Selectivity improvement and extractive removal by various pretreatment methods prior to oxygen delignification for *Acacia mangium* and mixed hardwood kraft pulps

The objective of this study was to evaluate different pretreatment methods prior to oxygen delignification on extractives removal and O-delignification selectivity. Four different pretreatment methods were used including ultrasonic treatment, hot water soaking, soda addition-preheating, and applying a high-shear mechanical pretretament. *Acacia mangium* and mixed hardwood (MHW) kraft pulps were used in this study. Mechanical pretreatment, prior to oxygen delignification, promoted a better selectivity for both *Acacia mangium* and MHW pulps. MHW kraft pulp did not show a significant extractive removal in all pretreatment methods during oxygen delignification. This was probably due to a low extractive content of pre O_2 MHW kraft pulp to begin with. A dramatic extractive removal occurred on the *Acacia mangium* pulp that was pretreated with ultrasonic. The ultrasonic pretreatment followed by filtering induced extractive removal.

Application: Control of extractives for tropical hardwood kraft pulp mills

INTRODUCTION

Wood extractives are known to be gummy materials which are difficult to remove in washing stages and may give sticky deposits on process equipment. In addition, modified extractives, chiefly chlorinated, have been shown to have a strong influence on brightness stability [1]. In the modern production of bleached kraft pulp, a large part of the lipophilic extractives originally present in wood is removed in the kraft cooking and oxygen delignification stages, i.e. in the closed part of the mill [1]. A minor part of the wood extractives are, however, carried over to the bleach plant with the brownstock pulp. In the bleach plant such wood extractives will, to various degrees, react with the bleaching chemicals to form oxidized and modified extractives [1].

A study by Bouchard et al [2] showed that pressing and washing of aspen kraft pulp after oxygen delignification stage can reduce extractive concentration in pulp. This result was in agreement to that of reported by Mahagaonkar et al [3] on bisulfite *Radiata pine*. This study also proved that none of the approaches involving caustic addition during oxygen delignification improve extractive removal [2]. An alkali pretreatment on *Radiata pine* bisulfite pulp prior to hydrogen peroxide bleaching was shown to give maximum extractive removal (86 %) as reported by Mahagaonkar et al [3]. Sun et al [4] reported that hot water treatment on wheat straw at 80-90 °C, pH 6.0-8.0 for 0.5 h released 41-53 % of original extractive. This study suggested that hot water treatment is a convenient method for dissolution of the lipophilic extractives. Ultrasonic treatment was reported to affect pulp Kappa number reduction and brightness improvement on unbleached alkaline sulfite pulp of *Tamlin flax* [5]. The use of linear alcohol ethoxylate surfactants at concentration of 0.25 kg/t in oxygen delignification of aspen kraft pulp was reported to reduce 12.5 % of DCM (dichloromethane) extractives [2]. Anionic surfactants such as naphthalene sulphonate or lignosulphonate, and non-anionic surfactants such as fatty alcohol ethoxylate or alkyl phenol ethoxylate have been reported to reduce 30 % of DCM extractives in peroxide bleaching stage of CTMP aspen pulp at concentration of 1 kg/t [6].

Acacia mangium has been recognized as an excellent source of short cellulose fibers for papermaking [7-10]. Extensive plantations are now growing in Southeast Asia, particularly Indonesia, supplying wood to the pulp and paper industry in that part of the globe [11]. The interesting properties of *Acacia mangium* fibers, together with its excellent adaptation to tropical humid climates [12] suggest that *Acacia mangium* plantations will soon spread to other regions of the world such as South America, competing with other hardwood fiber sources [13].

Despite the advantages of the *Acacia mangium* wood, its extractives content is known to be quite high when compared to that of other hardwoods as shown in Table 1 [14]. It was also reported by Pinto et al [13] that lipophilic extractives were quite abundant in *Acacia mangium*, as shown by the weight of dichloromethane extract (1.32%), and being composed essentially of aliphatic acids and long chain (>C20) aliphatic alcohol [14, 15].

