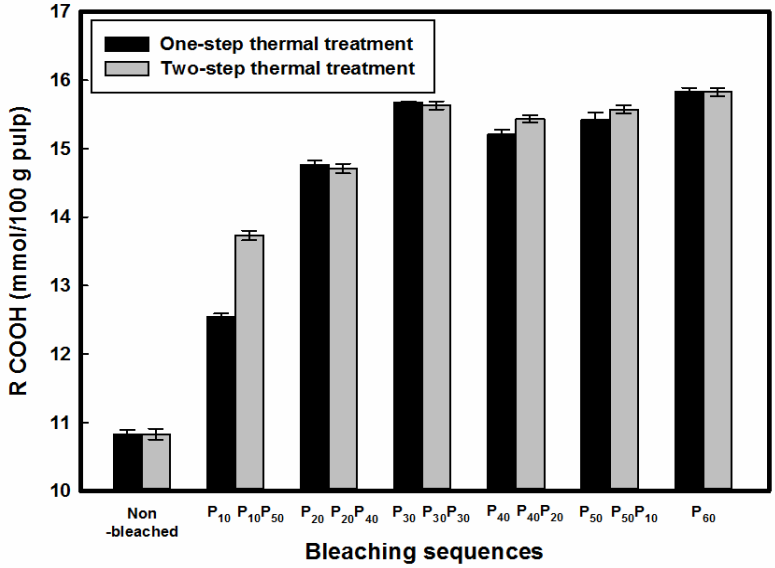

Fig. 5. The impact of bleaching sequences on the amount of carboxyl groups in TMP

Zero-span Tensile Index of TMP

Figure 6 presents the zero-span tensile index obtained for the bleached TMP by one- and two-step thermal treatments. The zero-span tensile index of $P_{30}P_{30}$ had the highest value among samples. In conventional hydrogen peroxide bleaching, zero-span tensile index increases gradually with reaction time. It is likely that the zero-span tensile index increases with chemical dosage, reaction temperature, and time because of the decrease in the number of hydrophobic groups and the increase in the number of hydrophilic groups. However, excessive chemical dosage or long reaction times at high temperature can induce a decrease in the zero-span tensile index due to the degradation of cellulose. (Liu *et al.* 2005). In these experiments, it is assumed that two-step thermal treatments have a little effect on the improvement of the zero-span tensile index.

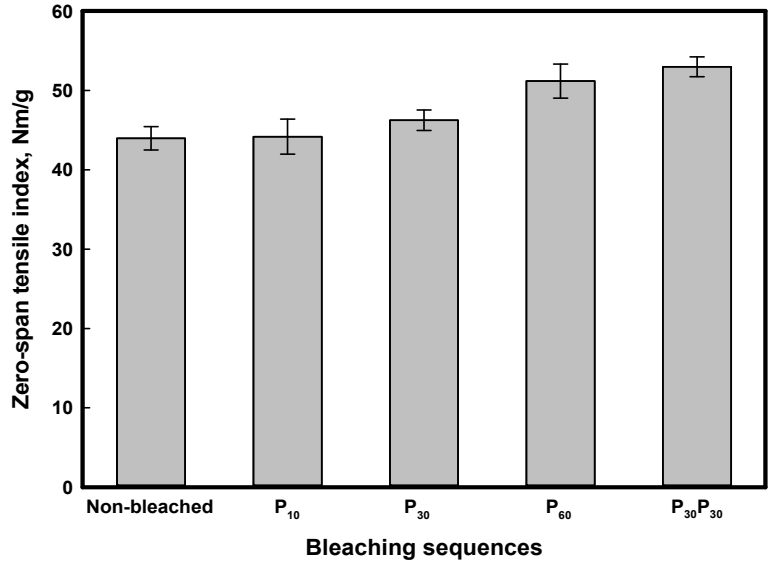

Fig. 6. The effect of bleaching sequence on the zero-span tensile index of TMP

Environmental Load of Effluents

To study the ecological effect of two-step thermal treatments, the environmental load of bleaching effluents was investigated. Figure 7 shows lipophilic extractives and COD in effluents by different bleaching sequences. COD load of effluents was not changed until 30 min of reaction time and considerably increased after 60 min. However, COD load of $P_{30}P_{30}$ was constantly maintained by applying low temperature in the latter phase of hydrogen peroxide bleaching. Lipophilic extractives were steadily increased by the increase of reaction time at high temperature, and its amounts were decreased by applying two-step thermal treatments. It is concluded that low temperature condition is an important factor to reduce lipophilic compounds extracted from TMP with low COD value of effluent. Lipophilic extracts of $P_{30}P_{30}$ and P_{60} were 1.1 and 1.7 mg/g of O.D. pulp.

