

# Ozone Based ECF Bleaching of Sulfate Pulp from Acacia

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## ABSTRACT

Acacia farnesiana willd is a species of growing-fast wood used for papermaking. Z(EOP)D bleaching of acacia sulfate pulp after oxygen delignification was researched in this paper, especially focused on effects of different ozone charges on kappa number, viscosity, brightness and HexA content of bleached pulp. In addition, the relationships between ozone charge and kappa drops, viscosity drops and brightness increase of pulp before and after EOP were analyzed, the change of final brightness after Z(EOP)D was measured respectively. Results showed that ozone delignification relax from intensity when ozone charge lie in the range of 4~6kg/odt; ozone charge has no much effects on viscosity drops and brightness increase of pulp before and after EOP, but incoming kappa number is opposite. Otherwise, the finally brightness increases steadily with the increasing ozone charge and the HexA content does not have big difference.

**Keywords:** acacia sulfate pulp; Z(EOP)D; brightness; HexA

## Introduction

Acacia farnesiana willd, a popular fast-growing hardwood specie in Southeast Asia. It was another new material for pulping and papermaking after the Eucalyptus was found, and widely distributed in the dry hot valley, sunny slopes, grassland or woodland in the river. The annual growth of acacia is 46m<sup>3</sup>/ha, 7~9 years can become useful. The fiber morphology and chemical composition of acacia were: the density was 0.52~0.68g/cm<sup>3</sup>, the average fiber length and width were 1.1 mm and 19.3μm, the lignin content in acacia was 19.4% and alpha-cellulose 44.1%, which was within the range of other acacias, but that of extractives was higher [1,2]. Thereby the acacia is a good fast-growing material for pulping also because of their smaller coarseness and larger density compared with eucalyptus fiber, so it has a great significance in the study of pulping and bleaching from acacia [3].

Although studies have shown that ozone application in ECF (Elemental Chlorine Free) process running hardwood pulp is attractive, certain issues have to be taken into consideration when deciding on the specific scheme on adding ozone to an existing ECF bleach plant. Replacement ratio, effectiveness of acid wash or chelating, and degree of oxygen delignification, etc are among the questions to be considered to achieve a successful implementation [4]. Many kraft pulp mills with ECF bleaching sequence use ClO<sub>2</sub> as the main delignification and bleaching chemical consume large amount of ClO<sub>2</sub> inevitably lead to a significant level of AOX, although already greatly decreased compared to the older elemental Chlorine bleaching process. Environmental management teams are attaching more importance to the effluent color and COD load. But without major, expensive modification of fiberline process, whatever other measures bring forth unsatisfying results. Meanwhile these mills often face the shortage of ClO<sub>2</sub> when production is kept at a level higher than its design capacity

continuously due to the limited capacity of ClO<sub>2</sub> production of its chemical plant [5].

Partial replacement of ClO<sub>2</sub> with ozone [6], especially in the first stage of bleaching, has proved capable of producing fully bleached pulp with comparable pulp strength with significantly lower consumption of ClO<sub>2</sub>, thus relieving the pressure on ClO<sub>2</sub> plant and reducing total chemical cost, as well as the load of COD, AOX and color in bleach plant effluent. Any replacement of chlorine chemicals in bleaching further reduces the production of AOX. The relative merits of ECF and TCF bleaching on toxicological properties of effluents are inconsistent. For example, biotests conducted in the same laboratory showed that chronic effects of effluents from TCF bleaching could greater than or less that ECF effluents. Collectively, the results indicate that effluents from ECF or TCF bleaching have the potential to cause biological effects only at high concentrations not likely encountered in receiving waters. But ozone delignification is not very different from chlorine dioxide delignification in environmental terms. Meanwhile, bleaching processes containing an ozone stage generated effluents having 25% less color than did effluents from ECF sequences [7].

Many studies have been carried out on the application of ozone in bleaching of softwood pulp from Scandinavian or North America or hardwood pulps from South America, but few studies have been done on Acacia [8]. This study aimed to research the effects of ozone application in the bleaching of Acacia pulp in terms of brightness, viscosity, pulp strength, and find the overall benefits of applying ozone to a typical existing ECF bleach plant. The acacia pulps were bleached in Z(EOP)D (where Z denotes ozone, E denotes oxygen and peroxide reinforced alkaline extraction, D denotes Chlorine dioxide) bleaching.

