Improving Bleachability of Thermomechanical Pulp by Ozone–Hydrogen Peroxide System

Ho Sang Lee,[a] Kang-Jae Kim,[b,]** and Jin-Ho Seo [c,]*

Thermomechanical pulp (TMP) was bleached with an ozone–hydrogen peroxide system, with the addition of hydrogen peroxide and ethylene glycol to enhance bleaching efficacy. The ISO brightness of TMP increased proportionally with higher concentrations of hydrogen peroxide across all sequences. Notably, TMP treated with the ozone and hydrogen peroxide sequence (ZP sequence) exhibited ISO brightness levels comparable to those of TMP bleached with hydrogen peroxide alone. However, the addition of hydrogen peroxide during the Z stage of the pZP sequence resulted in a 2.4% increase in ISO brightness and enhanced lignin solubility. A brief alkaline extraction step in the pZEP sequence led to a significant 4.3% increase in ISO brightness, though this improvement was accompanied by a yield loss due to removal of lignin in the E stage. Furthermore, the addition of polyethylene glycol alleviated yield loss by enhancing the selectivity of ozone bleaching, while effectively maintaining a stable ISO brightness.

DOI: 10.15376/biores.20.1.923-933

Keywords: Ozone; Hydrogen peroxide; Thermomechanical pulp; Polyethylene glycol; Brightness; Yield

Contact information: a: Division of Global Forestry, National Institute of Forest Science, Seoul, 02455, Republic of Korea; b: Major in Wood Science and Technology, School of Forestry, Science and Landscape Architecture & Agricultural Science and Technology Research Institute, Kyungpook National University, Daegu, Republic of Korea; c: Dept. of Paper Material Science and Engineering, Division of Forest Material Science and Engineering, Kangwon National University, 24341, Republic of Korea;
** Corresponding author: seojh97@kangwon.ac.kr; **Co-Corresponding author: jaeya0624@knu.ac.kr*

INTRODUCTION

According to global pulp price forecasts, pulp costs will continue to increase because of increasing demand, increasing primary costs of wood chips and oil, a weak dollar value, and high-income growth in China (Eu-Gene 2010). Therefore, the paper industry is making various efforts to reduce costs, such as increasing the dosage of inorganic materials, reducing the chemicals charge, improving the deinking process, and using low-grade pulp. In particular, the alternative use of low-grade pulp has a considerable advantage in mass production systems, and replacing some of the chemical pulp with low-grade pulp brings not only economic benefits but also environmental benefits. Among various pulps, mechanical pulp is a relatively low-grade pulp, and thermomechanical pulp (TMP) is a representative low-grade pulp produced in large quantities around the world. However, there are many problems associated with the use of TMP in high-grade papermaking, such as low fiber strength, low brightness of the final product, and a large number of shives. Specifically, the low brightness of TMP presents a significant challenge for its application in high-quality paper and other advanced uses. The TMP currently produced exhibits insufficient brightness for high-quality paper applications and is predominantly utilized in lower-grade products, such as newsprint and textbooks. One simple way to improve the quality of TMP is to increase the efficacy of the bleaching process.

Typically, TMP is bleached using hydrogen peroxide. Hydrogen peroxide acts as a strong oxidizing agent in bleaching, and there are limitations in selectivity and efficiency. As the concentration of hydrogen peroxide increases, brightness of pulp increases, but beyond a certain level, brightness does not increase. Additionally, hydrogen peroxide bleaching using a base is accompanied by an increase in brightness and a decrease in yield (Pan 2011). Therefore, bleaching using various bases such as sodium carbonate, magnesium oxide, magnesium hydroxide, and calcium hydroxide has been attempted. However, as the optical properties improved, the yield declined. So there was a trade-off between yield and optical properties (He and Ni 2008; Hou *et al*. 2010). Another bleaching agent, hydrosulfite is also commonly used for TMP bleaching; however, it has a well-defined limit on the achievable brightness of the pulp. Consequently, the use of various bleaching agents is necessary to enhance pulp quality while preserving existing benefits.

