IMPROVED OXYGEN DELIGNIFICATION: A WAY TO ENHANCE TOTALLY CHLORINE-FREE BLEACHING SELECTIVITY

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Why is totally chlorine-free bleached pulp not prevalence?

The application of totally chlorine-free bleaching (TCF) is well recognised for its environmental compatibility. However, its application is less well-established in comparison to conventional chlorine-based bleaching due to the TCF bleached pulp demonstrates relatively lower brightness and strength properties. Oxygen delignification (O-stage) plays an important role in establishing TCF bleaching and it is commonly used as the first bleaching stage in the pulp bleaching sequence. As compared to the conventional first bleaching stage—chlorination stage (C) followed by alkaline extraction (E), the bleaching selectivity between delignification and cellulose degradation of an O-stage is relatively lower. After the CE stage, up to 90% of the lignin can be eliminated from the pulp with merely slightly cellulose degradation; however, a reduction of kappa number of 50% or even lower by an O-stage is accompanied by a significant loss in pulp viscosity (Beyer et al., 1999; Smook, 1992). As a result, the TCF bleaching performance is restricted.

Improved Oxygen Delignification

For attaining a more efficient TCF bleaching, many studies have been carried out to improve the selectivity of the O-stage by two approaches which are either modifying the process or implementing a pretreatment. For the former approach, peroxide reinforced oxygen bleaching—OP –stage is one of the well-known modified O-stages, which is performed by adding hydrogen peroxide (H_2O_2) in the O-stage. It has been verified that OP stage is able to enhance the degree of delignification, a boost in brightness, lower brightness conversion, and maintain pulp viscosity at an acceptable level. In addition, the consumption of bleaching chemicals can be reduced with the application of the OP-stage as well (Ng *et al.*, 2011). Nevertheless, according to Parthasarathy et al. (1990), only a small amount of H_2O_2 (less than 0.5% on oven dry pulp) should be added to avoid serious loss of pulp viscosity.

For the second approach, it is believed that a simple pretreatment may activate the residual lignin in the pulp and thus enhance the degree of delignification in the subsequent O-stage. For instance, pretreating of pulp with peracetic acid (PAA) exercises a "stimulating" effect on O-stage as the reactive species generated by PAA—hydrosonium ion (OH^+) can react with both phenolic andon-phenolic types of lignin (Fossum and Marklund 1988; Kishimoto et al. 2003). With the capability of degrading non-phenolic lignin by PAA, therefore enhances lignin reactivity during succeeding stages (Obst *et al.* 1979; Minja *et al*. 1998).

New Findings of Improved Oxygen Delignification

The H_2O_2 reinforced oxygen delignification (O_P-stage) even though shows better performance than the ordinary O-stage, its beneficial effects is limited as only a small amount of H_2O_2 addition is allowed for the avoidance of serious cellulose degradation. Thus, in order to gain the full advantage of H_2O_2 upon delignification and pulp brightness, H_2O_2 charge higher than 0.5% may be required. With this in mind, an O_P-stage with H_2O_2 charge more than 1.0% was first studied by using oil palm empty fruit bunch (EFB) soda-anthraquinone pulp (Ng *et al.*, 2011). Different from ordinary O_P-stage, a small amount of anthraquinone (AQ)—less than 0.05% (on the basis of oven dry pulp weight) was added into the O_P system and it was found that the resultant pulp from the modified O_P-stage (known as AQ aided H_2O_2 reinforced oxygen delignification, O_{PAq}-stage) exhibited the highest selectivity (2.26) as shown in Table 1.

The research was continued and further verified by using commercial mixed tropical hardwood brown kraft pulp (supplied by Sabah Forest Industries Sdn. Bhd., SFI). It was found that the effective reduction of kappa number (K_n) by the optimum O-stage was limited to about 38%, and the pulp viscosity was 18.7 cP with selectivity less than 0.60 and ISO brightness of ca. 43% (Table 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 Kn reduction, but inevitable, it induced more serious cellulose degradation. In order to minimize the drop of pulp viscosity, an O_{PAq}-stage was applied by adding a small amount of AQ. The O_{PAq}-stage with the optimum amount of AQ was capable of retaining higher pulp viscosity.

Thus, with the same amount of alkaline charge, the selectivity of all of the OPAq-stages was greater than that of O stage and Op stage. It was also found that an excessive amount of AQ was not applicable as there are no positive effect to *Kn* reduction, pulp viscosity, selectivity and pulp brightness. Again, the result verified that the addition of AQ in an OP-stage enabled the employment of H_2O_2 with a higher amount to gain better *Kn* reduction and brightness increment without compromising on unwarranted drop of pulp viscosity.