## Experimental Materials

Cooking of acacia chips (Indonesian chips) was performed in lab batch rotary digester. After the washing and screening, water

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removal of pulp was done in a centrifuge before homogenization. The kappa of the pulp was 20.4, the yield was 52%, the viscosity was 858ml/g and the residual alkalin was 7.6g/L.

## Oxygen delignification

Both one and two stage oxygen delignifications were carried out in the CRS 1030 bleaching reactor with conditions as follows: 10% pulp consistency, 1.2% and 1.5% of NaOH respectively, 0.5 Mpa O<sub>2</sub> pressure and 0.5% MgSO<sub>4</sub>. The reaction time and temperature of two stages were 60min, 90 °C; 85 °C, 20min followed 95 °C 60 min respectively. pH of the filtrate after reaction was measured. All pulps after the two stages of oxygen delignification were washed with distilled water and dewatered using a Buchner funnel. After washing, pulps were homogenized for 15 minutes. Kappa number, HexA content, viscosity and brightness of oxygen delignified pulp were measured according to the following standards: Kappa number, SCAN-C 3:78; HexA content, HUT method; viscosity, SCAN-CM 15:88 ; brightness, SCAN-C 11:75. The measured results are in Table 1.

Table 1 The results of oxygen delignification of acacia pulp

	Kappa	Viscosity/ml·g <sup>-1</sup>	HexA content/mmol·kg <sup>-1</sup>	End pH
1 stage	9.7	793	43.0	10.3
2 stages	11.8	778	42.2	10.5

## Z(EOP)D bleaching

Bleaching will be carried out at Z(EOP)D sequences. The conditions are in Table 2. Z will be used as the first bleaching stage with different charge of ozone, followed by (EOP) and D. ClO<sub>2</sub> bleaching was carried out in plastic bags placed in water bath. The oxygen delignified pulps will be bleached with Z with varying ozone charge, 2, 4, 6, 8 kg/odt. Following prebleaching an alkali extraction stage reinforced with oxygen and peroxide was conducted on all pulps in the CRS 1030 reactor. Several charges of ClO<sub>2</sub> were used to determine the response of kappa number and the suitable kappa factor for achieving optimal kappa number (22.5) after the EOP extraction stage.

The pulps were first bleached with D<sub>0</sub> stage as the reference prebleaching at D<sub>0</sub>(EOP)D sequence. The conditions of D<sub>0</sub> were as follows: 10% consistency of pulp, 25kg/odt of ClO<sub>2</sub> as active Cl, the reaction time and temperature were 60min, 60 °C, and the End pH was 2.0-2.5. The conditions of other two stages were at same.

The end pH was measured and controlled. After these stages the pulp was again washed and dewatered as earlier. Then kappa number, HexA content, viscosity and brightness were measured with the same methods as mentioned above. Residual ClO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> were measured.

## Results and Discussion

### Ozone bleaching

The Kappa number of acacia pulp reduces steadily with the

Table 2 Bleaching conditions of acacia sulfate pulp.

	Z	EOP	D
Temperature/°C	50	90	70
Reaction time /min	40	90	180
Consistency/ %	10	10	10
ClO <sub>2</sub> as active Cl /kg·odt <sup>-1</sup>			10 <sup>b*</sup>
Ozone charge/ kg·odt <sup>-1</sup>	2, 4, 6, 8		
H <sub>2</sub> SO <sub>4</sub> / %	a*		
NaOH charge kg·odt <sup>-1</sup> pulp		15	2
H <sub>2</sub> O <sub>2</sub> /kg·odt <sup>-1</sup>		5	
MgSO <sub>4</sub> / kg·odt <sup>-1</sup>		3	
O <sub>2</sub> pressure/Mpa		4	
End PH	2.0-3.0	10-11.5	3.5-4.5

a\* Was adjusted to achieve the desired initial/End pH.

b\* Was adjusted to achieve a final ISO brightness of 89-90%.

