Application of Photo, Peracetic Acid, and Combination Pre-treatments in Improving Totally Chlorine-Free Bleaching Selectivity

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The application of totally chlorine-free bleaching (TCF) is well recognised for its environmental compatibility. However, its application is restricted in comparison to a chlorine-based bleaching sequence. TCF bleaching produces pulp with relatively lower brightness and strength properties. Oxygen delignification (O-stage) is commonly used as a first bleaching stage; therefore its selectivity influences TCF bleaching performance. In this study, the selectivity of the O-stage and hydrogen peroxide-reinforced O-stage (Op-stage) on tropical hardwood kraft pulp were 0.53 and 0.71, with 37.8% and 55.5% kappa number (K_n) reductions, respectively. The addition of photo pre-treatment prior to the O-stage and Op-stage improved the K_n reduction to 53.7% and 59.2%; consequently the selectivity was enhanced to 1.0 and 0.73, respectively. The Fourier transform infrared spectra showed that photo pre-treatments improved the selectivity by protecting the cellulose from carbonyl-induced degradation. This protective effect was more prominent in the O-stage than the Op-stage. However, the combination of peracetic acid and photo treatment did not further increase bleaching selectivity in either stage. In short, blue light and UV irradiation treatment with or without the prior addition of peracetic acid to ordinary or hydrogen peroxide-reinforced oxygen delignified pulp displayed a similar bleaching effect on the resultant pulp.

Keywords: Oxygen delignification; Peroxide reinforcement; Photo and peracetic acid pre-treatment; Selectivity; Pulp viscosity, Fourier transform infrared spectroscopy (FTIR)

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INTRODUCTION

Totally chlorine-free bleaching (TCF) is well recognised for its environmental compatibility; however, the application and development of TCF bleaching is restricted (Reeve and Weishar 1991; Nelson 1998; Reinstaller 2008). This is because in comparison to a conventional chlorine-based bleaching sequence, TCF bleaching has relatively low selectivity between delignification and cellulose degradation and therefore produces pulp with lower brightness and strength properties (Parthasarathy *et al.* 1990; Leroy *et al.* 2004 ; Ng *et al.* 2011).

Oxygen bleaching, which is also known as oxygen delignification (O-stage), was first introduced in the late 1960s and early 1970s to act as extended delignification prior to a conventional bleaching sequence. Thus, the major role of O-stage is to reduce the burden of the bleaching plant by reducing the consumption of chemicals and the pollution level of effluent (Agarwal *et al.* 1999; Gaspar *et al*. 2002; Sippola and Krause 2005). On the other hand, in a TCF bleaching sequence, an O-stage is commonly used as the first bleaching stage to eliminate the bulk of residual lignin from the brownstock. Thus, the selectivity of an O-stage provides a main influence on TCF bleaching performance.

In general, the degree of delignification of an O-stage is limited to 50% and below. It is far lower than that of the first two bleaching stages of the conventional bleaching sequence, wherein the chlorination stage (C) followed by an alkaline extraction (E) can eliminate up to 90% of the residual lignin. Previous studies reported that delignification by O-stage beyond the limit will decrease the selectivity by diminishing the reactivity towards lignin but increasing the cellulose degradation (Smook 1992; Beyer *et al.* 1999).

Thus, a number of studies have been carried out in an effort to enhance the performance of a TCF bleaching sequence, especially related to O-stage, so that it may present a high degree of delignification with relatively minimal cellulose degradation (high bleaching selectivity). Among these studies, the benefits of using hydrogen peroxide (H_2O_2) in conjunction with the O-stage, known as peroxide-reinforced oxygen bleaching (Op-stage), are well-recognized (Suchy and Argyropoulus 2002). It has been observed that the Op-stage shows the following benefits in comparison with the O-stage: improvement of the degree of delignification, a boost in brightness, lower brightness reversion, higher beatability, and maintenance of pulp viscosity at an acceptable level (Pedro *et al.* 2010). In the latest study (Ng *et al.* 2011), the addition of a small amount (0.02%) of anthraquinone (AQ) in an Op system with an H_2O_2 charge of more than 0.5% still enables the maintenance of a rather high pulp viscosity, provided sufficient alkalinity is supplied. This AQ-aided Op-stage shows potential for enhancing kappa number (K_n) reduction and pulp brightness while protecting the cellulose from serious degradation.

On the other hand, a number of studies report that the introduction of a pre-treatment prior to the O-stage can improve bleaching selectivity by increasing the degree of delignification (Roncero *et al.* 2002). Studies have verified that lignin macromolecules are reactive under acidic conditions in the presence of peracetic acid, probably through reactions involving free radicals. The reactive species of peracetic acid (PAA) is hydrosonium (OH^+), which is reactive to both phenolic and non-phenolic types of lignin (Fossum and Marklund 1988; Kishimoto *et al.* 2003). As only the phenolic type of lignin is degraded during the O-stage, the employment of peracetic acid pre-treatment, which is capable of degrading non-phenolic lignin, may enhance lignin reactivity during succeeding stages (Obst *et al.* 1979; Minja *et al.* 1998).

The exposure of the woody material to ultraviolet and visible light, known as photo treatment, has been regularly reported to cause the degradation of lignin and carbohydrates (Kringstad 1969; Hon 1983; Davidson 1996; Bikova and Treimanis 2004). Based on these studies, which mostly focus on the irradiation absorption by synthesized lignin of ultraviolet and visible light, it was found that during photo treatment, active species, especially radicals, are generated. Thus, lignin degrades into a lower molecular weight by radical-induced depolymerisation (Bikova and Treimanis 2004; Chong *et al.* 2013b). Lignin shows a higher absorbency of the radiation than carbohydrates, even at different wavelengths, as it contains various chromophoric structures.

