Effect of Hydrogen Peroxide and Anthraquinone on the Selectivity and Hexenuronic Acid Content of Mixed Tropical Hardwood Kraft Pulp during Oxygen Delignification

Yin Hui Chong, Wan Rosli Wan Daud, and Cheu Peng Leh *

In this study, the bleachability of commercial mixed tropical hardwood brown kraft pulp by oxygen delignification (O stage) was examined. It was found that the effective reduction of kappa number was limited to about 35%, and the pulp viscosity was 20.3 cP with a selectivity less than 0.60 and ISO brightness of *ca.* 43%. The selectivity and pulp brightness of the O stage were improved by adding H_2O_2 (O_P stage) because it decreased the kappa number to a greater extent. However, the addition of hydrogen peroxide caused more serious cellulose degradation. In order to minimize the drop of pulp viscosity during the O_P stage, a small amount (0.04%) of anthraquinone (AQ) was added. The results showed that the AQ-aided O_P stage was capable of preventing cellulose degradation and thus improved the bleaching selectivity about 60%, in comparison to the ordinary O stage. Moreover, the AQ-O_P pulps retained significantly less hexenuronic acid than the pulps from O and O_P stages.

Keywords: Oxygen delignification; Peroxide reinforcement; Anthraquinone; Hexeneuronic acid; Brightness; Pulp viscosity

*Contact information: Bioresource, Paper and Coatings Technology, School of Industrial Technology, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia; *Corresponding author: cpleh@usm.my*

INTRODUCTION

After the discovery of the formation of highly toxic and persistent by-products, such as chlorinated dioxins, furans, and other organic compounds, when using the conventional chlorine-based bleaching processes, an increase in demand for chlorine-free bleached pulp and paper products from the public has been observed since the late 1980s (Smook 1992) . Hence, the implementation of a totally chlorine-free (TCF) bleaching sequence has been widely promoted with the aim of completely eliminating the use of chlorine-containing chemicals in bleaching plants.

Among all the chlorine-free bleaching agents, oxygen delignification (O stage) plays an important role in developing and implementing TCF bleaching processes, as it is capable of removing residual lignin in bulk (Minja *et al*. 1998). However, in comparison to conventional bleaching, like most of the TCF bleaching stages, O stage shows lower selectivity, which is indicated by less delignifying power but more extensive degradation of carbohydrates. Generally, the removal of lignin by an O stage is limited to 50% or

lower, depending on the pulp. Beyond that limit, both lignin and carbohydrates are degraded unselectively, resulting in a relatively weak pulp.

Over the past 30 years, many attempts have been made to improve the selectivity of the O stage with minor modifications. One such attempt was hydrogen peroxide-reinforced oxygen bleaching (O_P), which is carried out by adding hydrogen peroxide (H_2O_2) to the O stage (Suchy and Argyropoulus 2002). Many reports have shown that the addition of H_2O_2 in an amount of no more than 0.5% (oven dry pulp weight) is beneficial to the O stage. It may increase the degree of delignification to a small extent and retain the pulp viscosity at an acceptable level. However, its effect on pulp brightness is negligible (Farley 1973; Parthasarathy *et al.* 1990; Sjödin and Nordén 1994; Boman and Reeves 1995; Stevens and Hsieh 1995; Asgari and Argyropoulos 1998; Argyropoulos *et al*. 2004). In order to attain promising effects of H_2O_2 on delignification and pulp brightness, a larger amount of H_2O_2 charge is required. Nevertheless, the addition of a higher charge of H_2O_2 will inevitably induce undesirable cellulose degradation due to the generation of unselective hydroxyl radicals (OH·)

In a more recent study, Ng and co-workers (2011) reported that an addition of a small amount of anthraquinone (AQ) to O, and O_P stages gave different beneficial effects on oil palm fiber soda-anthraquinone pulp. In the former case, the addition of 0.02% AQ favoured K_n reduction, but no effect was observed on pulp viscosity. However, with the presence of H_2O_2 up to more than 1% in the latter case (O_p stage), the addition of AQ exhibited a significant effect on retaining a higher pulp viscosity. Nevertheless, it diminished the positive effect of AQ on delignification.

