Trace Elements Content of Mangium Pulp throughout ECF Bleaching Stages as Measured by ICP

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Abstract

The fate of metals in pulp of the five years old mangium wood (*Acacia mangium* Wild) during bleaching process was investigated. The wood was divided into tree division, i.e. bottom, middle and upper divisions. The wood was chipped and kraft pulped to achieve a kappa number of 14 $\pm$ 0.5. The resulting pulps were then bleached following an elementally chlorine free (ECF) method of D_0, EO, D_1, D_2 and P sequences. The measurement of metals content was carried out with Inductively Coupled Plasma (ICP) type Optical Emission Spectrometry (OES) Optima 4300DV. Brightness and viscosity of bleached pulps were measured in accordance with TAPPI T 525 om - 92 and TAPPI T 230 om-89 standard procedures, respectively. It was found that, metals content of five years old *Acacia mangium* tended to increase from the bottom to the upper divisions of the stem. Beyond the EO stage, the content of Mn reduced to below detrimental limit required in peroxide bleaching, which is of 1 ppm. However, the content of Cu and Fe of pulp from every stage of bleaching sequences were much higher than their detrimental limit, i.e. 0.5 ppm and 2 ppm, respectively. Metals content were also found to reduce brightness gain in ECF bleaching.

Keywords: *Acacia mangium*, brightness, ECF bleaching, metals, viscosity

Abstrak

Dalam penelitian ini dilakukan pengukuran terhadap kadar logam pulp mangium (*Acacia mangium* Wild) hasil setiap tahap pemutihan. Batang mangium berumur 5 tahun dibagi menjadi tiga bagian, yaitu bagian pangkal, tengah dan ujung. Kayu dibuat serpih dan dimasak menggunakan proses kraft untuk menghasilkan bilangan kappa 14 $\pm$ 0.5. Pulp yang diperoleh kemudian diputihkan dengan metode pemutihan *elementary chlorine free* (ECF) $D_0EOD_1D_2P$. Pengukuran kadar logam pulp dilakukan dengan *Inductively Coupled Plasma* (ICP) *tipe Optical Emission Spectrometry* (EOS) Optima 4300DV. Derajat putih dan viskositas pulp masing-masing ditentukan mengikuti prosedur standar TAPPI T 525 om-92 dam TAPPI T 230 om-89. Hasil penelitian menunjukkan bahwa kadar logam mangium berumur 5 tahun cenderung meningkat dari bagian pangkal ke bagian ujung batang. Setelah tahap EO, kadar Mn menurun dibawah batas yang diijinkan (1 ppm) untuk pemutihan tahap P. Tetapi, kadar Cu dan Fe pulp dari setiap tahap pemutihan jauh melebihi batas yang diijinkan, yaitu masing-masing sebesar 0.5 ppm dan 2 ppm. Kandungan logam juga berdampak pada menurunnya peningkatan derajat putih pulp.

Kata kunci*:* *Acacia mangium*, derajat putih, logam, viskositas, pemutihan ECF

Introduction

An environmentally friendly bleached pulp production requires the application of elemental chlorine free (ECF) and totally chlorine free (TCF) bleaching methods. The methods have been well known capable of preventing the formation of toxic organochlorine compounds from elemental chlorine based pulp bleaching. Although in ECF bleaching Cl_2 is replaced by a more environmentally benign ClO_2 (Smook 1994), the final objective of pulp production technology is the application of the totally effluent free (TEF) technology. The main prerequisite of TEF technology is the use of close loop cycle where the application of TCF bleaching and counter current washing methods is unavoidable.

The presence of trace elements such as metallic component in mill systems will impede the practice of close loop cycle system. The trace elements content is dependent on its intake (from pulp wood, process water and chemical used in pulp production), process configuration, and operating conditions (Nurmesniemi *et al.* 2005). Many metal ions reduce the brightness and strength properties of pulp, mainly when pulp is bleached with oxygen, ozone and peroxide (Yokohama *et al*. 1999). Dahl (1999) reported that the detrimental limit of Cu^{2+}, Mn^{2+}, and Fe^{2+} and Fe^{3+} in peroxide bleaching were 0.5 ppm, 1 ppm, and 2 ppm, respectively. Furthermore, metal ions are corrosive and may damage iron or steel based equipment (Bryant & Edwards 1996).