Some studies report that lignin is capable of absorbing wavelengths in the range of 280 to 400 nm (Bikova and Treimanis 2004; George *et al.* 2005). According to Sun *et al.* (1996) and Chong *et al.* (2013b), the addition of peroxide-aided photo treatment in a TCF bleaching sequence can successfully increase bleaching selectivity and hence shows the potential to improve O-stage selectivity. In this study, the effects of photo, peracetic acid, and the combination of the two pre-treatments on the selectivity of O-stage and also Op-stage towards the mixed tropical hardwood brown kraft pulp would be carried out. Moreover, the reason for increasing bleaching selectivity with these pre-treatments would be clearly justified. The effect of pre-treatments on the carbohydrate content, extracted lignin and pulp functional groups were investigated by gas chromatography and Fourier transform infrared spectroscopy (FTIR).

EXPERIMENTAL

Materials

Sabah Forest Industries Sdn. Bhd, Sabah, Malaysia provided the mixed tropical hardwood brown kraft pulp with kappa number of 16.4, pulp viscosity of 30.4 cP, and 36% ISO brightness.

Methods

Photo pre-treatment with or without the addition of peracetic acid

The required quantity of pulp was soaked in a sulphuric acid solution at pH 5 for 15 min. After that, pretreatment was performed in plastic bags containing 0.125% $MgSO_4$, and the pH 5 solution was added until a consistency of 10% was reached based on the oven-dried weight of the pulp. The sample was placed under blue light with a spectrum range of 460 to 490 nm or an ultraviolet irradiation machine at 369 nm for the desired duration of time. The distance between the lamp and the specimens was 3 cm for blue light and 5 cm for the UV light. Meanwhile, the wattage of the blue light and UV light were 20 watt and 6 watt， respectively. The pulp was then transferred to a 200-mesh filter and washed thoroughly with filter water to remove all the residue chemicals and lignin. The experiment was continued with oxygen bleaching after pre-treatment. The procedure for PAA-aided photo pre-treatment was the same; the only difference was an additional 0.05% PAA was added to the pulp mixture while adjusting the consistency.

Oxygen delignification

Oxygen delignification was carried out using a 650-mL stainless steel autoclave equipped with a gas inlet and stirrer, manufactured by the Parr Instrument Company, USA. This was done by mixing 22 g (oven-dry) of pulp with 0.5% magnesium sulfate, 2.5% sodium hydroxide, and 1.4% hydrogen peroxide (only for the Op-stage), according to the conditions desired. Then, the pulp was adjusted to a 10% consistency using distilled water and the fibre-chemical mixture was placed into the autoclave. After the cover was fastened, the air in the autoclave was replaced by oxygen gas through a gas inlet, and the pressure inside the autoclave was kept at 0.55 MPa and 100 °C for 30 min for all conditions. At the end of the delignification process, the reactor was cooled and the oxygen pressure was released. The pulp was then washed, spin-dried, and analysed.

Pulp properties

The delignified pulp was analyzed by the Technical Association of the Pulp and Paper Industry TAPPI T236 (2013) to find the kappa number, TAPPI T230 (2008) to establish pulp viscosity, TAPPI T525 (2012) to determine pulp brightness and TAPPI T249 (2000) to analyse the carbohydrates composition of extractive-free wood and wood pulp by gas-liquid chromatography. Bleaching selectivity is defined as the relative reactivity of a bleaching process toward the lignin and carbohydrate components of pulp and it was calculated as the ratio between the difference in kappa number to the difference in pulp viscosity (cP) before and after the process (Bajpai 2005; Paul e*t al.* 2004). The delignified pulp was also used for carbohydrate analysis by gas chromatography (GC). The GC was equipped with a flame ionization detector (FID) and a 30 m x 0.25 mm x 0.25 μm DB-225 column (J&W Scientific, Folsom, CA, USA). The GC oven was programmed at a constant temperature of 220 ºC with a holding time of 30 min; helium was used as carrier gas with flow rate of 25 mL/min and a split ratio of 50:1; and a sample size of 1 μL was injected (Agarwal and Atalla 1993; Agarwal e*t al.* 2003; Woldesenbet e*t al.* 2013).

Enzymatic extraction of residual lignin in pulps

Residual lignin in the chemical pulp was isolated using an enzymatic procedure with a commercially available cellulolytic enzyme according to the method proposed by Chang (1992). A pH 4.5 acetate buffer solution (6.56 mL sodium acetate and 4.64 mL acetate acid in 4 L of distilled water) was prepared. Commercially cellulolytic enzyme was dissolved in 100 mL of the acetate buffer solution. A 20-g (oven-dried weight) sample of pulp was treated with 12 mL of enzyme solution at a 5% consistency using the acetate buffer solution in each of four 500-mL Erlenmeyer flasks with screw caps. The treatment was carried out in a shaking water bath at 45 ºC for 48 h with continuous shaking. Then, the hydrolysates were removed by centrifugation. The residues from two flasks were combined, then placed into one flask for the second enzyme treatment, which was performed by adding 12 mL of the enzyme solution at the same consistency and under the same conditions as before. The residues from the two flasks were collected by centrifugation and combined into one flask for the third enzyme treatment under the same conditions. The fourth enzyme treatment was carried out according to the same procedure as for the third. However, instead of using 12 mL of enzyme solution, only 6 mL of enzyme solution was used for the fourth enzyme treatment. Residue from the final enzyme treatment was washed and then freeze-dried to give a water-insoluble residual lignin.