The authors (Ng *et al.* 2011) claimed that under an O stage, similar to alkaline pulping, AQ was reduced to anthrahydroquinone (AHQ) by the oxidation of the cellulose reducing end groups. As AHQ is capable of catalyzing the cleavage of lignin β-aryl ether linkages in free phenolic phenylpropane units, it improved K_n reduction. However, under an O_P stage, AHQ might also react with the OH· generated through stepwise reduction of oxygen and decomposition of H_2O_2. Therefore, the amount of AHQ available for depolymerizing lignin was decreased (Fig. 1). On the other hand, the reaction between OH· and AHQ in the system might lessen the negative impact of OH· on cellulose degradation as well. Moreover, the study also found that to avoid an uncontrollable drop of pulp viscosity, a sufficient alkali charge was necessary during the O_P stage.

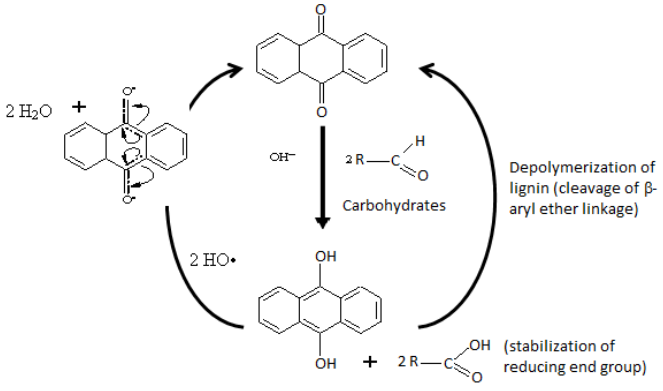

Fig. 1. Scheme for anthraquinone-anthrahydroquinone reactions with carbohydrates and lignin during oxygen delignification in the presence of hydrogen peroxide (Ng *et al.* 2011)

The addition of AQ to an O stage in the delignification of wheat straw soda-pulps was carried out by Liu *et al.* (2013). Different from the findings of Ng *et al.* (2011), the AQ added to O stage did not give any significant effects, neither on K_n nor pulp viscosity, but it improved pulp yield. Thus, although previous studies have verified that the addition of AQ resulted in positive effects on O_p and even O stages, the effects reported were varied as pulps from different non-wood sources were used. Therefore, in this study, the effect of the anthraquinone-aided O_P stage on a mixed tropical hardwood kraft pulp's properties (kappa number, pulp viscosity, brightness, and hexenuronic acid content) was investigated. Moreover, the optimum amount of AQ was also determined.

EXPERIMENTAL

Materials

Sabah Forest Industries Sdn. Bhd, Sabah, Malaysia provided the mixed tropical hardwood brown kraft pulp. Table 1 shows the properties of the material.

Table 1. Properties of Mixed Tropical Hardwood Brown Kraft Pulp

Kappa number	16.4
Pulp viscosity, cP	30.4
ISO brightness, %	36.0
Hexenuronic acid, μmol/gPulp	55.5

Methods

Procedure of oxygen delignification

Oxygen delignification was carried out using a 650 mL stainless steel autoclave equipped with a gas inlet and a stirrer, manufactured by Parr Instrument Company, USA. Twenty-two grams (o.d.) pulp was mixed with 1% $MgSO_4.7H_2O$ and an appropriate amount of alkali charge (NaOH) (1.5, 2.0, 2.5, or 3.0%) according to the conditions desired. The pulp mixture was then adjusted to 10% consistency using distilled water and placed into the autoclave. After fastening the cover, the air in the autoclave was replaced by oxygen gas through a gas inlet. The pressure inside the autoclave and the reaction temperature for all conditions were kept constant at 0.55 Mpa and 100 °C, respectively, for 30 min. At the end of delignification, the reactor was cooled and the oxygen pressure was released. The pulps were then washed, spin dried, and analyzed for pulp properties.

Procedure of hydrogen peroxide-reinforced oxygen delignification with or without AQ

The procedures of H_2O_2-reinforced oxygen delignification with and without the aid of AQ were the same; the only difference was that additional H_2O_2 (and AQ) was added to the pulp mixture, according to Table 2.

Pulp properties

The oxygen delignified pulps were analyzed by TAPPI UM-246 to find the kappa number, JPRI Standard 3015 (a modified method of TAPPI Standard T230 su-66) to establish pulp viscosity, ISO2470 to determine pulp brightness, and TAPPI T282 pm-07

to determine hexeneuronic acid content of the chemical pulp. The bleaching selectivity was calculated as the change of kappa number divided by the change to pulp viscosity (cP).

