

# IMPROVED OXYGEN DELIGNIFICATION SELECTIVITY OF OIL PALM (*ELAEIS GUINEENSIS*) EFB SODA-AQ PULP: EFFECT OF PHOTO- PRETREATMENT AND AQ-AIDED H<sub>2</sub>O<sub>2</sub> REINFORCEMENT

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The kappa number ( $K_n$ ) reduction of oil palm empty fruit bunch (EFB) soda-anthraquinone (AQ) pulp by oxygen delignification was limited to only 34% to avoid substantial cellulose degradation. Thus, a preliminary study of photo-pretreatment was performed to improve the bleaching selectivity, and its effect was compared with the AQ-aided H<sub>2</sub>O<sub>2</sub> reinforced O-stage (O<sub>p</sub>-stage). The results showed that both methods performed better selectivity than the ordinary O-stage. It was suggested that the photo-treatment improved selectivity by diminishing carbonyl-induced carbohydrate degradation. Conversely, the AQ-aided O<sub>p</sub>-stage delivered higher delignifying power with minimum cellulose degradation. For pulps with the  $K_n$  above 6.0, the effectiveness of both methods was about the same, but to achieve lower  $K_n$  (5.8 and below), the AQ aided O<sub>p</sub> pulps exhibited better selectivity.

**Keywords:** peroxide reinforced oxygen delignification, anthraquinone, oil palm EFB, pulp viscosity, photo-pretreatment

## INTRODUCTION

Oil palm (*Elaeis guineensis*) is an important crop for its oil in tropical countries, such as Indonesia, Malaysia, Thailand, Nigeria, Colombia etc. Since 2007, the production of palm oil has overtaken soybean oil as the world largest edible oil, the total production achieving 50 million tonnes in 2009. However, besides the oil, numerous biomass residues are also generated by the palm oil industry. For instance, in oil production mills, the fibrous and oily mesocarp and empty fruit bunches (EFB) are generated throughout the year; oil palm frond (OPF) is a by-product of pruning activity in oil palm plantation, and a large number of oil palm trunks (OPT) are available when replantation of new palm trees is necessary. Without proper management, these residues will cause environmental problems to the estates and oil mills.

Efforts in converting the oil palm biomass to pulp and paper on a lab scale have been made since the 1980s. Among biomass, EFB is one of the most preferred due to two main reasons: non-seasonal availability and ready availability in mills. Considering environmental concerns, sulphur-free pulping methods,

especially soda-anthraquinone (AQ) pulping, are the most preferable and suitable to be employed to cook the material. Hence, soda-AQ EFB pulping will be carried out in this research. Oil palm EFB is used as material since EFB fibres have lower lignin content than wood fibres – 17.2%<sup>1</sup> and 25.2%, respectively.<sup>2</sup> Therefore, lower kappa number ( $K_n$ ) of oil palm EFB pulp, compared to that of wood pulp, may be obtained from the same pulping process.

On the other hand, the increased concern about the generation of environmentally persistent polychlorinated dioxins and furans by conventional chlorine-based bleaching plants,<sup>3</sup> has driven the pulp and paper industry to approach totally chlorine free (TCF) bleaching process. Oxygen delignification (O) plays an important role in TCF bleaching as it is capable of removing up to 50% of the residual lignin from the pulp, without significantly reducing the pulp strength.<sup>4,5</sup> Hence, the effectiveness of oxygen delignification on chemical pulps, including dissolving pulp, produced from oil palm biomass, especially from its empty fruit bunches (EFB), has been studied extensively since the early

2000s.<sup>6,7,8</sup> However, it was found that to avoid substantial losses in pulp viscosity, the kappa number reduction of the soda-AQ EFB pulp by an O-stage should be limited to no more than 38%.<sup>9,10</sup>