Ozone, an oxygen-based bleaching agent, has gained attention as a potential substitute for chlorine-based agents, which pose environmental concerns. As a strong oxidizing agent, ozone reacts readily with a wide range of organic materials, including lignocellulosic substances, and it is typically employed in the middle of the bleaching sequence for chemical pulps (Doree and Healey 1938; Liebergott *et al.* 1992). Ozone reactions are generally selective towards lignin. However, hydroxyl radicals generated from ozone reactions or its decomposition in water can initiate free-radical chain reactions, which may lead to an undesirable reduction in the strength properties of the pulp (Jacobson *et al.* 1991; Johansson 2003). Nevertheless, pre-treatment of the pulp with alcohol prior to ozone bleaching has been shown to significantly improve the selectivity of the process (Johansson 2003). Based on this, ozone bleaching appears to be a viable method for TMP. In this study, ozone–hydrogen peroxide bleaching was used for TMP prepared from *Pinus densiflora* Siebold et Zuccarini to establish an optimal sequence. In addition, the effects of the addition of hydrogen peroxide or ethylene glycol in ozone bleaching to prevent yield loss were also analyzed.

EXPERIMENTAL

Materials and Methods

The bleaching trials were carried out with an industrial softwood TMP (containing lignin) supplied by a Korean papermill. The basic characteristics of the TMP are presented in Table 1. Standard methods were used to measure the ISO brightness (ISO 2470-1 2016), total lignin content (KS M 7045 2006), and CIELAB (ISO 5631-1 2022).

The polyethylene glycol (PEG, M_w 8,000 Daltons) used was reagent grade purchased from Sigma Aldrich. Hydrogen peroxide (30% solution), sodium hydroxide (powder), sodium silicate (water glass, solution), with a weight ratio between SiO_2 and Na_2O of 2.5 were supplied by Daejung Chemicals & Metals (South Korea).

Table 1. Basic Characteristics of Thermomechanical Pulp

	ISO Brightness (%)	*L**	*a**	*b**	Lignin Content (%)
TMP	47.63	82.98	0.1	15.13	28.4

Ozone–Hydrogen Peroxide Bleaching System

An ozone–hydrogen peroxide system was used to improve the TMP bleachability. Hydrogen peroxide was also used in the ozone stage to evaluate the TMP bleachability, and PEG was introduced in the Z stage to improve the pulp yield. The amount of chemicals and additives were based on oven-dried pulp. The bleaching temperature was 20 °C in the Z stage and 70 °C in the E and P stages. The reaction time was adjusted to 12 to 60 min in the Z stage, 10 to 60 min in the E stage, and 60 min in the P stage. The bleaching conditions are shown in Table 2, and the bleaching sequence is shown in Table 3. The abbreviation for each stage is as follows:

P: Hydrogen peroxide stage
Z: Ozone stage
E: Alkaline extraction stage
pZ: Ozone stage reinforced with hydrogen peroxide

Table 2. Thermomechanical Pulp Bleaching Conditions

Stage	Pulp Consistency (%)	Chemical Charge	Temperature (°C)	Time (min)	pH	Additives (% based on oven-dried pulp)
Z	10	1.0 to 5 kg/t	20	12 to 60	3	H_2O_2: 0.4% PEG: 0 to 50%
E	10	0.8%	70	10 to 60	-	-
P	10	1.5 to 4.5%	70	60	10.5	-

Table 3. Bleaching Sequences

Sequence	H_2O_2 Conc. in P-stage (%)	H_2O_2 Conc. in Z-stage (%)	Ozone Charge (kg/t)	E-treatment Time (min)
P	1.5 to 4.5	-	-	-
ZP			5	-
pZP		0.4	5	-
pZEP			5	10 to 60

Optical Properties of Thermomechanical Pulp

The ISO brightness of the pulp was determined according to the ISO 2470-1 (2016) standard, using a spectrophotometer (Elrepho, Lorentzen & Wettre, Kista, Stockholm, Sweden). The optical properties of the TMP mentioned above were also measured with the same device.