Table 2. Bleaching Conditions of Peroxide-reinforced Oxygen Delignification with and without Anthraquinone Aid

	Peroxide-reinforced				Anthraquinone-aided peroxide-reinforced							
NaOH, %	1.5	2.0	2.5	3.0	2.5	2.5	2.5	2.5	2.5	1.5	2.0	3.0
H_2O_2, %	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
AQ, %	-	-	-	-	0.02	0.04	0.06	0.08	0.15	0.04	0.04	0.04

RESULTS AND DISCUSSION

Comparison between Oxygen Delignification and H_2O_2 Reinforced Oxygen Delignification

Alkali charge (A_C) is one of the most influential parameters for oxygen delignification (O stage). An increase of A_C increases the amount of hydroxyl ions proportionally and thus intensifies the reaction rate with residual lignin and cellulose (Leh *et al.* 2008). As shown in Table 1, various O stages were carried out with different A_C (in the range of 1.5 to 3.0%) at a constant reaction temperature of 100 °C and reaction time of 30 min. The O stage with 1.5% A_C decreased the kappa number (K_n) of the tropical mixed hardwood kraft pulp from 16.4 to 10.7 (Fig. 2), which amounted to a 34.9% reduction of K_n (Fig. 3). Additionally, the ISO pulp brightness increased about 17% (Fig. 4).

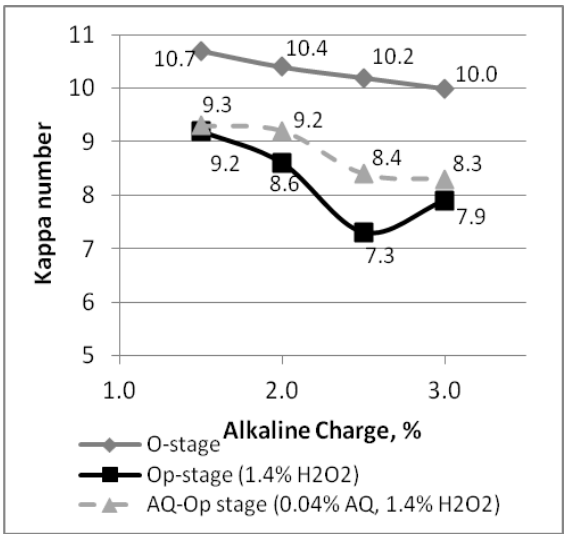

Fig. 2. Effect of alkaline charge on kappa number of mixed hardwood kraft pulp in different bleaching stages

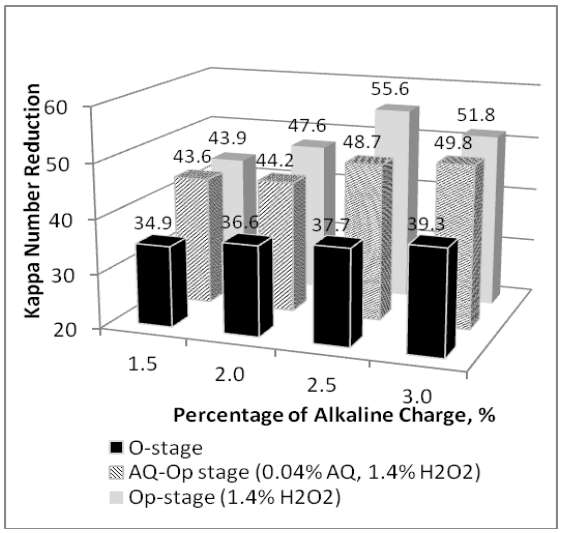

Fig. 3. Effect of alkaline charge on kappa number reduction of mixed hardwood kraft pulp in different bleaching stages

Quite notably, a further increase of A_C up to 3.0% only improved the K_n reduction and ISO brightness slightly, but the pulp viscosity decreased to a greater extent (Fig. 5). This indicated that the effectiveness and efficiency of the O stage toward the tropical mixed hardwood kraft pulp declined when more than 1.5% A_C was applied. Hence, the effective reduction of K_n was limited to about 35%, or K_n of 10.5, in which the pulp viscosity was 20.3 cP with a selectivity less than 0.60 (Fig. 5). Although the reduction was rather low, it was similar to a hardwood kraft pulp (*Eucalyptus globulus*) produced by a South American mill, wherein the O stage decreased the kappa number from 16.3 to 10.4 (Tavast *et al*. 2011). Nevertheless, as the first bleaching stage, the O stage should attain higher selectivity by increasing the delignifying power or retaining higher pulp viscosity, or both together to achieve a comparative bleaching effect to the conventional CE stage.