Analysis of residual lignin and delignified pulp by FTIR absorption spectroscopy

FTIR spectral data were obtained using the potassium bromide (KBr) pellet technique. Infrared spectra were recorded using a Shimadzu FTIR spectrometer, model 8201PC (Japan). Small amounts of sample pulp were mixed with the KBr powder at a concentration of 1 mg/100 mg KBr. The mixture was then ground for 3 to 5 min. The powder was pressed for 2 min to form a KBr pellet. The collar was placed with the pellet onto the sample holder. The spectra were recorded in the absorption band of 4000 to 400 cm^{-1}.

RESULTS AND DISCUSSION

Selectivity of Oxygen Delignification with and without Addition of Hydrogen Peroxide towards Tropical Mixed Hardwood Kraft Pulp

Figure 1 shows a typical selectivity curve (pulp viscosity (cP) against kappa number) of oxygen delignification (O-stage). The curve shows that the decrease in kappa number was accompanied by cellulose degradation (shown by the decrease in pulp viscosity). Moreover, the curve also shows a sharp decrease in viscosity when kappa number was approaching 9 (about 45% kappa number reduction). Hence, the efficiency of the ordinary O-stage towards the tropical mixed hardwood kraft pulp was limited to about 38% kappa number reduction, without serious cellulose degradation.

A modified O-stage achieved by adding 1.4% hydrogen peroxide (H_2O_2), known as H_2O_2-reinforced oxygen delignification (Op-stage), was found to be capable of decreasing the kappa number down to 7 (about 56% kappa number reduction) without causing serious cellulose degradation. According to Parthasarathy *et al.* (1990), the addition of H_2O_2 during an O-stage of more than 0.5% (on dry pulp weight) accelerates cellulose degradation. However, in the present case, even with the addition of 1.4% H_2O_2, the viscosity of the hardwood kraft pulp did not decrease dramatically. Thus, it can be seen that the selectivity curves of the two bleaching stages showed the same trend whereby the Op-stage method was improved by shifting towards the left (lower kappa number). Based on our previous results (Chong *et al.* 2013a), the maximum bleaching selectivity of the Op-stage (0.71) was higher than that of the O-stage (0.53). These selectivity curves are used as reference lines for the following research to observe the effect of pre-treatment on tropical mixed hardwood kraft pulp after an ordinary or improved O-stage.

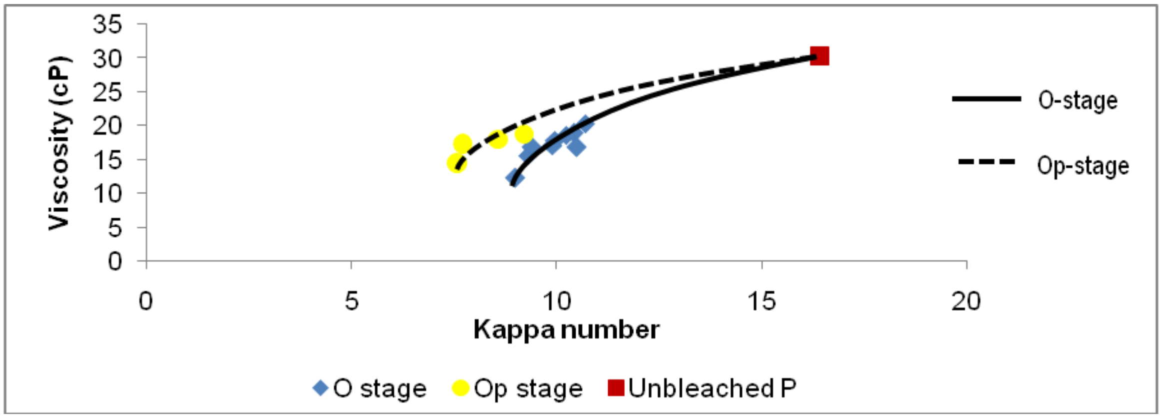

Fig. 1. Selectivity plot of O-stage and Op-stage on hardwood kraft pulp

Effect of Photo Pre-treatment on O-stage's Selectivity

Blue light has longer wavelengths (lower energy levels) than ultraviolet light; therefore, a shorter exposure time was applied for the latter (60 to 300 min) than the former (15 to 30 min) to minimise cellulose degradation (Bolton and Colton 2008). Based on Table 1 and Figure 2, the addition of blue light photo treatment (BL60-O) increased the degree of delignification from 37.8% to 44.5% and diminished cellulose degradation. Therefore, the selectivity increased from 0.53 to 0.77. When the reaction time was increased from 60 min to 300 min (BL300-O), however, the effectiveness of photo treatment remained unchanged, as there was no noticeable decrease in kappa number or pulp viscosity. Therefore, the selectivity of BL60-O and BL300-O were about the same, and the effect on pulp brightness was also negligible. Figure 2 clearly shows that the effect of blue light photo pre-treatment was similar to that of the improved O-stages (Op-stage).

Table 2 shows the FTIR spectra band absorption and the intensity of the distribution area of lignin extracted from unbleached and photo-treated pulp. FTIR spectroscopy at the mid infra-red region (4000 to 600 cm^{-1}) was carried out to detect the presence of chemical functional groups in various lignin samples. Table 2 shows that the band intensity at 3400 cm^{-1} of all the pre-treated lignin increased remarkably. This indicates that the presence of hydroxyl groups in this particular lignin increased, which can be attributed to the cleavage of β-ether bonds during the photo treatment process. The presence of hydroxyl groups allowed the lignin to be easily dissolved and degraded during the subsequent bleaching processes (Camarero *et al*. 1999). This explains why photo pre-treated pulp was more easily delignified during the succeeding O-stages.