Table 1. Extractives content of five hardwoods [14]

	Extractives, % (ethanol/toluene)
Acacia mangium	4.46
Betula pendula	2.24
Eucalyptus globulus	1.72
Eucalyptus urograndis	1.91
Eucalyptus grandis	2.10

Table 2. Kraft pulping conditions, Kappa number, and ClO_2 consumption during bleaching by sequence (DEDED) [14]. Final TAPPI brightness 90

Wood species	% Na_2O/wood	Unbleached pulp Kappa number	ClO_2 consumption %/pulp
Acacia mangium	24	15.9	7.4
Betula pendula	18	16.4	7.2
Eucalyptus globulus	16	15.0	4.4
Eucalyptus urograndis	20	15.7	5.3
Eucalyptus grandis	19	16.1	5.4

The high content of extractives may constitute a negative point of this species when used as a fiber source, because extractives increase the chemical consumption during pulping and bleaching processes, and may lead to pitch deposits in mill machinery and in pulp and paper; requiring high maintenance costs and decreasing the final product quality [16]. These issues were in agreement with a recent report by Neto et al [14] where *Acacia mangium* wood required the highest amounts of pulping and bleaching chemicals to achieve similar degree of delignification as shown in Table 2.

The present study was directed to evaluate different pretreatment methods prior to oxygen delignification with respect to selectivity and extractive removal. Fiber structural properties, including: fiber length, fines, fiber curl and fiber kink were also discussed.

Table 3. Metal profile of pre O_2 *Acacia mangium* and MHW (mixed hardwood) kraft pulps

Metal	*A. mangium*, mg/kg	MHW, mg/kg
Cu	4.19	1.69
Mn	2.21	19.4
Fe	7.76	5.34
Mg	38.5	281
Ca	282	2470
Ni	< 0.36	< 0.28
Co	< 0.30	< 0.20

EXPERIMENTAL

Pulps

A pre O_2 *Acacia mangium* and mixed hardwood (MHW) kraft pulps were acquired from APRIL's (Asia Pacific Resources International holdings Limited) mill Sumatra, Indonesia. These pulps were washed until the effluent was pH neutral and colorless. These wet pulps (a consistency of about 17 %) were kept in the cold room at 2 °C, prior to use. The metal profile of these pulps is shown in Table 3.

Pretreatments

Four different pretreatment methods were applied prior to oxygen delignification as follows:

1. Pulps (35 g o.d.) were ultrasonicated for 2 hours at 1 % consistency, temperature of 25 °C, amplitude 40 %, energy 1.0 MJ while being continuously stirred at 25 rpm, to keep the pulp slurry homogeneous. This pulp was then filtered and washed until the effluent colorless. The oxygen delignified pulp sample of this pretreatment was labeled as 1A for *Acacia mangium* pulp and 1M for MHW pulp.
2. Pulps (60 g o.d.) were premixed with 0.5 % $MgSO_4$ (5 % w/w solution) and hand stirred with plastic rod. This pulp mixture was preheated at 12.8 % consistency and temperature of 70 °C for 2 hours in the water bath. The oxygen delignified pulp sample of this pretreatment was labeled as 2A for *Acacia mangium* pulp and 2M for MHW pulp.
3. Pulps (60 g o.d.) were premixed with 0.5 % $MgSO_4$ (5 % w/w solution) and hand stirred with plastic rod. 2 % NaOH (1.00 N NaOH solution) was added to this pulp mixture and hand stirred with plastic rod. This pulp mixture was then heated at 12.8 % consistency and temperature of 70 °C for 2 hours, in the water bath. The oxygen delignified pulp sample of this pretreatment was labeled as 3A for *Acacia mangium* pulp and 3M for MHW pulp.
4. Pulps (100 g o.d.) were premixed with 0.5 % $MgSO_4$ (5 % w/w solution) and hand stirred with plastic rod. This pulp mixture underwent mechanical pretreatment in a laboratory Quantum mixer at speed 2200 rpm and 12.8 % consistency for 5 seconds. The oxygen delignified pulp sample of this pretreatment was labeled as 4A for *Acacia mangium* pulp and 4M for MHW pulp.

A control pulp samples were made without pretreatment prior to oxygen delignification and labeled as CA for *Acacia mangium* pulp and CM for MHW pulp.