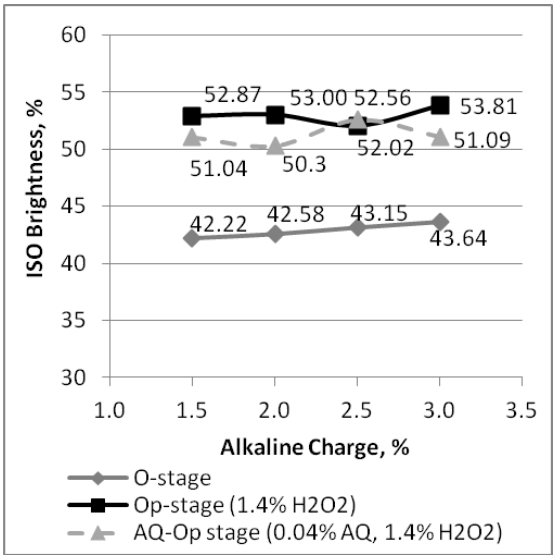

Fig. 4. Effect of alkaline charge on ISO brightness of mixed hardwood kraft pulp in different bleaching stages

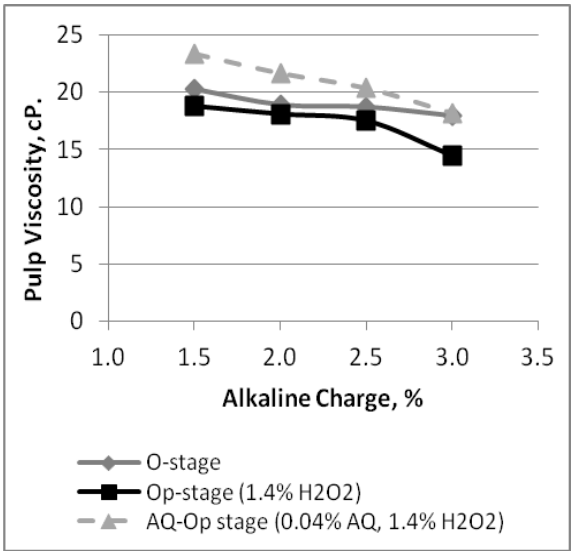

Fig. 5. Effect of alkaline charge on pulp viscosity of mixed hardwood kraft pulp in different bleaching stages

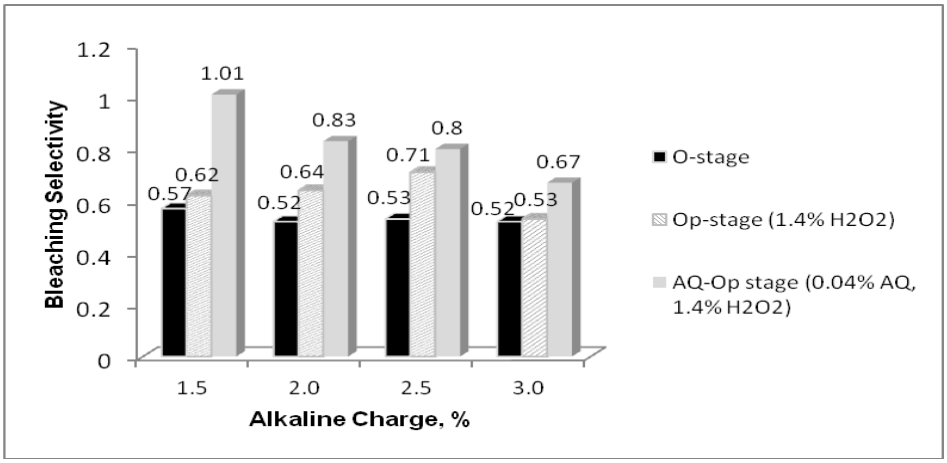

Fig. 6. Effect of alkaline charge on bleaching selectivity of mixed hardwood kraft pulp in different bleaching stages

The hexenuronic acid (HexA) content of the brown hardwood pulp was 55.5 μmol/gPulp, as shown in Table 1. Figure 6 demonstrates that the oxygen-delignified pulps retained a HexA content in the range of 48.4 to 51.5 μmol/gPulp. These results revealed that an O stage could remove a HexA content of only less than 10%. Furthermore, the increase of A_C would not enhance the removal of HexA by an O stage.