Table 1. Effect of Photo Pre-treatment with and without PAA Pre-treatment on the O-Stage

No.	**Type of Light**	**PAA Charge (%)**	**Time (min)**	**Type of Oxygen Bleaching**	**Selectivity**	***Kn* Reduction (%)**	**Brightness (ISO, %)**
		Unbleached P					36.00
$\mathrm{O_O}$	-	-	-	O	0.53	37.8	43.15
$\mathrm{Bl300_0}$	Blue light	-	300	-	-	4.3	-
$\mathrm{UV30_0}$	UV light	-	15	-	-	7.9	-
BL60-O	Blue light	-	60	O	0.77	44.5	45.10
BL300-O	Blue light	-	300	O	0.74	45.7	46.70
U15-O	UV light	-	15	O	0.87	42.9	48.25
U30-O	UV light	-	30	O	1.01	53.7	47.77
$\mathrm{A_1}$	-	0.05	15	O	0.63	47.0	47.19
BL60P-O	Blue light	0.05	60	O	0.80	49.4	48.61
BL300P-O	Blue light	0.05	300	O	0.70	50.6	50.20
U15P-O	UV light	0.05	15	O	0.64	43.9	44.48
U30P-O	UV Light	0.05	30	O	0.79	54.3	50.05

O = O-stage bleaching

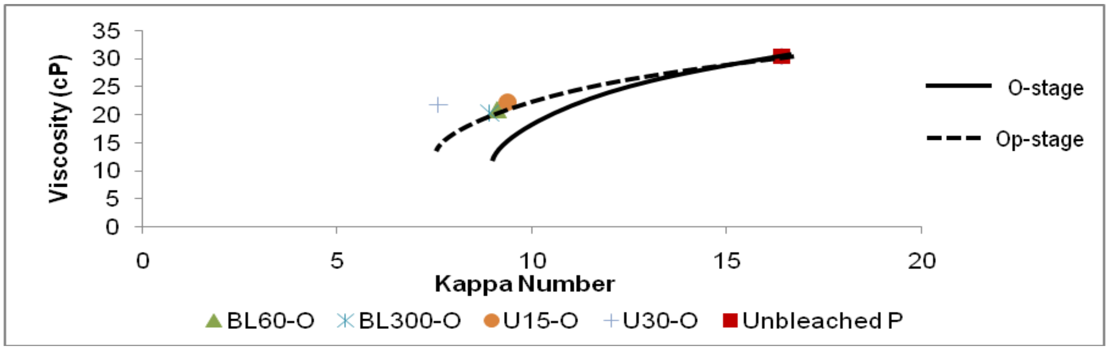

Fig. 2. Study of the selectivity plot of blue light and ultraviolet photo pre-treatment of the O-stage on hardwood kraft pulp

Because the exposure time of photo treatments was considered rather short, their effects on the reduction of the kappa number were negligible (Table 1). Nevertheless, the FTIR spectra show that photo treatment was capable of reducing the band intensity at 1500 cm^{-1} (aromatic skeleton stretching) from 1.91 to 1.00. This indicates that even though the lignin content of the pulp was not diminished by the photo treatments, the decrease in aromatic band intensity verifies the structural changes in the lignin, which are suspected to be caused by the opening of aromatic rings.

Previous studies have reported that lignin generates active species when exposed to ultraviolet (UV) and visible light, which cause photodegradation of lignocellulosic materials into materials with lower molecular weights (Kringstad 1969; Hon 1983; Davidson 1996; Bikova and Treimanis 2004). Thus, the detected changes in lignin structure are highly related to the degradation of lignin. This phenomenon is further supported by the slight decrease in band intensity absorption for wavelengths of 1380 cm^{-1} and 1280 cm^{-1}, which represent the presence of syringyl units (S unit) and guaiacyl units (G unit), respectively. Moreover, the reduction of C-O band intensity for wavelengths 1163 cm^{-1} from 7.86 down to 0.80 also indicated the structural change of lignin by photo treatment. Hence, using the same O-stage condition (O_O), the pulp exposed to photo treatment (both blue light and UV radiation) was more easily delignified than those without treatment, an observation attributed to the effects of photodegradation.

On the other hand, the increase of O-stage selectivity after undergoing a photo treatment is also attributed to a higher pulp viscosity retained. However, theoretically there are two factors that may explain why the pulp viscosity is preserved: 1) degradation and the removal of hemicellulose from the pulp, which may increase the average pulp viscosity; and/or 2) less cellulose degradation by random cleavage of the glycosidic bond of the cellulose chain. Thus, the analysis of carbohydrates and FTIR of the pulp were carried out to determine the reason.

Table 2. Summary of IR Bands and the Relative Intensity Observed in unbleached Lignin and the Single Stage of Photo Pre-treated Lignin

Type of band assignment	Band position (cm^{-1})	Unbleached Lignin	BL300$_{OL}$	UV30$_{OL}$
O-H stretching	3400	15.86	21.78	20.54
C-H stretch in methyl and methylene group	2900	6.28	6.31	5.12
C=O stretch in aldehyde	1650	9.32	8.74	9.14
Aromatic skeleton vibrations plus C=O stretching	1550	3.61	2.34	0.62
Aromatic skeleton vibrations	1500	1.91	1.17	1.00
C-H deformations (methyl and methylene)	1430	2.09	1.79	1.53
S unit	1380	3.85	3.28	3.59
G unit	1280	1.94	0.52	0.78
C-O stretching	1163	7.86	0 .80	0.80
Aromatic C-H in-plane deformation for GS unit	1113	5.46	4.83	4.72
C-O of secondary alcohols	1060	1.80	0.81	1.02
C-H out-of-plane	890	4.79	3.80	4.37

Carbohydrate analysis by gas chromatography (Table 3) clearly shows that oxygen-delignified pulp with and without photo treatment contained a similar percentage of glucose (about 75 to 80%), as well as other simple sugars from hemicellulose. This indicates that photo treatment did not induce the degradation and removal of hemicellulose. Hence, the high pulp viscosity can be attributed to less cellulose chain cleavage.