Hydrogen peroxide decomposition by Fe, Cu and Mn proceed through Fenton reaction. In Fenton reaction, metal ions continuously alter their oxidation degree and decompose hydrogen peroxide to produce hydroxyl radical and other radicals (Lidén & Ohman (1997). Hydroxyl radical reacts and depolymerizes cellulose, thus reducing the strength properties of pulp (*Et al*. 2000). In these ways, metal ions also increase the consumption of bleaching chemical and decrease the selectivity of oxygen based bleaching (Ni *et al.* 1996). At an excessive concentration, Ca, Mg and Al are corrosive to bleaching equipment. Nevertheless, Mg can act as a stabilizer for hydrogen peroxide; however, Ca possibly disturbs the performance of the digester heating elements and evaporator effects (Bryant & Edward 1996). Numerous lignin components such as veratryl alcohol, bis-eugenol, vanillyl alcohol and catechol formed complexes with metals (Yoon *et al.* 1999). Iron and lignin form colored complexes that reduce the brightness of pulp (Sunden *et al.* 2000). The appearance of color from lignin-metal complexes was because of the d-d interaction (between the d-electron of metal ion and ligan) or charge transfer between metal ion and ligan or both (Gosh & Ni 1998). These authors also found that the influence of Mn and Al on pulp brightness is negligible.

Fast growing tree such as mangium wood *(Acacia mangium)* is the preferred pulp wood plantation in Indonesia. It can be grown in both infertile and fertile lands. As for other tropical woods (Fengel & Wegener 1984), the ash content of mangium is relatively high and has been reported to reach 0.38-0.46 % with the lowest metal content was retained by the 5 years old (Wistara & Yustiana 2014). Ash content is indicative to the metals content of wood.

From the standpoint of its trace elements content, mangium wood will possibly be a challenging raw material for TEF based pulp production. Various methods have been developed to eliminate the negative effects of metallic component in the TEF pulping process. Chelating agents applied in acidic media reduced the metallic component through the formation of complexes with trace elements. The most commonly used chelating agents are ethylene diamine tetra acetic acid (EDTA) and diethylene triamine penta acetic acid (DTPA). DTPMP is another excellent chelating agent proven capable of effectively removing Mn, Ba, Mg and Zn (Kujala *et al*. 2004). The transition (Fe and Mn) and scale-inducing (Ba, Ca, Mg and Al) metals content determine the application of chelating stages (Bryant & Edwards 1996). Pulp washing at the pH of 1.5-3 capable of reducing metallic ions in a more environmentally friendly approach compared to that of using chelating agents because of acid is recyclable (Bouchard *et al.* 1995). Another environmentally friendly method of handling metal content in bleaching processes is by nanofiltration. Nanofiltration with polyamide membranes has been reported effectively filters metal complexes from TCF bleaching effluent (Lastra *et al*. 2004).

The present works were intended to determine the content and distribution of metal ions in every stage of an ECF bleaching sequences of the 5 years old mangium pulp. Prediction of pulp strength quality was carried out through the determination of pulp viscosity.

Materials and Methods

Metal content of chips, unbleached and bleached kraft of the mangium pulp was measured. Mangium wood of 5 years old used in the present experiments was donated by the state own company, PT. Perhutani BKPH Parung Panjang–Indonesia. The wood was divided into 3 divisions, i.e. bottom, middle, and upper division. Each division was chipped and screened. Chips of the accepted size distribution were then cooked to a kappa target of 14$\pm$0.5 by kraft pulping process. Pulping was carried out with L/W of 6/1 with active alkali of 22% and sulphidity of 30% at maximum temperature of 165 ^{o}C for 190 min. The resulting pulp was washed and screen for 1 hour. Kappa number, effective alkali and total solid content were determined based on the standard procedures of TAPPI 236 cm-85, Western Lab 4.1.1996 and TAPPI 625 cm-85, respectively. The screened pulp was then air dried, homogenized and oxygen delignified. Oxygen delignification (ODL) stage was carried out in an alkaline media (pH $\pm$ 11) at 100 ^{o}C for 60 min under 8 bars pressure and consistency of 10%. The pulp was bleached with ECF method consisting of $D_0(EO)D_1D_2P$ sequences proceeding oxygen delignification. Table 1 indicates the bleaching conditions and parameters.