In order to enhance the effectiveness of the O stage toward hardwood pulp, 1.4% hydrogen peroxide (H_2O_2) was added during the O stage. Figures 1 and 2 show that all of the H_2O_2-reinforced O stages (O_P stage) with different A_C yielded a higher degree of delignification, in which the reduction of K_n was improved perceptibly, ranging from 43.9% to 55.6%. It was remarkable that the kappa number of the O_P stage with only 1.5% A_C was 9.2, which could hardly be achieved by the O stage, even with a higher A_C.

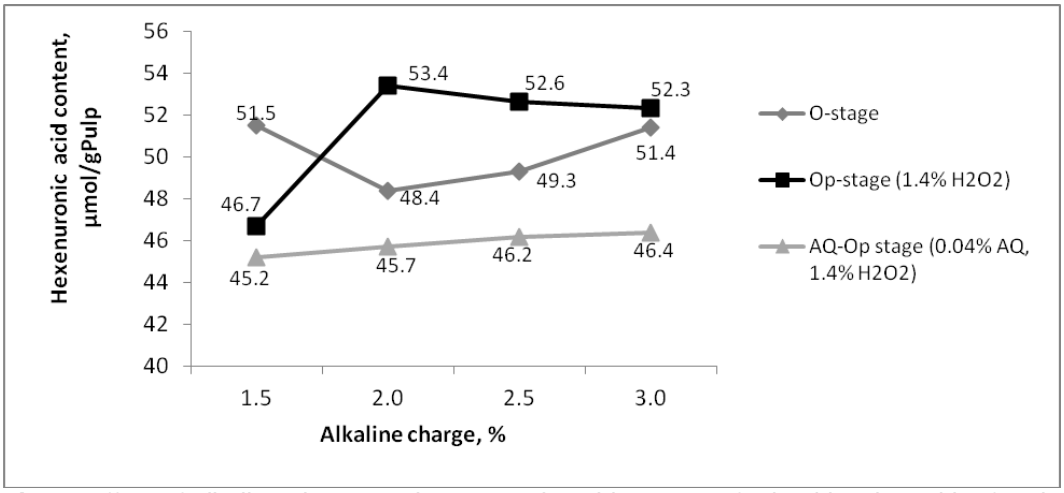

Fig. 7. Effect of alkaline charge on hexenuronic acid content of mixed hardwood kraft pulp in different bleaching stages

Moreover, since H_2O_2 is a well-known brightening agent, the brightness of the resultant pulps was increased to the range of 52% to 54% ISO brightness (Fig. 4). That is, the brightness increased more than 20% compared to its ordinary O stage counterparts. On the other hand, although Fig. 5 shows that the pulp viscosity of O_P stages was lower than that of the O stage counterparts, the bleaching selectivity of the former was higher than that of the latter for those conditions with A_C up to 2.5% (Fig. 6). This is because the O_P stage was capable of achieving lower K_n (Fig. 2). However, when the A_C was increased to 3.0%, no beneficial effect on further delignification was observed; rather it was accompanied by a substantial drop of pulp viscosity (Fig. 5).

Previous studies indicated that the addition of H_2O_2 in an amount less than 0.5% is favourable to an O stage. This is because the addition of more than 1% H_2O_2, without introducing other additives, will cause serious cellulose degradation due to more hydroxyl radicals (OH·) being generated. Although the unstable hydroxyl radicals are responsible for delignification, they also attack the cellulose chains, resulting in strength loss of the fibres (Sjöström 1993; Potùcek *et al.* 2000; Suchy and Agryropoulos 2002; Knill and Kennedy 2003; Ng *et al.* 2011). However, in this study, the addition of 1.4% H_2O_2 had yet to stimulate the degradation of cellulose to a large extent. This indicated

that the effect of H_2O_2 addition was also dependent on the origin of pulp. Additionally, Fig. 7 shows that the addition of H_2O_2 did not help in reducing the content of HexA compared to the ordinary O stage.