increasing of ozone charge (Fig. 1). For different incoming kappa number, the reduction of kappa number is almost same, about 0.5unit/kg O<sub>3</sub>. By increasing ozone charge, viscosity drops sharply in the beginning even with low ozone charge, 2unit/kg O<sub>3</sub>. Viscosity reduction is about 10-18 unit/kg O<sub>3</sub>. After certain ozone charge, reducing of viscosity becomes slow. At same ozone charge, the higher incoming kappa number, the higher viscosity after reaction with ozone. Meanwhile, the oxygen delignified pulp has much higher viscosity than ozone delignified pulp even at low ozone charge which means that ozone has very poor selectivity toward lignin. And the unwanted reactions with cellulose leading to the deterioration in pulp quality occur when large dosages are applied. A highly selective ozone treatment remains elusive despite the intensive efforts directed toward elucidating the mechanisms of ozone and carbohydrate reactions and the conditions required to minimize these reaction [9].

The brightness of acacia pulp increases slowly in the beginning, after certain amount of ozone charge it increases sharply (Fig. 2). Incoming kappa number has great effects on brightness. At same

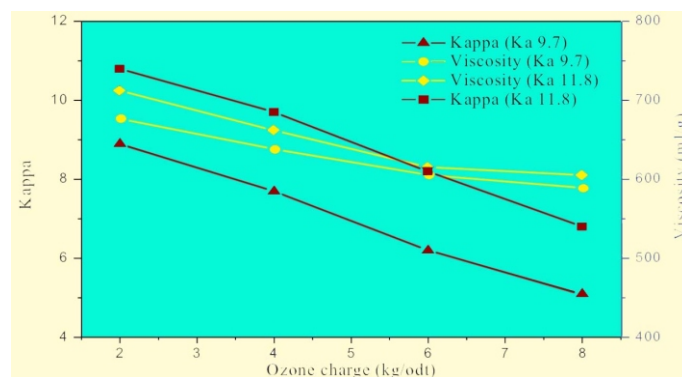


Fig. 1 Effects of ozone charge on Z kappa number and viscosity of acacia pulp

ozone charge, the higher incoming kappa number, the lower brightness after reaction. For ozone delignification, the highest brightness is achieved at the lowest incoming kappa number, 9.7, with the highest ozone charge, 8 kg/odt, while the lowest brightness happens at the highest incoming kappa number, 11.8, with the lowest ozone charge, 2 kg/odt. HexA content reduces steadily with the increasing ozone charge. HexA reduction is approximate 2-4 meq/kg  $O_3$ . Which means ozone can react with HexA and HexA can be removed by adding of ozone. Incoming kappa number also has great effects on HexA content. At the same ozone charge, the higher incoming kappa number, the higher HexA content. For ozone delignification, the highest HexA content happens at the highest incoming kappa number, 11.8, with the lowest ozone charge, 2 kg/odt. For oxygen delignification, HexA contents are almost same at kappa number 9.7 and 11.8 (Table 1), which means oxygen doesn't react with HexA.

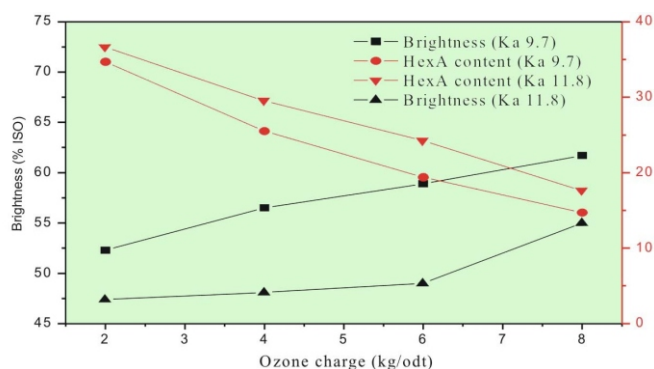


Fig. 2 Effects of ozone charge on Z brightness and HexA content of acacia pulp

Viscosity drops sharply in the beginning then reduces slightly with the reducing kappa number at Z stage (Fig. 3). Viscosities of some pulps are even lower than 500 ml/g. Viscosity drop is 20-35 unit/kappa drop. Kappa number after Z stage has great effect on viscosity. Pulps with higher Z kappa number have higher Z viscosity. Brightness increases slightly in beginning then goes up sharply with the reducing kappa number at Z stage. Kappa number after Z stage has great effect on brightness. Pulps with lower Z kappa number have higher Z brightness.