Analysis of Fiber Characteristics

The total lignin content of the pulp was measured according to KS M 7045 (2006), and the pulp yield was calculated from the weight change. The ratio of the absorbance at 1730 cm^{-1} to the absorbance at 2900 cm^{-1} was used as an indirect measure of the amount of carboxylic acid, using attenuated total reflection infrared spectroscopy (ATR-IR, Bruker Optics, Karlsruhe, Germany). A total of 64 scans per sample were performed from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

The effects of H_2O_2 concentration in each sequence and the addition of H_2O_2 in the Z stage were investigated. The amount of H_2O_2 used in the P stage was studied at three levels: 1.5%, 3%, and 4.5%. Figure 1 shows the changes in the ISO brightness value of the pulp for each sequence with changes in H_2O_2 concentration, with an ozone dosage of 5 kg/t in the Z stage and the E stage lasting 10 min. In all the sequences, as the H_2O_2 concentration in the P stage increased, the ISO brightness also increased. At the same H_2O_2 concentration, the ISO brightness of TMP bleached using the pZP sequence was higher than that using the ZP sequence. Peroxide addition in the Z stage improved the brightness by at least two points compared with that at the P and ZP sequences. These results suggest that there is potential for decreasing the H_2O_2 input in the final P stage. In addition, the E stage in the pZEP sequence further increased the ISO brightness. The addition of H_2O_2 in the Z stage converts carbonyl compounds to carboxylic acids and carboxylic acids are more soluble than carbonyl compounds in water; therefore, it is believed that their extraction in the E stage improved the ISO brightness of pulp (Leporini Filho *et al*. 2003).

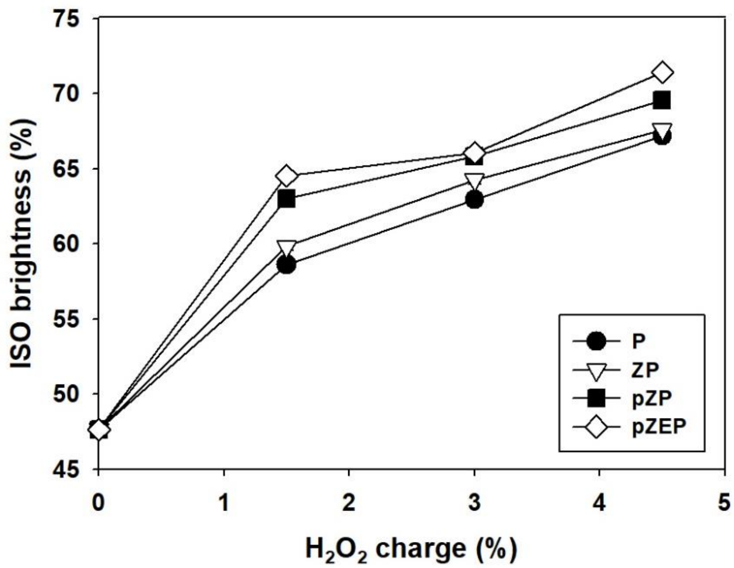

Fig. 1. Impact of H_2O_2 charge on ISO brightness of TMP for different sequences

Figure 2 shows the TMP yield in the pZEP sequence, based on H_2O_2 concentration in the P stage. As the H_2O_2 concentration was increased, the TMP yield decreased. The TMP yield was 92.1% for addition of 3% H_2O_2, and it sharply decreased to 86.3% for addition of 4.5% H_2O_2. A reduction in the amount of lignin in the Z stage may cause a decrease in the TMP yield, and it is concluded that large amounts of lignin were extracted from the TMP in the E stage. As shown in Fig. 3, the removal of lignin and carboxylic acids was dependent on the charge of H_2O_2 in the P stage, and the maximum removal was achieved with an H_2O_2 charge of 4.5%. For high concentrations of H_2O_2 in the P stage, the TMP yield decreased dramatically due to total lignin content removal in the pZEP sequences. Therefore, it may be necessary to adjust the H_2O_2 concentration in the P stage to a level suitable for the final use of the pulp.