Effects of Anthraquinone Charge on H_2O_2 Reinforced Oxygen Delignification

According to Ng *et al.* (2011), the addition of 0.02% AQ to an O_p stage of oil palm EFB soda-AQ pulp resulted in the positive effect of increasing the bleaching selectivity through retaining higher pulp viscosity. In the current case, because a different type of pulp was used, the optimum amount of AQ required was probably different, thus requiring identification. The effects of different AQ charges (0.02% to 0.15%) of O_p stage on pulps' properties are demonstrated in Fig. 8. It was very interesting to see that at a constant A_C of 2.5% and H_2O_2 of 1.4%, K_n and brightness of all the resultant pulps were of similar values, which were in the range of 8.4 to 8.5 and 48.3 to 48.7% ISO, respectively, regardless of the amount of AQ added to the O_P stage. This was in agreement with the findings of Ng *et al.* (2011). According to them, even though an increase of AQ and H_2O_2 charges individually to an O stage contributed to a decrease of K_n, the beneficial effect became insignificant when the two chemical additives were added as one.

Under alkaline conditions, AQ is reduced to anthrahydroquinone (AHQ) by the oxidation of the cellulose-reducing end group. Since AHQ is capable of catalyzing the cleavage of lignin β-aryl ether linkages in free phenolic phenylpropane units, it improves delignification. On the other hand, the addition of H_2O_2 increased the amount of HO· generated through its decomposition reaction, and thus contributed a decrease of K_n as well. However, when AQ and H_2O_2 were added together, both the amount of AHQ and radicals that caused the depolymerisation of lignin might have decreased due to mutual reaction. Since the H_2O_2 charge added in this study was rather high (1.4%), it caused the effect of the AQ on delignification to become negligible, even though up to 0.15% AQ was added.

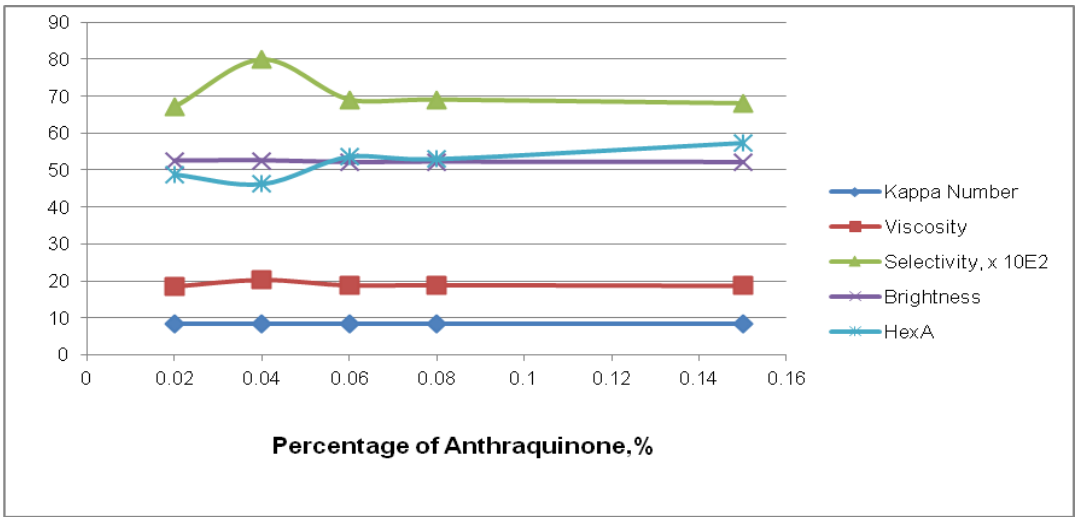

Fig. 8. Study of optimizing AQ-aided O_p stage (1.4% H_2O_2) on hardwood kraft pulp

In comparison to O_P (with 2.0% $A_{C,}$ Fig. 4) bleached pulp with similar K_n, all pulps from AQ-aided O_P stages (Fig. 8), regardless of the AQ charge, exhibited higher viscosity. This indicated that the addition of AQ was capable of reducing the severity of cellulose degradation. As mentioned earlier, the reduced AQ (AHQ) present in the bleaching system readily reacts with the hydroxyl radicals, and therefore, the amount of hydroxyl radicals was reduced. Since the radicals attack both lignin and cellulose unselectively, the reduction of the radicals possibly minimized cellulose degradation. This also explains why the K_n reduction and the brightness of the AQ-aided O_P bleached pulps were lower than the ordinary O_P stage with the same A_C (Ng *et al*. 2011). The increase of AQ charge had a negligible effect on pulp brightness as well.