During the last three decades, numerous studies<sup>4,11,12,13,14,15</sup> were reported to enhance the effectiveness of oxygen delignification, which included the addition of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) during the O-stage, known as peroxide reinforced oxygen bleaching, and written as O<sub>p</sub>, and also photo-treatment prior to or during the O-stage. It was well recognized that, compared to a conventional O-stage, an O<sub>p</sub>-stage is capable of improving the delignification rate and maintaining the pulp viscosity at an acceptable level, merely with the addition of a small amount of H<sub>2</sub>O<sub>2</sub> (less than 0.5% on oven dry pulp).<sup>4,11,12</sup> However, for attaining the beneficial effect of H<sub>2</sub>O<sub>2</sub> upon delignification and pulp brightness, a H<sub>2</sub>O<sub>2</sub> charge higher than 0.5% was proposed. Nevertheless, in the absence of any pretreatment, a high H<sub>2</sub>O<sub>2</sub> charge leads to a substantial loss of pulp viscosity, and thus lowers the selectivity between delignification and cellulose degradation.<sup>13,15</sup> In the latest study,<sup>10</sup> it was reported that with sufficient alkalinity, the addition of only a small amount of anthraquinone (0.02% on oven dry pulp) to an O<sub>p</sub>-stage makes it possible to obtain a higher pulp viscosity of the oil palm EFB soda-AQ pulp.

On the other hand, a number of researches reported that when lignocellulosic materials absorb ultraviolet (UV) and visible light, they will generate active species, and thus cause photo-degradation of lignocellulosic materials into lower molecular weight materials.<sup>16,17,18,19,20</sup> In addition, photo-irradiation may also affect the optical properties of lignocellulosic materials, e.g. by photo-bleaching on pulp, especially on unbleached high-yield pulp.<sup>21</sup>

Due to their high absorbency, cellulose and lignin are able to absorb different types of wavelength, as they contain various chromophore structures. Some studies reported celluloses are capable of absorbing the wavelength shorter than 340 nm, while lignin absorbs wavelength in the range of 280 nm up to 400 nm.<sup>22,17,19,20</sup> In order to verify the responsibility of each lignin-containing group towards light absorption, model lignin compounds are used for the experimentation.<sup>23,24,25,26,27,28,29</sup> On the other hand, some research has also been carried out directly on the pulp rather than on extracted lignin.<sup>30,31,32,33</sup>

In this study, the photo-pretreatment and H<sub>2</sub>O<sub>2</sub> reinforcement of oxygen delignification on oil palm EFB soda-AQ pulps were carried out with the aim to improve the selectivity of the O-stage. The photo-pretreatment was carried by using blue light in the visible spectrum range of 400-500 nm. Meanwhile, a small amount of anthraquinone was added for the H<sub>2</sub>O<sub>2</sub> reinforced O-stage (known as O<sub>p</sub>-stage).

## EXPERIMENTAL

### Materials

The oil palm empty fruit bunch (EFB) fibre was provided by EcoFibre Bhd., Johore, Malaysia, in the mat formation. The EFB was soaked in water for one day and washed, in order to remove contaminants (such as sand, dust and oil), then it was air-dried and kept in plastic bags prior to pulping.

### Soda-anthraquinone pulp preparation

Pulping of EFB was carried out in a 4-Liter stationary stainless steel digester (with neither external circulation mixing, nor internal agitation), manufactured by NAC Autoclave Co. Ltd., Japan, fitted with a microcomputer-controlled thermocouple. 0.250 kg of oven-dried (o.d.) EFB was placed in the digestion vessel and then sodium hydroxide (25% or calculated as active alkali – 19.4% on o.d. raw material), anthraquinone (0.1% on o.d. raw material) and distilled water were added, to reach a material-to-liquor ratio of 1:7. For assuring homogeneous cooking, the material in the vessel was squeezed to soak completely in the liquor. The digester was then heated to 160 °C, at a time-to-temperature of 90 min and a time-at-temperature of 120 min. Upon completion of pulping, the resultant pulp was collected and defiberized in a hydro-pulper for 10 min. Finally, it was washed thoroughly with tap water and screened with Somerville flat-plate screen (0.15 mm).

### Oxygen delignification and AQ-aided H<sub>2</sub>O<sub>2</sub> reinforced oxygen delignification

Oxygen delignification (O-stage) was carried out in a 650 mL stainless steel autoclave, equipped with a gas inlet and a stirrer, manufactured by the Parr Instrument Company, USA. 22 g (o.d.) of the brown stock was mixed with 0.5% MgSO<sub>4</sub> and different percentage of NaOH (as listed in Table 1) based on oven-dry weight of the material. The pulp mixture was then adjusted to 10% consistency by using distilled water. After placing the mixture in the autoclave, the cover was fastened and the air in the autoclave was replaced by oxygen through the gas inlet, the pressure inside the autoclave being kept at 689.48 kPa for appropriate temperature and time values, as shown in Tables 1 and 3. After the completion of delignification, the oxygen pressure was released. The pulps were then washed thoroughly with distilled water and followed by spin drying and

analysis of properties. The procedure of H<sub>2</sub>O<sub>2</sub> reinforced oxygen delignification (O<sub>p</sub>-stage) with AQ was similar with oxygen delignification, except that

different percentages of NaOH, H<sub>2</sub>O<sub>2</sub> and AQ were added to the pulp mixture, according to Table 4.