Lignin kappa reduces steadily with the increasing ozone charge (Fig. 4). Lignin kappa reduction is approximate 0.5-0.8 unit/kg  $O_3$ .

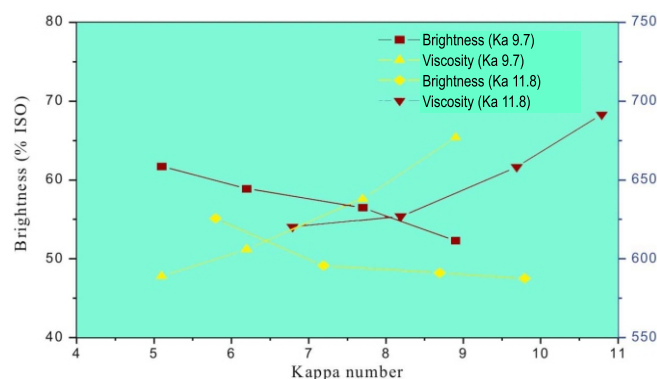


Fig. 3 Effects of Z kappa number on Z brightness and viscosity of acacia pulp

Incoming kappa number has great effects on lignin kappa number. At same ozone charge, pulps with higher incoming kappa number have higher lignin kappa number

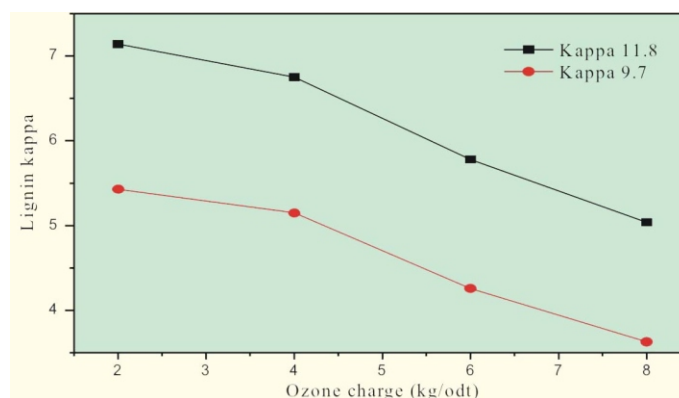


Fig. 4 Effect of ozone charge on lignin kappa of acacia pulp

### EOP stage

In bleaching, extractives react to some extent with the bleaching chemicals to form oxidized and/or otherwise modified products. The extractives remaining in the pulps are detrimental to the pulp quality. Major lipophilic components of unbleached kraft pulps are triterpenoids, fatty acids, and fatty alcohols. Among the minor components are resin acids and diterpene alcohols. In general, due to the diversity of compounds and different bleaching stages involved, the bleaching behavior of extractives-based compounds is rather complex and remains not fully understood. For TCF bleaching using  $H_2O_2$  or  $O_3$ , the knowledge of the reactions of the different extractives during pulp bleaching is still quite limited [10]. There are conflicting reports about the merits of extracting a pulp with alkali after ozone stage. The general consensus is that alkali extraction stage decreases the kappa number of an ozone-delignified pulp by about 1.5-5 units and is beneficial to the bleaching process by reducing the need for application of more costly bleaching chemicals in later oxidizing stages.

At EOP stage, pulps with lower ozone charge have more kappa drops (Fig. 5). Incoming kappa number also has effect on kappa drop. Kappa number reduces sharply in the beginning with the increasing of ozone charge. After certain amount of ozone charge, kappa reduction becomes slow. Pulps with higher incoming kappa