Table 3. Carbohydrate Composition of Pre-treated and Ordinary Oxygen-delignified Pulp

	Arabinose (%)	Xylose (%)	Mannose (%)	Galactose (%)	Glucose (%)
Unbleached P	2.67	16.94	8.32	4.37	67.69
O_O	1.99	12.67	7.02	3.87	74.46
BL300-O	1.10	14.61	2.35	0.79	81.16
UV30-O	1.73	14.93	3.01	1.05	79.28
BL300P-O	1.54	13.93	3.34	1.44	79.75
UV30P-O	1.92	14.10	3.68	1.32	78.98

FTIR spectra of the unbleached, pre-treated, and bleached hardwood kraft pulps are shown in Figure 3. It is obvious that after photo pre-treatment, the peak at 1600 cm^{-1}, which is assigned to the carbonyl (C=O) stretching vibration of aldehyde groups, was reduced. Similar peak reduction was also observed for pre-treated pulp after the O-stage. As stated by Sjöström (1993), the presence of carbonyl groups in carbohydrates tends to promote carbohydrate degradation in an alkaline treatment as the glycosidic bond becomes more alkali-labile.

This clearly reveals that both photo pre-treatments (blue light and UV irradiation) are capable of reducing the amount of carbonyl groups in the carbohydrates (cellulose and hemicellulose) and thus prevent carbohydrate degradation through the random cleavage of glycosidic bonds in cellulose. Thus, without a photo treatment to reduce the carbonyl group content, such as sample O_O, the cellulose is easily degraded by the β-alkoxy elimination mechanism during the O-stage, which results in pulp with lower viscosity and retains relatively higher transmittance at 1600cm^{-1}. In short, the protective effect of photo pre-treatment on pulp viscosity is verified by the elimination of carbonyl groups.

Moreover, it is interesting to note that transmittance peaks in the region for aromatic groups (in the range of 1550 to 1500 cm^{-1}) for the pulp pre-treated solely with photo treatments almost disappear. As mentioned earlier, photo pre-treatment does not cause a considerable reduction in kappa number. Thus, it is again verified that photo pre-treatment can cause a ring-opening reaction in lignin. As a result, the lignin of the photo pre-treated pulp was more easily attacked and degraded during the O-stage (compared with unbleached pulp without photo pretreatment), which resulted in pulp with a lower kappa number. At the same time, it is believed that the enhancement of delignification indirectly diminishes unwarranted carbohydrate degradation. Thus, the pulp preserves a higher viscosity.

Effects of PAA and PAA-aided Photo Pre-treatments on O-stage's Selectivity

Figure 4 shows the effect of peracetic acid (PAA) and PAA-aided photo pre-treatment on the selectivity of oxygen-delignified pulp. With the addition of only 0.05% peracetic acid at pH 5 for 15 min at 80 ºC (A_1), the kappa number was reduced to 8.7 and the pulp retained a viscosity of 18.2 cP. Therefore, the selectivity increased from 0.53 (O_0) up to 0.63 (A_1) (Table 1). Peracetic acid produces hydroxonium ions (OH^+), which are highly reactive and degrade both phenolic and non-phenolic lignin structures by degrading the ether linkage; therefore, it is believed that the degradation of lignin structures may enhance the efficiency of subsequent alkaline bleaching (Suss and Helmling 1987; Fossum and Marklund 1988; Kishimoto *et al.* 2003). Thus, the addition of peracetic acid increased bleaching selectivity.

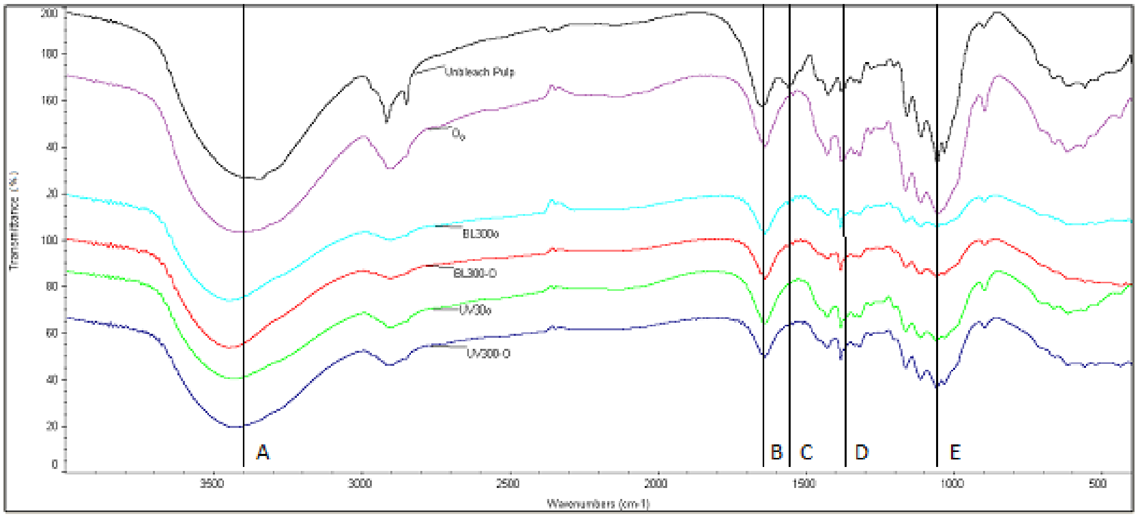

Fig. 3. Distribution area for the assignment band of the signal in the FTIR spectra of photo pre-treated oxygen-delignified pulp. (A refers to hydroxyl groups (3400 cm^{-1}); B refers to carbonyl groups (1650 cm^{-1}); C refers to aromatic groups (1550 cm^{-1}); D refers to S unit (1380 cm^{-1}), and E refers to carbon-oxygen bond (1160 cm^{-1}))