Table 1  
Effects of O-stage on EFB Soda-AQ pulp properties

Order	Conditions			Responses				
	NaOH (%)	Temp. (°C)	Time (min)	Kappa number, $K_n$	Pulp viscosity (cP)	Brightness (%)	$K_n$ reduction (%)	Selectivity
	Brown stock			10.1	17.5	45.4		
OD <sub>1</sub>	1	85	60	7.8	16.1	53.7	22.8	1.64
OD <sub>2</sub>	1	105	30	7.0	15.4	55.5	30.7	1.48
OD <sub>3</sub>	1.2	90	30	7.1	15.5	55.9	29.7	1.50
OD <sub>4</sub>	1.5	90	30	6.7	14.9	57.4	33.7	1.31
OD <sub>5</sub>	2	85	30	6.8	14.9	57.2	32.7	1.27
OD <sub>6</sub>	2	95	60	5.9	13.0	61.4	41.6	0.93
OD <sub>7</sub>	2	105	60	5.8	12.6	62.9	42.6	0.88
OD <sub>8</sub>	3	105	60	5.8	10.7	65.9	42.6	0.63
OD <sub>9</sub>	4	90	30	6.3	12.0	62.3	37.6	0.69
OD <sub>10</sub>	4	95	60	5.8	10.3	61.4	42.6	0.60

Table 2  
Photo-treatments prior to O-stage in different pH media

No.	Conditions			Responses		
	pH of medium	Reaction time, (hour)	H <sub>2</sub> O <sub>2</sub> , (%)	Kappa number	Pulp Viscosity (cP)	Brightness (%)
Ph1	Neutral	24	0	9.0	17.3	48.04
Ph2	pH 12	1	0.5	8.7	17.4	49.57
Ph3	pH 12	3	5.0	8.2	16.4	55.88
Ph4	pH 12	24	0	8.7	16.7	49.41
Ph5	pH 3	5	0	9.4	16.4	48.47

Table 3  
Effect of oxygen delignification on photo-pretreated pulps

No.	Response after oxygen delignification				
	Kappa Number $K_n$	Pulp Viscosity (cP)	Brightness (%)	Selectivity	$K_n$ Reduction (%)
Ph1-OD <sub>4</sub>	6.4	14.6	59.2	1.28	36.63
Ph2-OD <sub>4</sub>	6.3	15.5	57.5	1.90	37.62
Ph3-OD <sub>4</sub>	6.3	14.3	62.8	1.19	37.62
Ph4-OD <sub>4</sub>	6.6	16.0	58.4	2.33	34.65
Ph5-OD <sub>4</sub>	6.7	14.6	58.1	1.17	33.66
Ph2-OD <sub>9</sub>	5.5	11.1	62.9	0.72	45.54
Ph4-OD <sub>9</sub>	5.2	11.2	65.9	0.78	48.51
Ph5-OD <sub>9</sub>	5.2	10.9	65.9	0.74	48.51

#### Photo-pretreatment

Blue light, with the spectrum range of 460-490 nm and the intensity around 30  $\mu\text{W}/\text{cm}^2/\text{nm}^{-1}$ , was used as pretreatment on the EFB pulp. 8 g (o.d.) of pulp was weighed, and then the pulp was dispersed in distilled water to 1.0% consistency. Table 2

shows the three process variables of the photo-treatment: pH of medium, reaction time and percentage of H<sub>2</sub>O<sub>2</sub>. The pH of the medium was adjusted to the required pH: pH 12 and pH 3, by adding 0.5M NaOH and 0.1M of H<sub>2</sub>SO<sub>4</sub>, respectively. For some conditions, an appropriate

amount of  $H_2O_2$  was added to the pulp suspension before it was placed in a reaction cylinder (inner diameter = 4.7 cm, thickness = 0.3 cm, length = 50.5 cm). The cylinder was then exposed to blue

light in an irradiation chamber (Figure 1) for a desired time, as shown in Table 2. The experiment was continued with an O-stage.