On the other hand, the oxidation of the cellulose-reducing end groups (mainly generated due to the cleavage of glycosidic bonds along the cellulose chain) by AQ to alkali-stable aldonic acid groups, and thus, further end groups peeling reaction will be retarded (Löwendahl and Samuelson 1978). Based on pulp viscosity and selectivity, the optimum charge of AQ for the hardwood kraft pulp was 0.04%, in which the resultant pulp retained a viscosity of 20.4 cP and the selectivity increased to 0.80, as shown in Fig. 8. Adding 0.02% AQ was insufficient to give substantial protection to the pulp viscosity whereas an overload of AQ (0.06% to 0.15%) did not improve pulp viscosity. A further study is required to investigate whether the limitation of AQ addition on pulp viscosity is due to its nature or the presence of H_2O_2 in the system.

An interesting phenomenon was observed concerning the HexA content. The increase of AQ charge from 0.02 to 0.15% seemed to preserve the HexA. As exhibited by Fig. 8, when the AQ charge was 0.04% and below, the HexA content decreased, resulting in an amount below 50 μmol/gPulp. However, when the AQ charge was increased to 0.06% and above, the HexA content remained above 53 μmol/gPulp. The content increased to 57.4% when the AQ charge was increased to 0.15%. This occurrence indicated that a large dosage of AQ in the O_P stage possibly preserved HexA indirectly through the stabilization of carbohydrates, and it also supported the fact that the optimum charge of AQ was 0.04% in the present study.

Effect of Anthraquinone on Hydrogen Peroxide Reinforced Oxygen Delignification

The effect of AQ during the O_p stage was further investigated by adding 0.04% AQ to O_P stages with different A_C. Figure 1 illustrates that the K_n of the AQ-aided O_p stages was about 1.4 to 1.8 units lower than that of O stages, but slightly higher than that of O_P stages. As explained earlier, owing to the reaction between the hydroxyl radicals and AHQ, which diminished the effectiveness of delignification, the K_n reduction of the AQ-aided O_P stage did not exceed 50% (Fig. 3). Nevertheless, the pulp brightness was comparable to that of O_P stage (Fig. 4).

The most beneficial effect of AQ is clearly demonstrated by Fig. 4; the pulp viscosity of the AQ-aided O_P stage was higher than those of O and O_P stages. As illustrated by Fig. 5, with the same amount of A_C, the selectivity of all of the AQ-aided O_p stages were greater than those of the other two stages. The selectivity of O_P stage increased significantly by adding a small amount of AQ, which was in agreement with the findings of Ng *et al.* (2011). Even so, it was found that the pulp viscosity still dropped

with 3.0% A_C. This indicated that the extra charge of A_C would cause serious carbohydrate degradation with the presence of AQ.

Among the four AQ-aided O_p stages (Fig. 6), the stage with 1.5% A_C exhibited the greatest selectivity of 1.02, but the K_n of the resultant pulp was quite high. For achieving the aim of bleaching, the condition with 2.5% A_C was considered the best because it exhibited the most advantageous properties: satisfactory low kappa number of 8.4 and rather high pulp viscosity of 20.4 cP. In comparison to ordinary O stage, the selectivity was improved by about 60%. Figure 7 shows that the addition of 0.04% AQ significantly decreased the HexA content to a greater extent in comparison to both O and O_P stages. On the other hand, the results also showed that, similar to the other two stages, the increase of A_C did not produce any effect on the HexA content.

CONCLUSIONS

1. The selectivity of the O stage on mixed tropical hardwood kraft pulp was improved by adding H_2O_2 (O_p stage), as it offered a greater effect on kappa number reduction, but induced more serious cellulose degradation.
2. The optimum amount of anthraquinone (AQ) for the hardwood kraft pulp was 0.04%. An excessive amount of AQ was not beneficial in terms of pulp viscosity, hexenuronic acid content, and selectivity.
3. The O_P stage with the optimum amount of AQ was capable of retaining higher pulp viscosity. Thus, with the same amount of A_C, the selectivity of all of the AQ-aided O_P stages was greater than that of O stage and O_p stage. This indicated that the addition of AQ is capable of reducing the severity of cellulose degradation.
4. Moreover, the HexA content of pulps from the AQ-aided O_P stage was significantly lower than that of pulps from O and O_P stages. However, the increase of A_C did not have any effect on the HexA content.

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