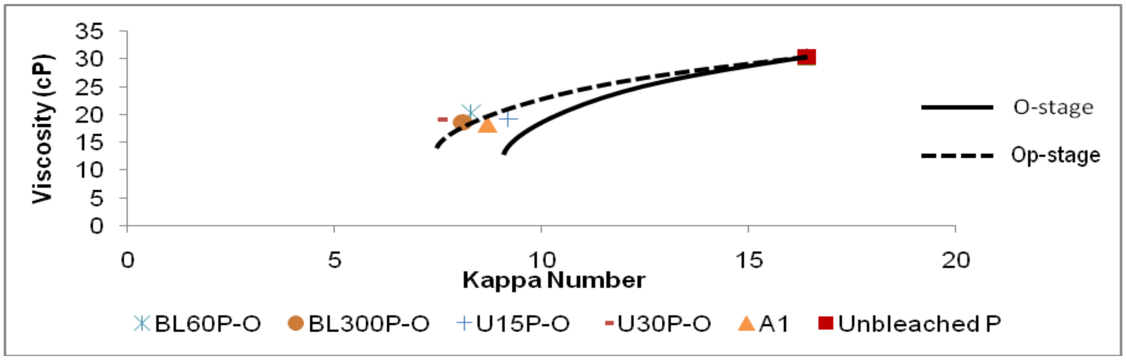

Fig. 4. Selectivity plot of PAA-aided blue light and ultraviolet photo pre-treatment with the O-stage on hardwood kraft pulp

However, when PAA was added to photo pre-treatments (combination pre-treatment), the kappa number was reduced by 2% and the pulp brightness only increased by 3.5%. Nevertheless, the photo treatments were still capable of protecting the carbohydrates from undergoing serious degradation. The results indicate that even though both the photo treatment and PAA treatment alone noticeably improve the bleaching selectivity of the O-stage, the combination of these two treatments in one step (PAA-aided photo pre-treatment) did not exhibit beneficial effects on selectivity; an even lower selectivity was attained for U15P-O and U30P-O. This phenomenon suggests that the reactive species from PAA and that generated from UV irradiation exist in one step, which counteracts and thus weakens its efficiency and effectiveness on delignification.

The results of carbohydrate composition for both PAA-aided photo treatment and photo treatment alone demonstrate a similar percentage of glucose and other simple sugars from hemicellulose, as shown in Table 3. This indicates that the addition of PAA does not have any effect on carbohydrate composition in the pulp resulting from the dissolution of hemicellulose.

The FTIR spectra of PAA-aided photo pre-treated hardwood kraft pulps are shown in Figure 5. PAA-aided photo pretreated pulp shows a lower peak intensity at 1600 cm^{-1} (carbonyl group) in comparison with unbleached pulp, and a similar peak intensity to those treated with photo irradiation. This clearly reveals that the addition of PAA to both photo pre-treatments (blue light and UV irradiation) did not induce an additional reduction of the amount of carbonyl groups in the carbohydrates. Moreover, aromatic groups (in the range of 1550 to 1500 cm^{-1}) in the PAA-aided photo pretreated pulp cannot be detected from the spectra. This verifies that the introduction of PAA into photo pre-treatment had the same effect as photo pretreatment alone on lignin aromatic structures.

Effect of Photo, PAA, and Combination Pre-treatments on the Op-stage's Selectivity

Table 4 and Figure 6 show the effect of photo pre-treatment prior to the Op-stage on pulp properties in terms of bleaching selectivity, kappa number reduction, and pulp brightness. It is interesting to note that the addition of 60-min blue light photo treatment prior to an Op-stage (BL60-Op) neither improved the degree of delignification nor induced cellulose degradation; moreover, a prolonged blue light photo treatment of 300 min (BL300-Op) started to decrease pulp viscosity without a noticeable decrease in kappa number. Thus, the bleaching selectivity of BL300-Op decreased. The most prominent benefit of blue light photo treatment prior to the Op-stage was the increase in pulp brightness by about 8% and 19%, which are from 52% of the Op-stage to 56.2% of BL60-Op and 59.8% of BL300-Op, respectively. On the other hand, UV photo treatments of 15 min and 30 min had more effect on bleaching selectivity. As shown in Figure 5, UV pre-treated pulp can achieve a lower kappa number (below 7) while retaining a pulp viscosity above 17 cP. However, no noticeable improvement in pulp brightness was observed.

The effect of PAA pre-treatment prior to the Op-stage was not as promising as pre-treatment prior to the O-stage (Figure 7). The introduction of PAA treatment decreased the bleaching selectivity to 0.67 even though it increased the kappa number reduction to 61% (Table 4). The results listed in Table 4 also show that PAA-aided photo pre-treatments (combination pre-treatment) slightly improved bleaching selectivity as compared with PAA treatment alone. However, the addition of 0.05% PAA to both blue light and UV photo treatments did not show a significant improvement in bleaching selectivity, and the reduction in kappa number and increase in pulp brightness most likely achieved their maximum extents, which were 61% and 63% ISO brightness, respectively.