Metal content, brightness, and viscosity of pulp resulted from each bleaching stage were determined. Pulp brightness and viscosity were determined following the standard procedures of TAPPI T 525 om-92 and TAPPI T 230 om-89, respectively. In metal content determination, an ashing process of the sample at 525 ^{o}C for 5 hrs was initially carried out, and 3 drops of HNO_3 was then added and diluted into 250 ml of volume. The solution was then injected into Optical Emission Spectrometry (OES) Optima 4300 DV Inductively Coupled Plasma. The wave length of each metal ion radiation was detected and converted into concentration unit (mg/l). The concentration in mg/L was then converted into ppm following the formulae of:

$$ppm = \frac{total\ element\ \left(\frac{mg}{L}\right) x \frac{250}{1000}}{oven\ dried\ weight\ of\ sample\ (Kg)}$$

Table 1 Parameters and condition of bleaching processes

Parameter	Stage				
	D_0	(EO)	D_1	D_2	P
Temperature, ^oC	65	80	80	80	80
Time, min	60	90	180	180	180
pH	2.5 – 3.5	10.8 – 11	4 – 5	4 – 5	4 -5
Consistency, %	10	10	10	10	10
ClO_2, ml	66-67	-	3-7	2-3	-
NaOH, ml	-	26-33	-	-	-
H2O2, ml	-	-	-	-	0.12
Brightness, %	65 – 75	78 – 80	89 – 90	90 – 91	>91

Results and Discussion

Ash content

The ash content represents inorganic substances in wood and pulp. Ash content of wood is usually not more than 1 % of the oven dried weight of wood (Chirat & Lanchenal 1997). Table 2 indicates the ash content of wood and pulp resulted from every bleaching stage and division of wood.

It can be seen in Table 2 that proceeding the post oxygen delignification (Post-ODL), the ash content tends to decrease with the advancing of bleaching sequences. It seemed that metal was washed out in every bleaching stage. Ash content tended to increase from the bottom division to the upper division of the stem. Upper division is dominated by sapwood that consists of physiologically active wood cells. These cells require higher amount of metal ion to carry out metabolic processes (Sunden*et al*. 2000). Greater content of ash in sapwood of red meranti has been reported (Sukowati 2013). Furthermore, silviculture treatment on *Leucaena leucocephala* also increased the ash content (Al-Mefarrej *et al.* 2011) might be because of increasing the proportion of sapwood. Pulp at the stage of Pre- and Post-ODL contained highest amount of metal possibly due to the higher level of residual lignin content as indicated by the kappa number of pulp in Table 3. Metal ions in wood attached to the functional groups of lignin and acid of hemicelluloses (Bryant & Edwards 1996).

Table 2 The ash content (%) of wood and pulp

Stage	Division of Wood		
	Bottom	Middle	Upper
Wood	0.44	0.47	0.60
Pre - ODL	0.52	0.65	0.61
Post - ODL	0.69	0.70	0.92
D_0	0.10	0.42	0.63
EO	0.31	0.33	0.38
D_1	0.02	0.02	0.05
D_2	0.02	0.02	0.02
P	0.02	0.02	0.02

Table 3 The Kappa Number of Oxygen Delignified Pulp

Stem Division	Oxygen Delignification Stage		
	Pre-ODL	Post-ODL	EO
Bottom	13.97	7.03	0.84
Middle	14.50	8.23	2.87
Upper	14.50	7.70	0.55