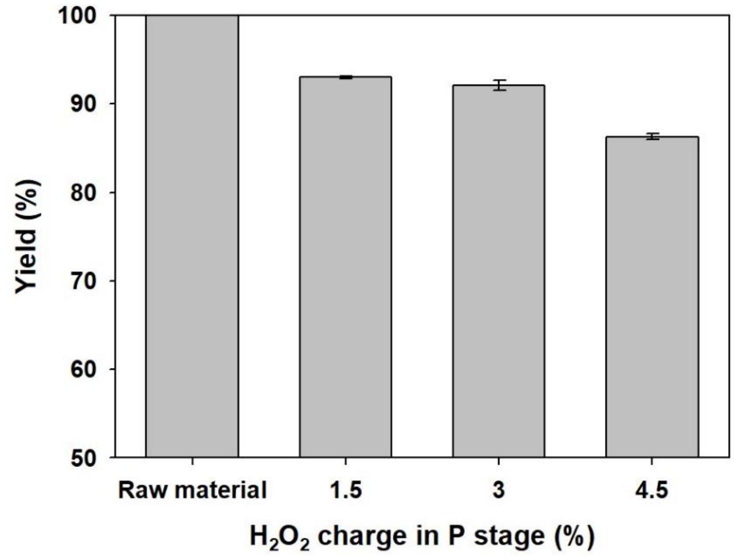

Fig. 2. Impact of H_2O_2 charge on yield of TMP in pZEP sequence

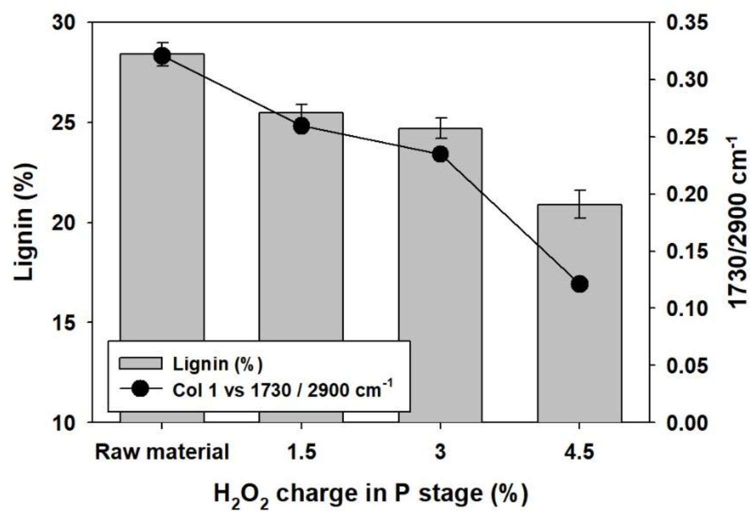

Fig. 3. Impact of H_2O_2 charge on lignin and carboxylic acid contents of TMP in pZEP bleaching

Figure 4 shows the ISO brightness and yield of TMP in each sequence at the same charge of H_2O_2 and NaOH. In the P and ZP sequences, the amount of H_2O_2 from the pZ stage and the NaOH from the E stage were additionally added to the P stage to equalize the total amount of chemicals added. There was a clear increase in ISO brightness when ozone and hydrogen peroxide bleaching were performed together in the ZP sequence. However, these values were approximately 3% to 4% lower than TMP for the pZP and pZEP sequences, and peroxide addition in the Z stage significantly increased the ISO brightness. Therefore, an increase in ISO brightness can be induced without increasing the total H_2O_2 usage. When an E stage was included, the yield of TMP dropped to about 9% compared with that of TMP in the P sequence. The individual values of yields were reported as 95% in P, 93% in ZP, 92.6% in pZP, and 86.3% in pZEP. In stage E, a greater amount of alkali-soluble lignin can be extracted, which is believed to reduce yield and increase brightness.

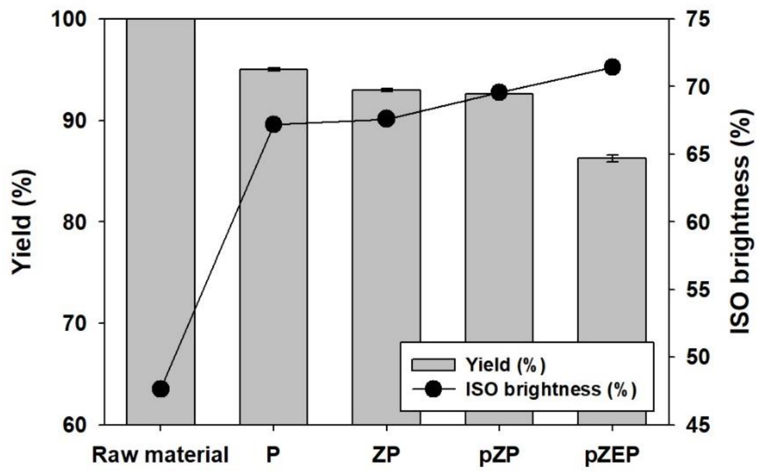

Fig. 4. Impact of different sequences on ISO brightness and yield of TMP. (H_2O_2 charge: 4.5%)

The total lignin and carboxylic acid contents of the bleached TMP obtained from each sequence were determined and compared, and the results are presented in Fig. 5. For bleached TMP of the pZP sequence, the total lignin content was similar to the initial lignin content of the unbleached pulp. However, the carboxylic acid content increased due to the generation of carboxylic acids by peroxide addition in the Z stage.