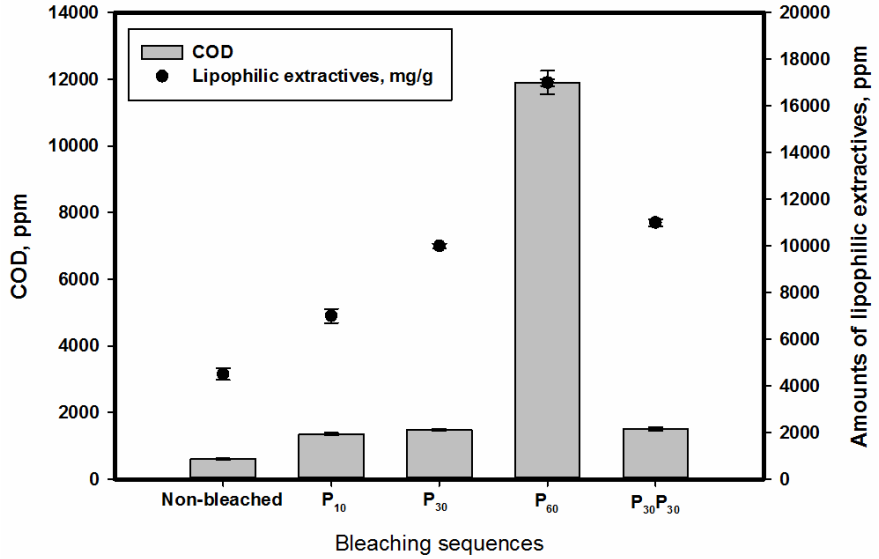

Fig. 71. Lipophilic extractives and COD of effluents by different bleaching sequences

CONCLUSIONS

1. Sufficient time was required for completion of the bleaching reaction between reactive species and pulp components and this reaction occurred at low temperature during the last 30 min.
2. The PC number of TMP was sharply increased after bleaching at 80 °C for 40 min. The PC number of TMP bleached by two-step thermal treatments was lower than that of TMP bleached by a one-step thermal treatment. The increase in severity of bleaching conditions for the one-step process decreased the stability of brightness.
3. The zero-span tensile index was improved by applying two-step thermal treatments.
4. The decomposition of hydrogen peroxide depends strongly on reaction temperature, and 30 min is enough to ionize hydrogen peroxide.
5. Lipophilic compounds and COD value were decreased by applying two-step thermal treatments.

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REFERENCES CITED

Andrade, M. F., and Colodette, J. L. (2010). "Influence of final bleaching stage on ECF brightness development, refineability, and pulp properties," *Scientia Forestalis* 38(86), 135-146.

Argyropoulos, D. S., and Rojas, O. (2004). "Lignin structural insights during pulping & bleaching," Ibero american Congress on Pulp & Paper Research, Madrid-Cordoba.

Asgari, F., and Argyropoulos, D. S. (1998). "Fundamentals of oxygen delignification. Part II. Functional group formation elimination in residual kraft lignin," *Can. J. Chem.* 76(11), 1606-1615. DOI: 10.1139/v98-132

Dence, C. W. (1996). *Pulp Bleaching Principles and Practice*, TAPPI press, Atlanta, Georgia.

Fu, Y. J., Qin, M. H., Guo, Y. Z., Xu, Q. H., Li, Z. Q., Liu, N., Yuan, Z. W., and Gao, Y. (2013). "Location and fate of carboxyl groups in aspen alkaline peroxide-impregnated chemithermomechanical pulp fibres during alkaline peroxide bleaching," *Wood Sci. Technol.* 47(3), 557-569. DOI: 10.1007/s00226-012-0510-y

Giust, W., Mclellan, F., and Whiting, P. (1991). "Alkali darkening and its similarities to thermal reversion," *J. Pulp Pap. Sci.* 17(3), J73-J79.

Gellerstedt, G. (2007). "Bleaching chemistry and post-color formation in kraft pulps," 3rd International Colloquium on Eucalyptus Kraft Pulp, Belo Horizonte, Brazil, 1-13.