Metal content in wood and pulp

Metal in wood is classified into micro and macro element dependent on its content. Macro element content is more than 100 ppm and that of micro element is below 100 ppm. The distribution pattern of macro and micro elements content of mangium wood of the present works is shown in Figure 1. The content of most metal in mangium wood tended to increase from the bottom to the upper division of its stem. Upper division of stem was thought to consist of more sapwood with its physiologically active cell. As the component of ash, metal ion is required more by these physiologically active cells for their metabolic process purposes (Sunden*et al*. 2000). Ca, Na, K and Mg are classified as macro element, thus with higher content compared to these of the micro elements. This finding agreed to that stated by Sjostrom (1993). Ca, Na, K, and Mg content (ppm) of the presently investigated mangium wood were in the range of 769.42-1015.93, 141.10-310.95, 233.14-720.16, and 104.87-203.32, respectively. Although Ca is important for the growth of wood, however at an excessive amount, it is very corrosive to the digester, bleaching and evaporator effect equipment (Bryant & Edwards 1996). Fe was the dominant micro element in the 5 years old mangium wood with its content of 26.08-36.31 ppm. Mn and Cu content were also found substantial to bring about a problem in the application of the future TEF technology based pulp production. It was not understood why Al noticed just in the middle part of the wood. Though Al and B are present in mangium wood, they are not considered to influence the bleaching properties of wood pulp.

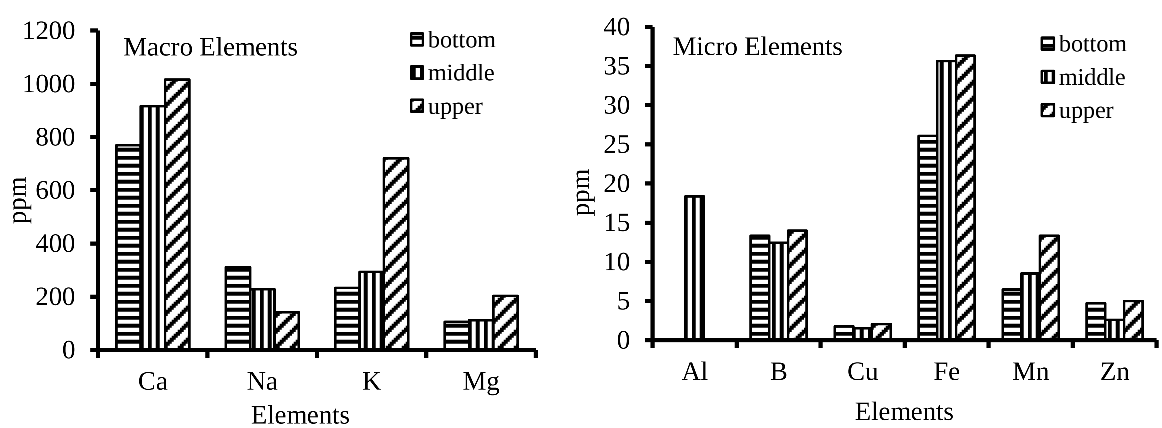

Figure 1 Macro and micro elements content of mangium wood based on stem division.

The present results indicated that the content of Ca and Mg reached 1000 ppm and 200 ppm, respectively. This result was on the contrary to those found by Wistara and Yustiana (2014), in which the content of Ca of the 5 years old wood was the lowest and Mg was the highest. As reported by Mayer and Koch (2007) for American black cherry wood, differences in growing site could be the origin of this variation. Metal content is influenced by factors such as wood species, soil type, wood maturity, cooking chemical and process water.

Figure 2 exhibits the content of Ca, Na, K, and Mg in wood and an ECF bleached pulp. The unbleached pulp (Pre-ODL) contained the highest amount of Ca, and its content tended to decrease with the following bleaching stages. An increasing amount of Ca in the Pre- and Post-ODL compared to that of wood was thought due to the used of mill white liquor in the pulping processes and it was not totally washed out in the Post-ODL stage. Mill white liquor contains traces of Ca from previously recovered cooking liquor. Increasing amount of Na in the post-ODL, EO and P bleached pulp was assumed because of the use of NaOH (Bryant & Edwards 1996). Oxygen delignification was carried out in an alkaline media, in which NaOH was used to increase the pH of the pulp slurry being delignified. Mg is a stabilizer of hydrogen peroxide in oxygen based bleaching (O, P and Z stages). The present results indicated that its highest content was in the pre-ODL and then kept decreasing afterward.