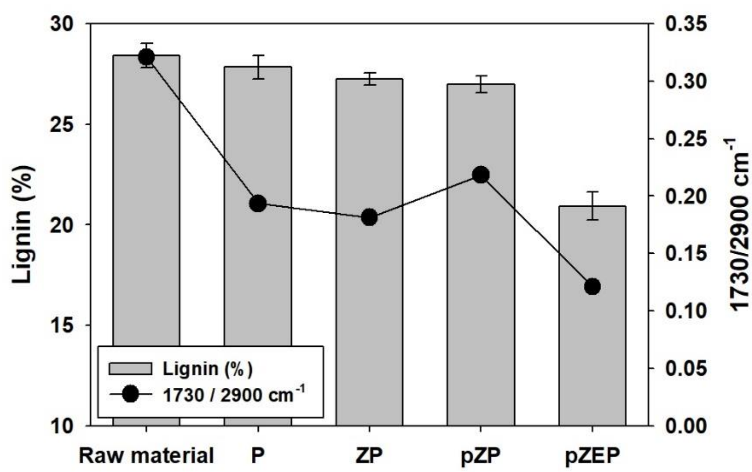

Fig. 5. Impact of different sequences on lignin and carboxylic acid contents of TMP

According to Leporini Filho *et al*. (2003), the addition of an oxidizing compound to the ozone reaction shifts the reaction to the generation of carboxylic acids. Furthermore, the carboxylic acid content decreased significantly due to alkaline extraction in the E stage of pZEP sequence. Carboxylic acids are much more soluble in water than carbonyl compounds are, and their extraction results in a lower amount of residual lignin and higher brightness (Leporini Filho *et al*. 2003). In this study, it was determined that the total lignin content was significantly reduced by 7.5% as the carboxylic acid generated in the pZ stage was extracted in the E stage.

Figure 6 illustrates the variation in yield with lignin content, highlighting the selectivity of the bleaching stages. As anticipated, yield decreased with a reduction in lignin content. Notably, a minor decrease in lignin content during the Z stage resulted in a substantial reduction in yield. Additionally, during stage E, both yield and lignin content decreased in nearly a 1:1 ratio. Specifically, the Z stage reduced lignin content by 0.6% but led to a 2% decrease in yield, indicating a lack of selectivity for this stage. Although the pZ stage is similar to the Z stage, the subsequent E stage effectively and selectively removes carboxylic acid compounds produced earlier. This suggests that while some carbohydrates may have been lost during the Z stage, the dissolution of hemicellulose by alkali in the E stage was minimal. In summary, while the Z stage enhances ISO brightness, it necessitates optimization to improve yield.