Gellerstedt, G., Pettersson, I., and Sundin, S. (1983). "Light-induced and heat-induced yellowing of mechanical pulps," *Svensk Papperstidning-Nordisk Cellulosa* 86(15), R157-R163.

Gellerstedt, G., and Pettersson, B. (1980). "Autoxidation of lignin," *Svensk Papperstidning-Nordisk Cellulosa*, 83(11), 314-318.

Gratzl, J. S. (1987). "Degradation reactions of carbohydrates and lignin by non-chlorine bleaching agents - Mechanisms as well as potential for stabilization," *Papier* 41(3), 120-130.

Katz, S., Beatson, R. P., and Scallan, A. M. (1984). "The determination of strong and weak acidic groups in sulfite pulps," *Svensk Papperstidning-Nordisk Cellulosa* 87(6), R48-R53.

Lachenal, D. (2005). "Influence of pulp colour on bleachability. Ways to improve the bleaching response of alkaline pulp," *ATIP* 59(3), 6-11.

Lai, Y. Z., Suzuki, T., and Omori, S. (1993). "Discoloration of high-yield pulps I. Influence of pH and bleaching on spruce TMP," *Cellulose Chem. Technol.* 27(1), 79-85.

Liu, Z., Ni, Y., Li, Z., and Court, G. (2005). "Peroxide bleaching of low-freeness TMP," *Pulp Pap. Can.* 106(3), 34-37.

Mclellan, F., Colodette, J. L., Fairbank, M. G., and Whiting, P. (1990). "Factors affecting ambient thermal reversion of high-yield pulps," *J. Pulp Pap. Sci.* 16(6), J173-J178.

Moldenius, S. (1983). "Light absorption coefficient spectra of hydrogen peroxide bleached mechanical pulp," *Paperi ja Puu* 65(11), 747-756.

Narvestad, H., Gregersen, O. W., and Kure, K. A. (2013). "Filler clay induced discolouration of bleached mechanical pulp," *Nord. Pulp Paper Res. J.* 28(1), 68-81. DOI: 10.3183/NPPRJ-2013-28-01-p068-081

Narvestad, H., Axelsson, P., and Kure, K. A. (2011). "Full scale experiences with magnesium hydroxide based peroxide bleaching and TMP brightness loss at Norske Skog Saugbrugs," International mechanical pulping conference, China Light Industry Press, Xian, China.

Ni, Y. H., Sommerville, J., and Van Heiningen, A. R. P. (2001). "Bleaching of recycled fibers by adding sodium borohydride to a peroxide reinforced oxygen stage," *J. Tappi* 84(6), 67-67.

Orsa, F., and Holmbom, B. (1994). "A convenient method for the determination of wood extractives in papermaking process waters and effluents," *Journal of Pulp and Paper Science* 20(12), J361-J365.

Poirier, N. A., Pikulik, I. I., Labadie, M., and Pageau, A. (1996). "The effect of pH on the optical properties of paper," *J. Pulp Pap. Sci.* 22(11), J419-J423.

Polcin, J., and Rapson, W. H. (1972). "Sapwood and heartwood groundwood of western hemlock and jack pine. 3. Influence of solvent-extraction on bleaching of pulps," *Pulp Pap. Can.* 73(1), 86.

Smook, G. A. (2002). *Handbook for Pulp and Paper Technologists*, Second Ed., Angus Wilde Publications Incorporated, Vancouver, Canada.

Süss, H. U., Nimmerfroh, N. F., and Kronis, J. D. (1998). "The naked truth on hot peroxide bleaching," *Pulp Pap. Can.* 99(4), 63-66.

Stevens, J. A., and Hsieh, J. S. (1997). "Achieving maximum peroxide bleaching response through proper selection of pH," 1997 Pulping Conference, TAPPI Press, San Francisco, CA.

Wojciak, A., Kasprzyk, H., Sikorska, E., Khmelinskii, I., Krawczyk, A., Oliveira, A. S., Ferreira, L. F. V., and Sikorski, M. (2010). "Changes in chromophoric composition of high-yield mechanical pulps due to hydrogen peroxide bleaching under acidic and alkaline conditions," *J. Photoch. Photobio. A* 215(2-3), 157-163. DOI: 10.1016/j.jphotochem.2010.08.005

Yoon, B. H., and Wang, L. J. (1999). "Optimizing and modeling brightness development on peroxide bleaching of thermomechanical pulp," Proceeding of Fall conference of the Korea Technical Association of the Pulp and Paper Industry, Korea TAPPI, Seoul, Korea.

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