Pulping decreased the content of Fe and Mn; however it increased the content of Cu and Zn as indicated by Figure 3. Oxygen delignification and subsequent bleaching stages tended to decrease the micro elements of pulp. During the bleaching stages (after Post- ODL), the highest content of Fe (15.96 ppm), Cu (5.03 ppm), and Mn (1.67 ppm) was found in the D_1, P and D_0 bleached pulp, respectively. These three metals ion can decompose hydrogen peroxide through Fenton reaction to form hydroxyl radical (Lidén & Ohman 1997). Hydroxyl radical is very reactive and brings about the depolimerization of cellulose.

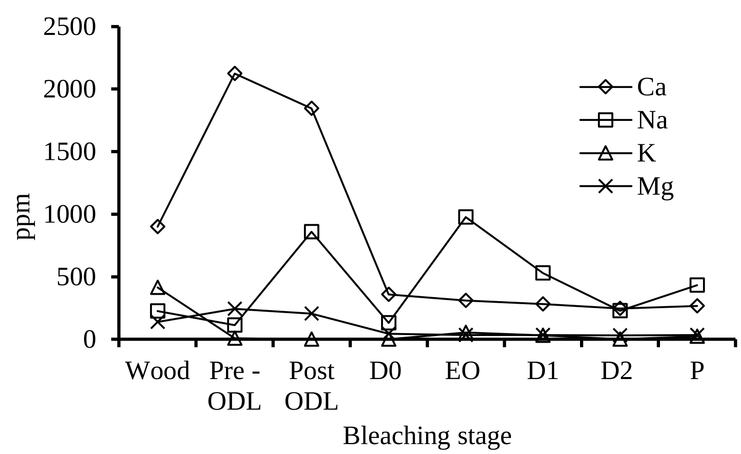

Figure 2 Macro elements content in mangium wood and its $D_0(EO)D_1D_2P$ bleached pulp.

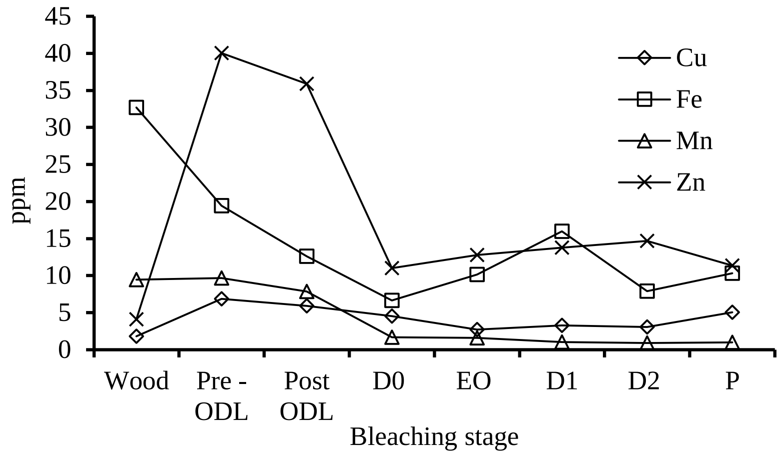

Figure 3 Micro elements content of mangium wood and its D_0(EO)D1D2P bleached pulp.

Dahl (1999) reported that the detrimental limit of Cu^{2+}, Mn^{2+}, and Fe^{2+} and Fe^{3+} to P bleaching stage was 0.5 ppm, 1 ppm, and 2 ppm, respectively. The content of Fe and Cu found in the present works were much higher than those of the reported detrimental limit. Furthermore, Fe, Cu and Mn do not just increase the consumption of bleaching chemical, but also reduce the reaction selectivity of oxygen toward lignin (Ni*et al*. 1996).

The brightness and viscosity of pulp

The efficiency and selectivity of oxygen based bleaching is strongly influenced by the presence of transition metals in the system. Transition metals decrease the stability of hydrogen peroxide and can bring about cellulose degradation (Yokohama*et al*. 1999). Figure 4 indicates that a significant increment of pulp brightness occurred from Post-ODL treatment to the subsequent bleaching stages. However, the brightness increment among D_0, EO, D_1, D_2 and P stages were not significant. The content of Fe and Cu sharply decreased after oxygen delignification of pulp. Fe in pulp negatively affects pulp brightness more than that of Cu. Meanwhile the influence of Mn and Al on brightness is negligible (Gosh & Ni 1998).