Similar to the O-stage, PAA-aided photo treatment did not exhibit better delignification, although it is well-recognized that it degrades both phenolic and non-phenolic lignin.

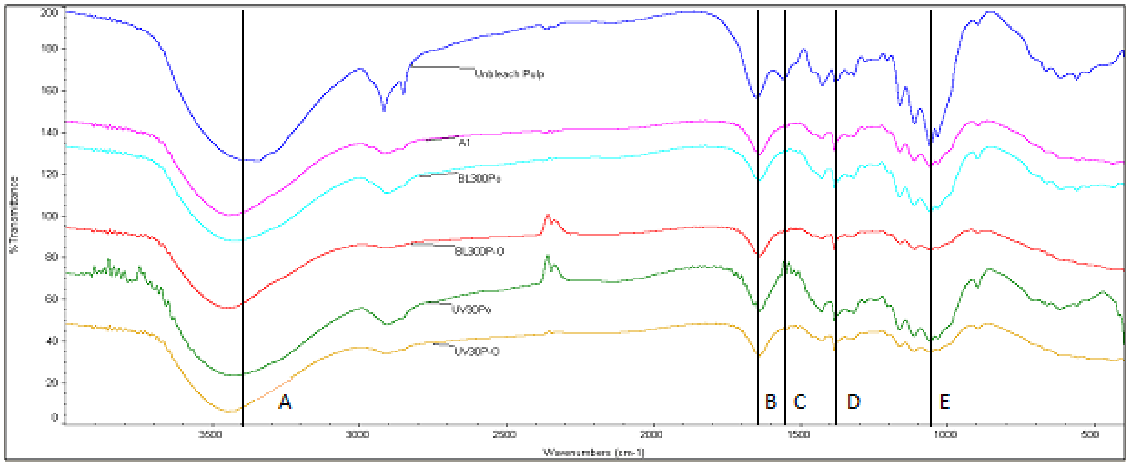

Fig. 5. Distribution area for the assignment band of the signal in FTIR spectra of PAA-aided photo pre-treated oxygen delignified pulp (A refers to hydroxyl groups (3400 cm^{-1}); B refers to carbonyl groups (1650 cm^{-1}); C refers to aromatic groups (1550 cm^{-1}); D refers to S unit (1380 cm^{-1}), and E refers to carbon-oxygen bond (1160 cm^{-1}))

Table 4. Effect of Photo Pre-treatment with and without PAA Pre-treatment on the Op-Stage

No.	Type of Light	PAA Charge (%)	Time (min)	Type of Oxygen Bleaching	Selectivity	Kn (%)	Brightness (ISO, %)
	Unbleached P						36.00
Op	-	-	-	Op	0.71	55.5	52.00
BL60-Op	Blue light	-	60	Op	0.74	56.1	56.21
BL300-Op	Blue light	-	300	Op	0.65	57.3	59.81
U15-Op	UV light	-	15	Op	0.73	57.3	60.51
U30-Op	UV light	-	30	Op	0.73	59.2	60.31
A_2	-	0.05	15	Op	0.67	61.0	61.00
BL60P-Op	Blue light	0.05	60	Op	0.69	59.4	62.39
BL300P-Op	Blue light	0.05	300	Op	0.68	61.3	63.45
U15P-Op	UV light	0.05	15	Op	0.73	57.3	61.09
U30P-Op	UV light	0.05	30	Op	0.69	56.7	58.39

FTIR spectra of PAA-aided photo pre-treated Op-stage hardwood kraft pulp are shown in Figure 8. Similar to the O-stage, the peak reduction of carbonyl groups at 1600 cm^{-1} was observed for all pre-treated Op pulp. Moreover, the transmittance peaks in the region for the aromatic groups (in the range of 1550 to 1500 cm^{-1}) for all pre-treated pulp also were shown to disappear in the spectra. However, it is remarkable that the photo-pretreated pulp with the addition of PAA showed a different transmission spectra from that of photo-pretreated pulp without PAA, especially in the spectra region between 1400 and 1000 cm^{-1}.

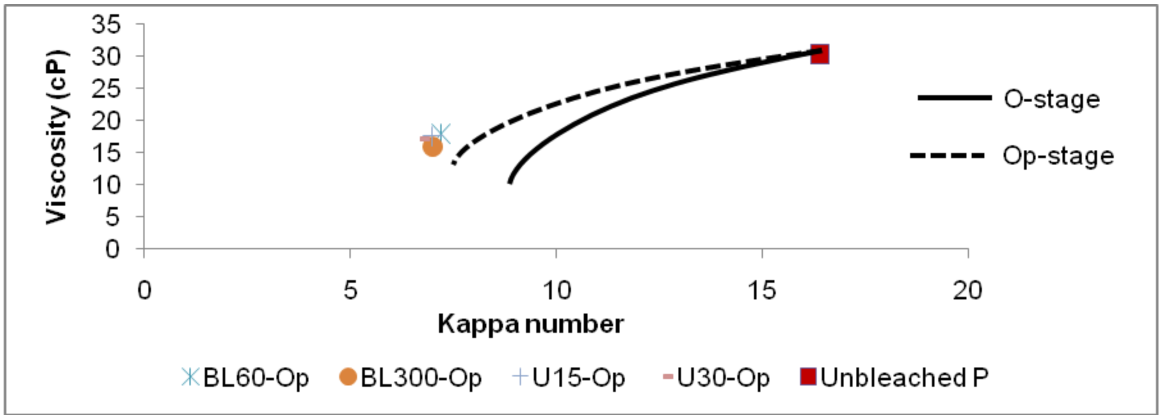

Fig. 6. Selectivity plot of blue light and ultraviolet photo pre-treatment with the Op-stage on hardwood kraft pulp