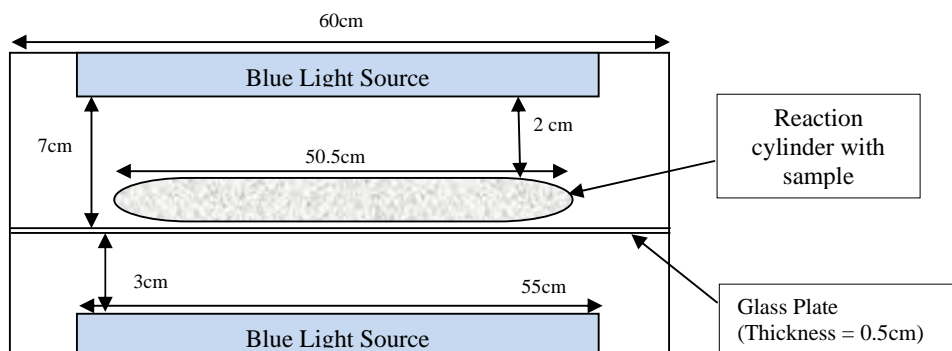


Figure 1: Design of blue light irradiation chamber

Table 4  
Effect of AQ-aided hydrogen peroxide reinforced oxygen delignification

	Order	H1	H2	H3	H4	H5
Conditions	Alkali charge (%)	1.2	1.5	2.0	2.4	2.5
	Temp. (°C)	90	90	92.5	100	100
	Time (min)	30	30	45	30	60
	$H_2O_2$ (%)	0.25	0.50	1.00	1.40	2.00
	AQ (%)	0.02	0.04	0.01	0.02	0.02
Responses	Kappa number, $K_n$	6.9	6.9	5.8	5.4	5.3
	Pulp viscosity (cP)	16.1	15.5	13.6	13.0	11.7
	Brightness (% <sub>ISO</sub> )	58.5	58.2	63.9	66.7	68.9
	$K_n$ reduction (%)	31.7	31.7	42.6	46.5	47.5
	Selectivity	2.29	1.60	1.10	1.04	0.83

### Pulp analyses

The oxygen delignified pulps were analyzed by the TAPPI Useful Method UM-246 Micro Kappa Number – to determine the kappa number, JPRI Standard 3015 (a modified method of TAPPI Standard T230 su-66) – to establish pulp viscosity, and TAPPI T218 om-02 – to determine pulp brightness. Bleaching selectivity was calculated as the ratio of kappa number to pulp viscosity (cP).

### RESULTS AND DISCUSSION

Table 1 shows the properties of brown stock oil palm empty fruit bunch (EFB) soda-AQ pulp and also of pulps that had been bleached by a number of O-stages under various conditions. In comparison with the EFB soda-AQ pulp prepared in the previous study<sup>10</sup> (with the kappa number and pulp viscosity of 14.2 and 15.0cP, respectively), although the same pulping method and

conditions were used, the pulp obtained in this study had a lower kappa number ( $K_n$ ), but higher pulp viscosity. The diversity of the resultant pulp properties was basically due to the different batch and freshness of the raw material used.

Based on the results obtained, it was found that, without considering pulp viscosity, the kappa number ( $K_n$ ) reduction of EFB soda-AQ pulp by an O-stage was considered quite low. It was limited to no more than 43%, the minimum  $K_n$  obtained being 5.8, even though rather severe bleaching conditions, for instance conditions OD<sub>8</sub>, OD<sub>9</sub> and OD<sub>10</sub>, were employed. Furthermore, the selectivity curve plotted for pulp viscosity against  $K_n$  (Figure 2) clearly illustrated that any attempts to decrease the  $K_n$  below 6.8 by increasing the O-stage process severity, and namely reaction

temperature and alkali charge ( $A_c$ ), led to a sharp decrease of pulp viscosity. This indicated that the  $K_n$  reduction of the pulp during the O-stage should not be higher than 34% in order to avoid serious cellulose degradation. It was

very interesting to see that even though the initial  $K_n$  was different, the optimum  $K_n$  reduction was in the same range as that reported in a previous study.<sup>10</sup>

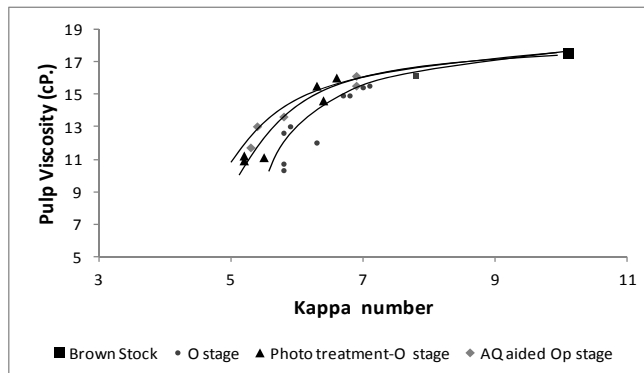
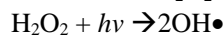