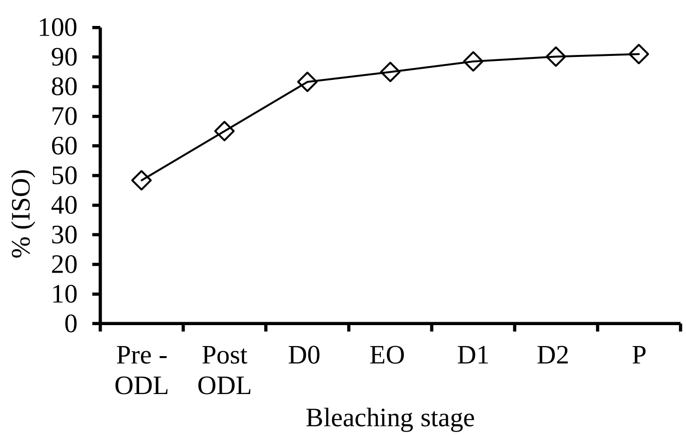

Figure 4 Brightness of unbleached and bleached pulp.

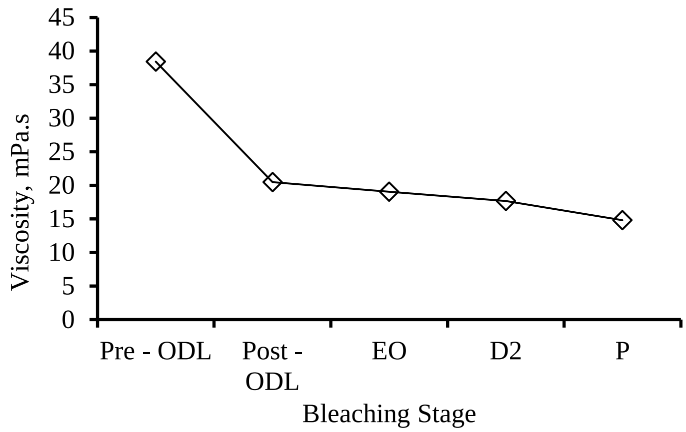

Figure 5 Pulp viscosity of unbleached and bleached pulp.

Transition metal has been reported also to reduce strength properties of pulp (Yokohama *et al*. 1999). However, in the present works, pulp viscosity was measured instead of directly measuring pulp strength. Viscosity of pulp is indicative of the depolimerization degree of cellulose, thus can be related to the strength of pulp. Strong pulp is generally made up of pulp with high viscosity value (Smook 1994). Figure 5 indicates the viscosity of pulp at selected bleaching stages of the present works. It can be seen that pulp viscosity decreased with the proceeding bleaching stages. Cellulose degradation is unavoidable when delignification proceeds in pulping and bleaching processes.

In peroxide based bleaching, transition metal can oxidize hydrogen peroxide and results in radical formation that bring about cellulose degradation and reduce pulp strength (Sunden *et al*. 2000). Figure 5 indicates that starting from oxygen delignification, the viscosity of pulp was sharply decreased. It could be due to the degradation of lignin carbohydrate complex and the presence of high concentration transition metals. It has been indicated early that the concentration of harmful metal ion to hydrogen peroxide bleaching were beyond the stated detrimental limit.

Conclusions

Metal content of 5 years old *Acacia mangium* wood tended to increase from the bottom division to the upper division of the stem. The increasing content of Ca after Pre-ODl and Post-ODL stages was thought due to the use of mill cooking liquor during pulping stage. Na increased in the EO and P stages because of the used of NaOH to activate oxygen and peroxide bleaching agents. Subsequent to the EO bleaching stage, Mn content of pulp decreased and was found lower than its detrimental limit of 1 ppm in peroxide stage. However, the content of Cu and Fe was higher than its detrimental limit in every bleaching stage. Metal content decreased the brightness and viscosity of pulp in the present ECF bleaching of pulp.

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