Oxygen delignification

A laboratory inclined Parr reactor was used in this study at constant oxygen pressure (1,034 kPa) and consistency (12 %). The mixer speed was kept constant at 20 rpm. The Parr reactor was warmed up to 70 °C. The reactor was then charged with pulp sample (60.00 g o.d.), 0.5 % $MgSO_4$ (5 % w/w solution, only for pretreatment 1 and control), 2 % of NaOH 1.00 N (only for pretreatment 1, 2, 4, and control) and deionized water so that the final pulp consistency of 12 % was reached. The reactor was secured while heating was continued. The oxygen pressure was applied after the temperature reached the set point (90 °C) and the timer was started at the same time. When the desired time was reached (60 min), the applied oxygen pressure, heating and mixing were stopped, and the reactor was allowed to cool to room temperature. The pressure in the reactor was released by opening the pressure release valve. The oxygen delignified pulps were then washed with de-ionized water until the effluent was pH neutral and colorless.

Pulp testing

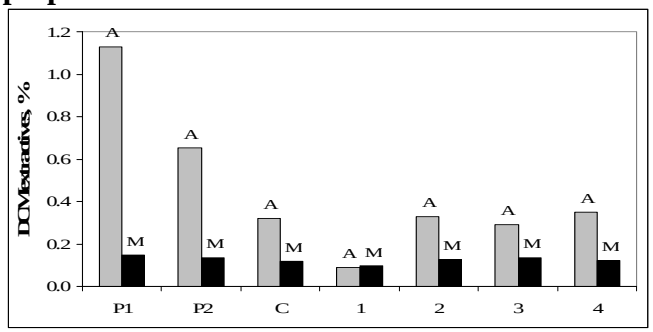
DCM (dichloromethane) extractives, Kappa number and viscosity of pulps were tested according to TAPPI methods T204 [17], T236 [18], and T230 [19], respectively. The standard deviation errors associated with each test were 7.2, 1.2, and 1.8 % for DCM extractives, Kappa number and viscosity, respectively. Fiber length, fines, fiber curl index and fiber kink were measured with Fiber Quality Analyzer (FQA), OpTest Equipment [20]. The standard deviation errors associated with each measurement were 1.1, 3.1, 2.1, and 1.6 % for fiber length, fines, fiber curl index, and fiber kink, respectively.

RESULTS AND DISCUSSIONS

In this experimental study, the oxygen delignification reactions were performed immediately after pretreatment of the pulp samples were completed. The concentrations of $MgSO_4$ (0.5%) and NaOH (2%) in pulps prior to oxygen delignification reaction were kept constant for all experiments. There was no washing and/or filtering between the pulp pretreatment and oxygen delignification reaction, with the exception of the pulp sample labeled number 1 (see the description in the experimental section). Thus, the pre O_2 pulp was filtered and washed after pretreatment number 1 prior to oxygen delignification. Figure 1 summarized the DCM extractives of pre O_2 and oxygen delignified pulps for each pretreatment. *A. mangium* pulp had significantly higher DCM extractives content than MHW pulp. It is evident as shown in Figure 1 that ultrasonic pretreatment on *A. mangium* pulp followed by filtering and washing induced extractive removal of 42 %. Pressing and washing was also reported to be the best combination to reduce extractive content [2]. Oxygen delignification of this pulp (pretreatment number 1) further reduced extractive content by additional 87 %. This result was found to be the best method to remove extractive content among the other pretreatment methods studied. A similar result was obtained for ultrasonic pretreatment of MHW pulp, even though only a total of 33 % extractive removed from pre O_2 MHW pulp. A low extractive content of pre O_2 MHW pulp was probably one reason why significant extractive removal was not observed in this study. Further study is needed to prove this hypothesis. The oxygen delignification stage itself reduced the extractives content by 51 and 19 % for *A. mangium* and MHW pulps, respectively (pulp sample labeled C), see Figure 1. The NaOH pretreatment (pulp sample labeled 3) proved to be inefficient to remove extractive [2]. Efficient extractive removal was also not obtained by hot water pretreatment and mechanical pretreatment of pulp (pulp sample labeled 2 and 4, respectively).