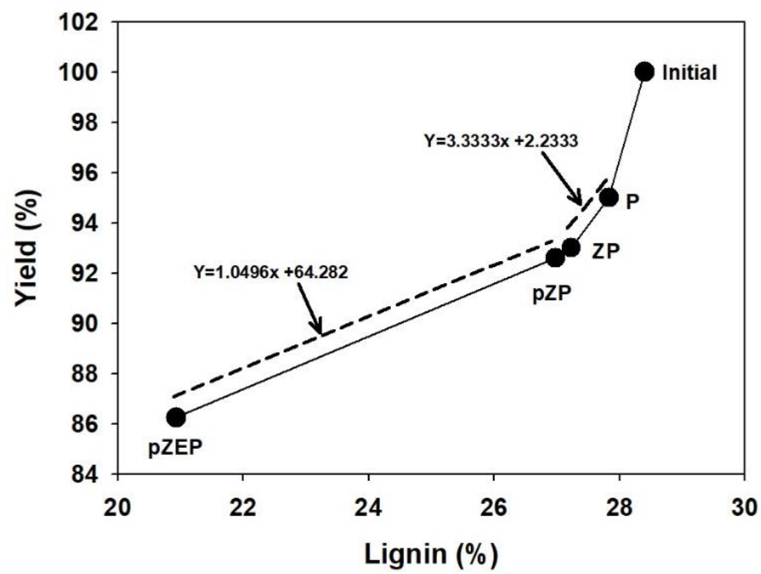

Fig. 6. Selectivity of pZEP sequence

Figure 7 shows the yield, ISO brightness, and lignin contents of TMP by alkali treatment time. The ISO brightness of the bleached TMP increased slightly. However, as the alkali-treatment time increased, the yield of TMP decreased: 86.3% for 10 min, 83.6% for 20 min, 82.1% for 30 min, and 81.2% for 60 min. The lignin content of the TMP decreased as the alkali-treatment time increased, which is the identical trend to the yield. The traditional TMP process generally excludes an alkaline extraction step and produces high-yield pulp with satisfactory brightness. However, due to the declining demand for newsprint, which predominantly uses high-yield pulp, exploring new applications for this pulp type has become essential. Although identifying new uses for existing TMP is important, enhancing pulp quality through minor process improvements could provide opportunities to broaden TMP applications. Consequently, incorporating an alkaline extraction step is anticipated to significantly impact TMP applications.

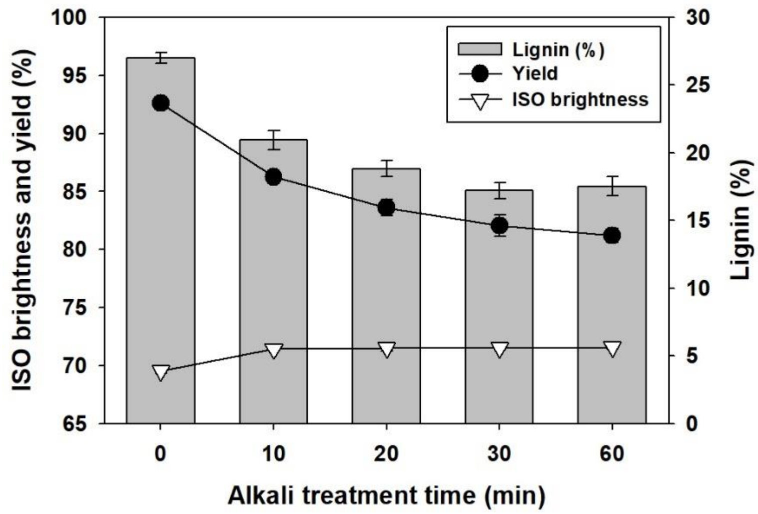

Fig. 7. Impact of alkali treatment time on yield, ISO brightness, and lignin content of bleached TMP in pZEP bleaching

In general, ozone molecules preferentially attack double bonds in the lignin. They do not directly degrade much of the carbohydrates. However, strong cellulose-degrading hydroxyl radicals are formed in ozone bleaching and hydrogen peroxide bleaching processes. These problems arise because of the radical reactions and not due to the reactions with ozone itself (Liebergott *et al*. 1992a,b; Ragnar 2000; Johansson 2003). Most alcohols have a positive effect on lignin removal and they simultaneously prevent carbohydrate degradation during ozone bleaching. The alcohols used are generally methanol and ethanol (Kamishima *et al*. 1982, 1983, 1985; Griffin and Van Heiningen 1998; Bouchard *et al*. 2000). In this work, the cellulose-protecting effect of PEG addition during pZEP bleaching was studied. The effect of PEG addition on the ISO brightness of TMP was not significant, but the ISO brightness decreased slightly at 50% of PEG charge (Fig. 8).

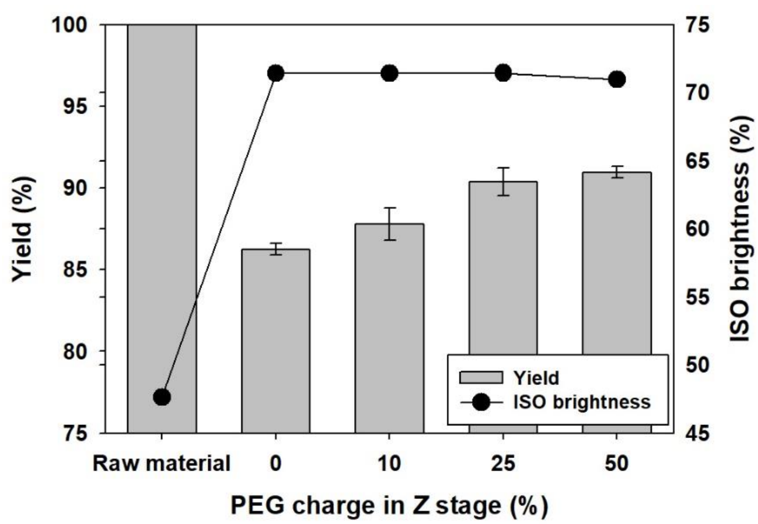

Fig. 8. Impact of PEG addition on yield and ISO brightness of TMP in pZEP bleaching