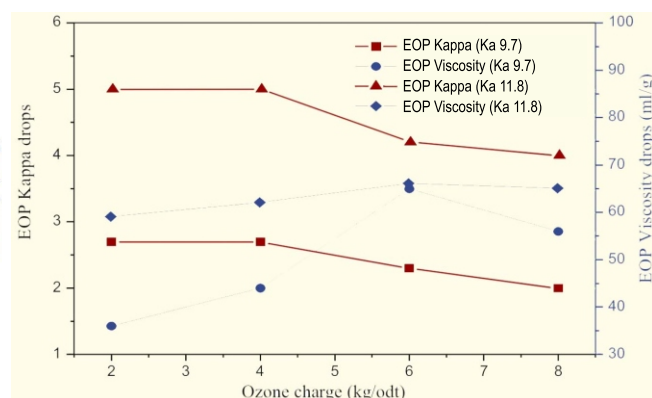


Fig. 5 Effects of ozone charge on EOP kappa drops and viscosity drops of acacia pulp



number have more kappa drops. Otherwise, by increasing ozone charge, viscosity drops sharply in the beginning even with low ozone charge, 2 kg/odt. After certain ozone charge, reducing of viscosity becomes slow. Incoming kappa number also has great effects on viscosity. For pulp after Z(EOP), the highest viscosity also is achieved at the highest incoming kappa number, 11.8, with the lowest ozone charge, 2 kg/odt. Viscosity drops very much at EOP stage, 30-60 units. Incoming kappa number has great effects on viscosity drops. Pulp with higher incoming kappa number have more viscosity drop..

Brightness increases steadily with the increasing of ozone charge (Fig. 6). Incoming kappa number has great effect on brightness. At same ozone charge, the higher incoming kappa number, the higher brightness after reaction. For pulp after Z(EOP), the highest brightness is achieved at the lowest incoming kappa number, 9.7, with the highest ozone charge, 8 kg/odt. At EOP stage, brightness increases approximately 14-20 units. Ozone charge does not show many effects on brightness increase. Incoming kappa number also does not have clear effects on brightness increase. For high kappa number, HexA content reduces steadily with the increasing ozone charge. For low kappa number, HexA reduces sharply in the beginning. After certain amount of ozone charge, HexA decreases marginally. Incoming kappa number also has great effects on HexA content. At the same ozone charge, the higher incoming kappa number, the higher HexA content. For pulps after Z(EOP), the highest HexA content happens at the highest incoming kappa number, 11.8, with the lowest ozone charge, 2 kg/odt, while the lowest HexA content occurs at the lowest incoming kappa number, 11.8, with the highest ozone charge, 8 kg/odt. At EOP stage, HexA content drops 0.5-6 meq/kg. Pulp with higher ozone charge give more HexA drops. Incoming kappa number does not show clear effects on HexA drops.

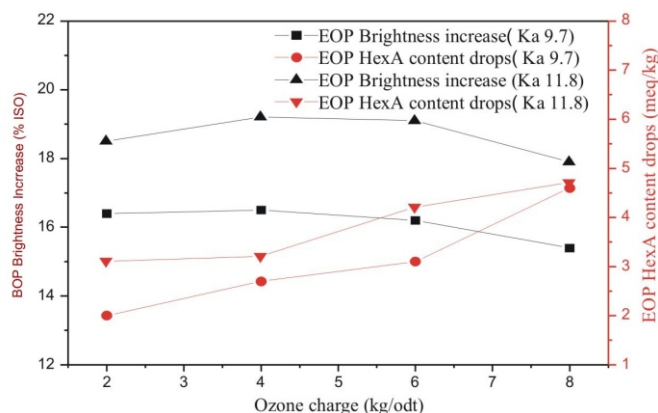


Fig. 6 Effects of ozone charge on EOP brightness increase and HexA drops of acacia pulp

Lignin kappa drops at EOP stage is related to ozone charge (Fig. 7). By increasing ozone charge, lignin kappa drop reduces slightly. Incoming kappa number has great effects on EOP lignin kappa drop. Pulp with higher incoming kappa number have more lignin kappa drops.

### Final bleaching

An advantage of using an ozone stage in a sequence is that contrary to bleaching with chlorine chemicals, its filtrate can be