Figure 2: Selectivity plots of O-stage, photo-treatment O-stage and AQ-aided O<sub>p</sub>-stage on EFB soda-AQ pulp

It was remarkable to see that the increase of chemical charge and temperature higher than 1.5% and 95 °C, respectively, would not further lead to satisfactory delignification of the O-stage, although the pulp brightness might improve by ca. 9 points (Table 1). On the other hand, beyond the limit, the bleaching selectivity also decreased dramatically. For instance, the selectivity of OD<sub>4</sub> was 1.31, whereas those of OD<sub>6</sub>, OD<sub>7</sub> and OD<sub>10</sub> were only 0.93, 0.88 and 0.60, respectively.

### Oxygen delignification with photo-pretreatment

By comparing Ph2 and Ph1 (Table 2), it was found that one-hour irradiation with the addition of 0.5% H<sub>2</sub>O<sub>2</sub> gave the same effect on the properties of the resultant pulps treated with 24-hour irradiation without H<sub>2</sub>O<sub>2</sub>. On the other hand, the addition of 5.0% H<sub>2</sub>O<sub>2</sub> (Ph3) only improved  $K_n$  reduction to a small extent and pulp brightness by about 6 points, without serious degradation of pulp viscosity in comparison to that with 0.5% H<sub>2</sub>O<sub>2</sub>. It is well understood that H<sub>2</sub>O<sub>2</sub> generates hydroxyl radicals under ultra-violet irradiation, as illustrated by Eq. 1. The hydroxyl radical is highly reactive and non-selectively attacks both lignin and carbohydrates, hence the mild decrease of  $K_n$  and pulp viscosity elucidated that the blue-light irradiation was not sufficient to dissociate H<sub>2</sub>O<sub>2</sub>.



Eq. 1

By comparing Ph4 in an alkaline medium and Ph1 in a neutral medium, it was observed that the reduction of  $K_n$  of the former was higher, although to a small extent. According to Sun and co-workers,<sup>26</sup> the reaction rates of lignin model compounds and of pine and eucalypt kraft pulp lignin treated with UV-peroxide at pH 11 are 2 to 4 and, respectively, 1.4-1.6 times higher than those at pH 5. This might be due to the fact that residual lignin in acid form is basically easier to dissolve in an alkaline medium.<sup>34</sup> Thus, it also explains why the photo-treatment in an acidic medium (Ph5) did not have any advantageous effect on  $K_n$  reduction.

Table 3 shows the effect of photo-treatments on pulp properties after the O-stage under two different sets of conditions. Under the first O-stage conditions (OD<sub>4</sub>: 1.5% alkali charge, 90 °C, 30 min), it was found that the pH of the medium during photo-pretreatment did not affect  $K_n$  after the O-stage, as the resultant pulps of Ph1-OD<sub>4</sub>, Ph4-OD<sub>4</sub> and Ph5-OD<sub>4</sub> exhibited similar values of  $K_n$ . Nevertheless, it was obvious that the photo-treatment in alkaline medium, even though with the addition of 0.5% H<sub>2</sub>O<sub>2</sub> (Ph2-OD<sub>4</sub>), could retain higher pulp viscosity. Hence, Ph4-OD<sub>4</sub> and Ph2-OD<sub>4</sub> gave the highest selectivity. On the other hand, the addition of 5.0% H<sub>2</sub>O<sub>2</sub> (Ph5-OD<sub>4</sub>) did not give any beneficial effect to  $K_n$  after the O-stage, but adversely accelerated cellulose degradation.

Under more severe O-stage conditions (OD<sub>9</sub>: 4.0% alkali charge, 95 °C, 60 min), the reduction of  $K_n$  was improved to more than 48% (Ph4-O<sub>2</sub> and Ph5-O<sub>2</sub>), but still it was not perceptible. This might be due to the remaining residual lignin in the pulps in the form of lignin-carbohydrate complex (LCC), and the linkages of benzyl ethers and phenyl glycosides of LCC are difficult to cleave under alkaline conditions.<sup>35</sup> Therefore, the decrease of  $K_n$  was low even in an O-stage with a high alkali charge. Furthermore, some other compounds, which were generated from carbohydrates under alkaline conditions, such as hexenuronic acid (HexA), carbonyls and double bond containing structures, are believed to be involved as  $K_n$  contributors.<sup>36,20</sup> On the other hand, it was not expected that the pH of the photo-pretreatments would have an insignificant effect on pulp viscosity under such conditions.