Condition				Result				
Type of Sample	NaOH %	H2O2 %	AQ %	Kappa Number	Pulp Viscosity cP	Kappa Number Reduction %	Selectivity	Brightness %
	2.5	-	-	8.2	11.6	42.3	1.76	55.11
EFB	2.5	2	-	6.2	11.3	56.3	2.16	66.63
	2.5	1.4	0.02	6.5	12.4	54.2	2.26	61.92
	2	-	-	10.4	18.9	36.6	0.52	42.58
Hardwood	2.5	-	-	10.2	18.7	37.8	0.53	43.15
	2	1.4	-	8.6	18.1	47.6	0.64	53.00
	2.5	1.4	-	7.3	17.5	55.6	0.71	52.02
	2	1.4	0.04	9.2	21.7	44.2	0.83	50.30
	2.5	1.4	0.04	8.4	20.4	48.7	0.8	52.56
	2.5	1.4	0.06	8.4	18.8	48.7	0.69	52.04

Table 1 Study of O-stage, Op-stage and OpAQ stage on EFB and hardwood kraft Pulp

On the other hand, the application of a simple UV radiation pretreatment prior to the O-stage and O_P-stage was also capable of enhancing the selectivity in comparison to the ordinary O-stage and OP-stage (Figure 1). As shown in Table 2, the improvement of bleaching selectivity of O-stage was attributed by the increase of Kn and retaining of pulp viscosity. It was noted that the Kn reductions of both O-stage and OP-stage increased from 37.8% and 55.5% to 53.7% and 59.1%, respectively, after the UV pre-treatment. Moreover, the UV treated pulps also showed higher resistant to alkaline degradation during the subsequent bleaching stage and resulted in a higher pulp viscosity after O-stage and retained an acceptable pulp viscosity after O_P-stage.

In order to verify the effect of UV pre-treatment, spectroscopy analysis of Fourier transform infrared (FTIR) was carried on the pulp before and after pre-treatment. Based on the FTIR spectra, it was found that advantages of photo pretreatment were causing structural and /or functional groups changes in both carbohydrates and lignin. Consequently, the carbonyl-induced degradation of carbohydrates (random cleavage ofglycosidic bonds in cellulose chain) was diminished and thus, increased the selectivity by protecting the cellulose from carbonyl-induced degradation and stimulating more lignin degradation (Chong *et al*. 2015).

Besides selectivity, the application of an UV pretreatment was also enhanced the brightness increment of the pulps. For O-stage, the addition of the pre-treatment increased about 5 units of the pulp brightness in comparison to the unpretreated one, whereas the brightness of the UV pretreated O_P bleached pulp attained brightness up to 60% ISO. In short, it can be concluded that application of a simple UV pretreatment, the Kn reduction can be improved up to 48% for O-stage and only no more than 5% for O_P-stage. Although the protective effect was more prominent in the O-stage than the O_P-stage, the latter could achieve about 12 units higher brightness.

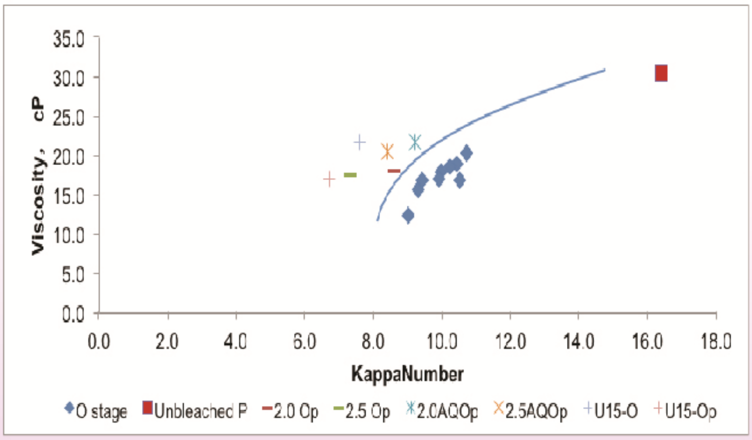

Figure 1: Selectivity curve of ordinary oxygen delignification and various improved oxygen delignification.

No	PAA Charge (%)	Temp. (°C)	Time (min)	Type of Oxygen Bleaching	Kappa Number	viscosity (cP)	Selectivity	Kn (%)	Brightness (ISO, %)
Unbleached P					16.4	30.4			36
-	-	-	-	2.0 Op	8.6	18.1	0.64	47.6	51
-	-	-	-	2.5 Op	7.3	17.5	0.71	55.5	52.02
-	-	-	-	2.0AQOp	9.2	21.7	0.83	44.2	50.30
-	-	-	-	2.5AQOp	8.4	20.4	0.80	48.8	52.22
U15-O	-	-	30	O	7.6	21.7	1.01	53.7	47.77
U15-Op	-	-	30	Op	6.7	17.1	0.73	59.1	60.31

Table 2: Effect of additive and pre-treatment on oxygen delignified hardwood kraft pulp

Conclusion

Maximizing of bleaching selectivity as well as pulp brightness in the first stage of TCF bleaching sequence should become an important conception nowadays. The major intention of shifting the pulp bleaching technology from conventional chlorine-based to TCF is to minimize the environmental pollution caused by pulp and paper industry. In the production of high brightness pulp (90% ISO brightness and above), a series of bleaching stage is required and the number of bleaching stages basically will increase proportionally to achieve a higher brightness. Thus, to produce a brighter pulp, more chemicals, energy and cost are required and at the same time the strength property of the pulp and paper produced might be diminished, especially by using TCF bleaching sequence with relatively low selectivity. Hence, in the context of environmental conservation, due to the implementation of government policy, printing and copying A4 papers with the brightness of 70-75% ISO brightness made from chlorine-free bleached pulp and up to 70% recycled paper are well accepted in Japan. This indicated that the acceptance of the paper consumers towards lower brightness paper products (70-80% ISO brightness) is a key factor to promote TCF bleached pulp and paper products as pulps with 70% ISO brightness can be produced by a short TCF bleaching sequence with no more than four bleaching stages. Moreover, by implementing the improved O-stage in a TCF bleaching sequence, it is believed that an even shorter bleaching sequence with three stages or lesser can easily attain the desired brightness without sacrificing pulp viscosity.

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