In addition, as shown in Fig. 9, lignin and carboxylic acid slightly increased only at 50% of PEG charge. The PEG forms a formyl-methyl radical, which can terminate the free radical chain reaction. Furthermore, ethylene glycol exhibits a low rate constant with ozone and a rate constant with OH radicals of 2.4×10^{9} $M^{-1}s^{-1}$, which is higher than the rate constant between cellulose and OH radicals, which is 1.5×10^{9} $M^{-1}s^{-1}$ (Johansson, 2003). Therefore, the increased selectivity by PEG addition results from a decrease in the cellulose degradation process rather than an increase in delignification (Johansson *et al*. 2000; Johansson 2003). Taking into account both yield and ISO brightness, a 25% addition of PEG based on oven-dried pulp is considered appropriate.

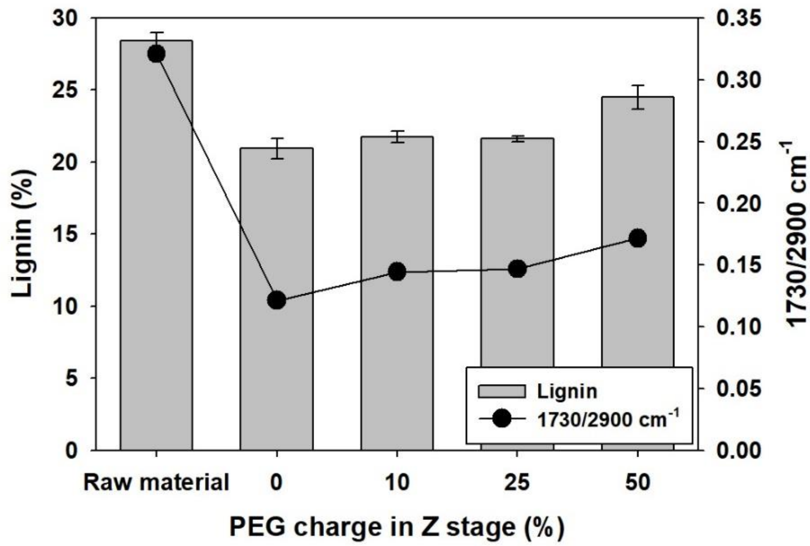

Fig. 9. Impact of PEG addition on lignin and carboxylic acid contents of TMP in pZEP bleaching

CONCLUSIONS

This study investigated the bleachability of thermomechanical pulp (TMP) using an ozone (Z)–hydrogen peroxide bleaching system, and the effect of H_2O_2 addition in the Z bleaching stage to improve the TMP characteristics such as brightness, yield, and total lignin content.

1. Increasing the H_2O_2 dose improved the ISO brightness of TMP for all sequences.
2. The H_2O_2 addition in the Z stage increased the brightness and delignification, however, it made the lignin more soluble. The yield of TMP still decreased because of the reduction in the amount of lignin.
3. The optimum alkali-treatment times were 10 min for high brightness and yield.
4. The 25% addition of PEG improved the selectivity of ozone in the pZEP sequence. The PEG appeared to decrease degradation of cellulose by protection from free-radical chain-reactions.

REFERENCES CITED

Bouchard, J., Morelli, E., and Berry, R. M. (2000). "Gas-phase addition of solvent to ozone bleaching of kraft pulp," *Journal of Pulp and Paper Science* 26(1), 30-35.

Doree, C., and Healey, A. C. (1938). "5-the action of ozone on cellulose and modified cellulose," *Journal of the Textile Institute Transactions* 29(3), T27-T42. DOI: 10.1080/19447023808658836

Eu-Gene, K. (2010). *A Change in Profitability of Domestic Paper Manufacturing Industry with Mid-Term Forecast for Global Pulp Prices*, Hana Institute of Finance, Seoul, Korea.