#### **Anthraquinone-aided hydrogen peroxide reinforced oxygen delignification**

The results in Table 4 show that the AQ-aided O<sub>p</sub>-stage achieved lower  $K_n$  (less than 5.8) in comparison with the ordinary O-stage. The maximum  $K_n$  reduction approached 47.5%, while pulp viscosity remained higher than 11.5 cP. On the other hand, although hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is a well-known brightening agent, which acts by eliminating the chromophore structures in pulp, the results denoted that the amount of H<sub>2</sub>O<sub>2</sub> added should be larger in order to give noteworthy brightness improvement. However, an increase of H<sub>2</sub>O<sub>2</sub> charge to 2.0% (Condition H5) tended to accelerate cellulose degradation with only a little contribution to the  $K_n$  reduction, thus resulting in a low selectivity of merely 0.83. The selectivity curve shown in Figure 2 demonstrates an improvement in selectivity on EFB soda-AQ pulp, when AQ-aided O<sub>p</sub>-stage was adopted. Nevertheless, in comparison with the results reported by Ng and co-workers,<sup>10</sup> the beneficial effect observed was not so profound.

#### **Comparison of effect of oxygen delignification with photo-pretreatment and AQ-aided H<sub>2</sub>O<sub>2</sub> reinforcement on selectivity**

In comparison with the ordinary O-stage (Figure 2), both the photo-pretreatment O-stage and AQ-aided O<sub>p</sub>-stage improved the selectivity of the O-stage, but with different

approaches. The former improved the selectivity by retaining higher pulp viscosity, but lowered  $K_n$  to a lesser extent. During an O-stage, cellulose is degraded mostly by random chain cleavage reaction, which involves oxidation of a hydroxyl group on the cellulose chains to a carbonyl group. It was reported that the presence of carbonyl groups in cellulose chains promotes the cleavage of glycosidic bonds in an alkali medium.<sup>37,38</sup> Hence, it was suspected that during the photo-pretreatment, especially under alkaline conditions, parts of the carbonyl groups in the brown stock were oxidized into carboxylic groups, and diminished the carbonyl-induced cellulose degradation of the photo-pretreated pulps. For the latter, the presence of H<sub>2</sub>O<sub>2</sub> enhanced the delignifying power and thus improved the selectivity. Furthermore, the addition of AQ was also capable of minimizing the degradation of cellulose, caused by the non-selective anion hydroxyl radical.

The effectiveness of the two methods in improving the O-stage selectivity was about the same for the resultant pulps with a  $K_n$  above 6.0. Nevertheless, by comparing the pulps with a  $K_n$  of 5.8 and below produced from both AQ-aided O<sub>p</sub> and photo-pretreatment O-stages, the former gave a better effect in improving the O-stage selectivity than the latter, as the O<sub>p</sub> treated pulps retained higher pulp viscosity.

#### **CONCLUSION**

The degree of delignification of oil palm EFB soda-AQ pulp by oxygen bleaching was limited to 34%, as exceeding this limit would accelerate cellulose degradation without satisfactory delignification. Photo-pretreatment under alkaline conditions gave the best effect on O-stage selectivity in comparison with neutral and acidic conditions. However, the pH of photo-pretreatments did not have a significant effect on the selectivity under more severe O-stage conditions. Both the photo-pretreatment O-stage and AQ aided O<sub>p</sub>-stage presented better selectivity in comparison with the ordinary O-stage. The photo-treatment, although could not enhance the reduction of  $K_n$ , diminished carbonyl-induced carbohydrate degradation and thus improved the selectivity. In contrast, the AQ-aided O<sub>p</sub>-stage improved the selectivity by delivering higher delignifying power and minimizing the cellulose degradation caused by hydroxyl

radicals. Both methods had the same effect in improving the O-stage selectivity for the resultant pulps with a  $K_n$  above 6.0. Nevertheless, for pulps with a  $K_n$  of 5.8 and below, the AQ aided  $O_p$  pulps exhibited better selectivity.

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