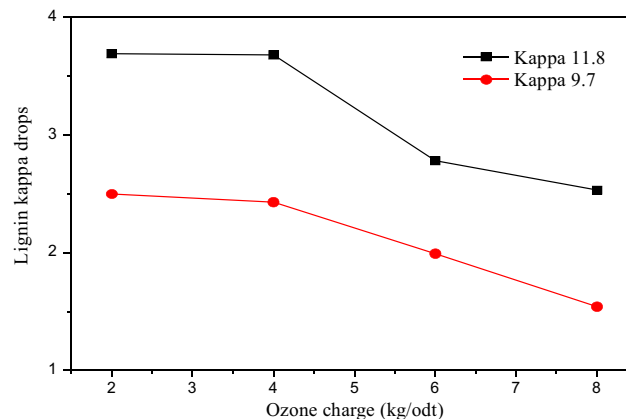


Fig. 7 Effects of EOP on lignin kappa of acacia pulp

easily recycled to existing chemical recovery processes. However, because many mills are limited in their recovery capacity, processing this filtrate may not be possible [9]. D stage was used as the final bleaching stage. The chemical charges were adjusted to achieve a final ISO brightness of 89-90%. Final brightness increases steadily with the increasing ozone charge (Fig. 8). In this figure, D ClO<sub>2</sub> charges are all 2.5%. Incoming kappa number has great effects on final brightness. At the same ozone charge, the higher incoming kappa number, the higher final brightness.

The results of final bleaching are in Table 3. For each incoming kappa number, final brightness after D<sub>0</sub>(EOP)D is much higher than after Z(EOP)D even at ozone charge 8 kg/odt. For pulp after Z(EOP)D, the highest final brightness happens at the lowest incoming kappa number, 9.7, with the highest ozone charge, 8 kg/odt, while the lowest final brightness occurs at the highest incoming kappa number, 11.8, with the lowest ozone charge, 2 kg/odt. For acacia chip, it is difficult to achieve high enough final brightness, 89%ISO. Without consideration of environmental issues, ClO<sub>2</sub> is a much better bleaching chemical than ozone. Ozone delignification requires low incoming kappa number, with high ozone dosage. Otherwise, it is impossible to achieve high enough final brightness. Therefore, the application of ozone in the mill must be considered carefully.

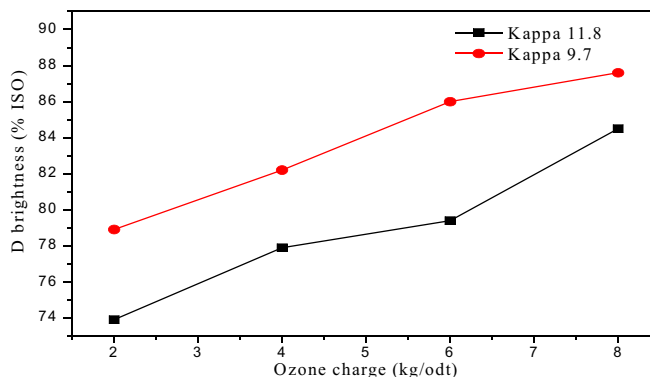


Fig. 8 Effects of ozone charge on D brightness of acacia pulp

### Conclusions

Acacia chips have very high cooking yield, more than 52% even at low kappa number. HexA content does not reduce in O<sub>2</sub> delignification stage which means HexA cannot react with O<sub>2</sub>.

Table 3 Results of final bleaching of acacia pulp.

Kappa before Z	O3 charge /kg*t <sup>-1</sup>	ClO <sub>2</sub> charge in D as active Cl	Viscosity /ml*g <sup>-1</sup>	HexA content /meq*kg <sup>-1</sup>	End pH	Brightness /% ISO
9.8	Reference bleaching	2.0	667	2.1	3.5	88.2
	2	2.5			3.3	78.9
	4	2.5			3.2	82.2
	6	2.5			3.0	86.0
	8	2.5			2.8	87.6
11.7	Reference bleaching	2.0	678	2.0	3.5	88.0
	2	2.5			3.3	73.9
	4	2.5			3.3	77.9
	6	2.5			3.2	79.4
	8	2.5			3.1	84.5

Ozonation and incoming kappa number have great effects on viscosity. Viscosity of ozonation pulp is much lower than that of reference bleaching. Selectivity of ozone toward lignin is very poor. At same ozone charge, pulp with higher incoming kappa number has higher viscosity. Without consideration of environmental issues, ClO<sub>2</sub> is a much better bleaching chemical than ozone. Ozone delignification requires low incoming kappa number, with high ozone dosage. Otherwise, it is impossible to achieve high enough final brightness. Application of ozone in the mill must be considered carefully. HexA content does not have big differences.

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