Griffin, R., Ni, Y., and Van Heiningen, A. P. (1998). "The development of delignificatior and lignin-cellulose selectivity during ozone bleaching," *Journal of Pulp and Paper Ccience* 24(4), 111-115.

He, Z., and Ni, Y. (2008). "Peroxide bleaching of eucalyptus CTMP using magnesium hydroxide as the alkali source," *Appita: Technology, Innovation, Manufacturing, Environment* 61(6), 1-7.

Hou, Q. X., Yuan, W., Zhang, S. Y., Zhao, J. P., Yang, B., and Zhang, H. J. (2010). "Partially substituting MgO for NaOH as the alkali source in the second-stage impregnation of triploid poplar P-RC APMP," *Industrial & Engineering Chemistry Research* 49(7), 3088-3093. DOI: 10.1021/ie901639p

ISO 2470-1 (2016). "Paper, board and pulps — Measurement of diffuse blue reflectance factor Part 1: Indoor daylight conditions (ISO brightness)," International Organization for Standardization, Geneva, Switzerland.

ISO 5631-1 (2022). "Paper and board — Determination of colour by diffuse reflectance Part 1: Indoor daylight conditions (C/2°)," International Organization for Standardization, Geneva, Switzerland.

Jacobson, B., Lindblad, P. O., and Nilvebrant, N. O. (1991). "Lignin reactions affect the attack of ozone on carbohydrates," in: International Pulp Bleaching Conference, Stockholm, Sweden: SPCI, pp. 45-58.

Johansson, E. E. (2003). *Free Radical Mediated Cellulose Degradation*, Doctorial Dissertation, Kungliga Tekniska Högskolan, Stockholm, Sweden.

Johansson, E. E., Lind, J., and Ljunggren, S. (2000). "Aspects of the chemistry of cellulose degradation and the effect of ethylene glycol during ozone delignification of kraft pulps," *Journal of Pulp and Paper Science* 26(7), 239-244.

Kamishima, H., Fujii, T., Akamatsu, I., and Nakayama, S. (1982). "The effect of organic acids on carbohydrate protection during ozone bleaching of kraft pulp," *Journal of the Japan Wood Research Society* 28(6), 370-375.

Kamishima, H., Fujii, T., and Akamatsu, I. (1983). "Influence of the addition of oxalic acid on the rate of cellulose degradation and delignification during ozone bleaching of kraft pulp," *Journal of the Japan Wood Research Society* 29(6), 422-427.

Kamishima, H., Fujii, T., Akamatsu, I., and Nakyama, S. (1985). "Protective agents for carbohydrates in ozone bleaching of unbleached kraft pulps. III. Screening of protective agents for carbohydrates in ozone bleaching," *Shikoku Kogyo Gijutsu Shikensho Kenkyu Hokoku* 17(9), 15-30.

KS M 7045 (2006). "Testing method for lignin in raw materials of pulp," Korean Standards Association, Seoul, Korea.

Leporini Filho, C., Suess, H. U., Degussa, A. G., da Silva, M. R., Peixoto, M. A. L., Papel, V. C., and Jacarei, U. (2003). "Addition of hydrogen peroxide to ozonation for

improved bleaching results," in: *ABTCP-TAPPI Congresso Internacional de Cellulose e Papel*, San Paulo, Brazil, pp. 1-7.
Liebergott, N., Van Lierop, B., and Skothos, A. (1992a). "A survey of the use of ozone in bleaching pulps, part 1," *TAPPI Journal* 75(1), 145-152.
Liebergott, N., Van Lierop, B., and Skothos, A. (1992b). "A survey of the use of ozone in bleaching pulps, part 2," *TAPPI Journal* 75(2), 117-124.
Pan, G. (2011). "Improving hydrogen peroxide bleaching of ASPEN CTMP by using aqueous alcohol media," *BioResources* 6(4), 4005-4011. DOI: 10.15376/biores.6.4.4005-4011
Ragnar, M. (2000). *On the Importance of Radical Formation in Ozone Bleaching*, Doctorial Dissertation, Kungliga Tekniska Högskolan, Stockholm, Sweden.

Article submitted: July 25, 2024; Peer review completed: August 18, 2024; Revised version received: August 22, 2024; Accepted: October 17, 2024; Published: November 27, 2024.
DOI: 10.15376/biores.20.1.923-933