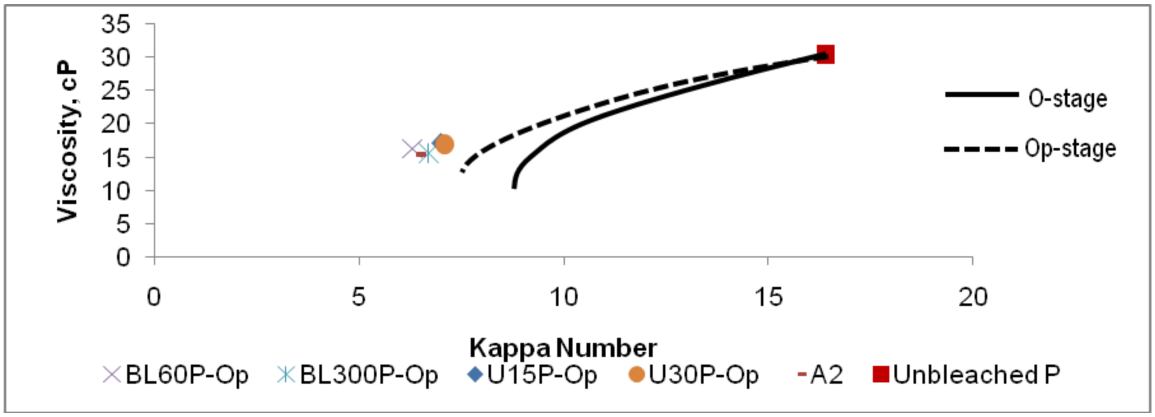

Fig. 7. Study of PAA-aided blue light and ultraviolet photo pre-treatment with the Op-stage

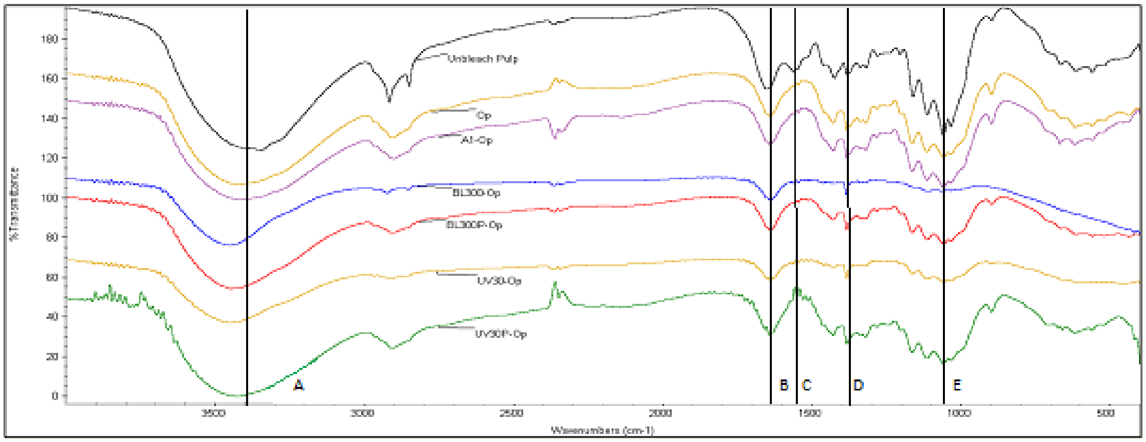

Fig. 8. Distribution area for the assignment band of the signal in FTIR spectra on photo pre-treated Op-stage pulp (A refers to hydroxyl groups (3400 cm^{-1}); B refers to carbonyl groups (1650 cm^{-1}); C refers to aromatic groups (1550 cm^{-1}); D refers to S unit (1380 cm^{-1}), and E refers to carbon-oxygen bond (1160 cm^{-1}))

The transmission peaks within this range were reduced or completely disappeared when photo pre-treatment alone was applied. However, when PAA was added, the transmission peaks were, again, similar to un-pretreated Op pulp. This phenomenon suggests that the reactive species formed during photo treatment, which can react with functional groups such as G and S units, C-O stretching, and C-O of secondary alcohols, were counteracted by PAA. As a result, PAA-aided photo pre-treatment demonstrated a low efficiency for improving bleaching selectivity.

CONCLUSIONS

1. The application of photo pre-treatment (blue light or UV radiation) before an oxygen delignification stage was capable of retaining higher pulp viscosity and therefore improved totally chlorine free (TCF) bleaching selectivity.
2. FTIR analysis of the pulp and its extracted lignin indicated that photo irradiation caused lignin degradation and reduced the amount of carbonyl groups in the carbohydrates.
3. The findings obtained verify the positive effect of photo pre-treatment protecting carbohydrates from major degradation during the subsequent O-stage or Op-stage through the carbonyl-induced random cleavage of glycosidic bonds in cellulose chain.
4. Although peracetic acid (PAA) pre-treatment alone improved bleaching in the O-stage, the combination of PAA and photo treatment did not show a beneficial effect in comparison with photo pre-treatment alone.
5. The application of a photo pre-treatment, kappa number reduction can be improved up to 40% for O-stage and no more than 7% for Op-stage. Between the two different light sources of photo treatments, excluding the irradiation time applied, the resultant pulp obtained showed basically similar properties.

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