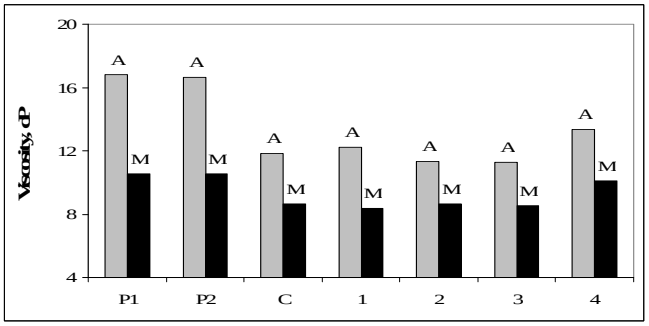
Pulp viscosity measurement was performed to see how pulp pretreatment prior to oxygen delignification affected the cellulose degradation. Figure 2 summarizes the viscosity of pre O_2 and oxygen delignified *A. mangium* and MHW pulps. Figure 2 shows that, in most cases, pulp pretreatment methods did not induce cellulose degradation. A slight viscosity reduction occurred on the hot water and NaOH pretreatments.
It was also shown, in Figure 2. that ultrasonic pretreatment did not degrade fiber cellulose. This was in accord with results reported by Thompson et al [21].

Fig.1. DCM extractives content of pre O_2 and oxygen delignified *A. mangium* (A) and MHW (M) pulps



Note: P1 denotes original pre O_2 pulp, P2 denotes pre O_2 pulp after ultrasonic pretreatment followed by filtering and washing, while C, 1, 2, 3, 4 are as described in the experimental section

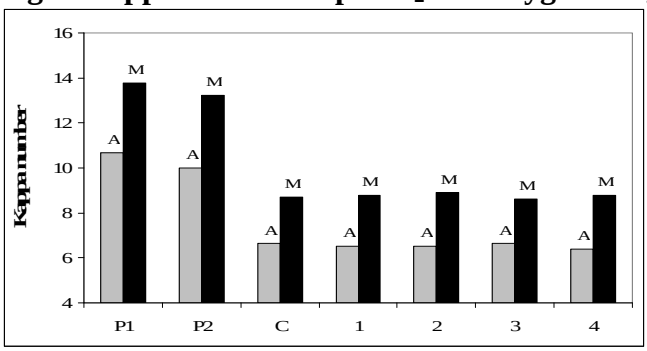
Fig.2. Viscosity of pre O_2 and oxygen delignified *A. mangium* (A) and MHW (M) pulps



Note: P1 denotes original pre O_2 pulp, P2 denotes pre O_2 pulp after ultrasonic pretreatment followed by filtering and washing, while C, 1, 2, 3, 4 are as described in the experimental section

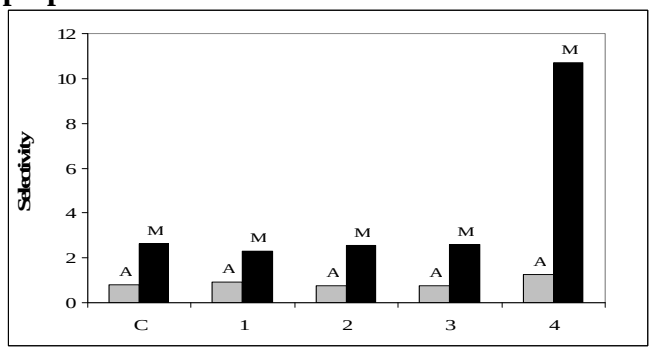
To investigate how the pulp pretreatments prior to oxygen delignification affected the lignin removal, Kappa number of the pulps was determined. Figure 3 summarized the pulp Kappa number of pre O2 and oxygen delignified *A. mangium* and MHW pulps. In general, the Kappa number of the oxygen delignified pulps with pretreatment was at a similar level to those without pretreatment. Figure 3 also indicttes that ultrasonic pretreatment, followed by filtering and washing, released to a small amount residual lignin from the pulp (pulp sample labeled P2). This was indicated by Kappa number reduction of 7 and 6 % for A. mangium and MHW pulps. Cell wall breakage and pores formation due to ultrasonic effect could be reasons why the Kappa number decreased [21].

Fig.3. Kappa number of pre O_2 and oxygen delignified *A. mangium* (A) and MHW (M) pulps



Note: P1 denotes original pre O_2 pulp, P2 denotes pre O_2 pulp after ultrasonic pretreatment followed by filtering and washing, while C, 1, 2, 3, 4 are as described in the experimental section

Fig.4. Selectivity (Δ Kappa / Δ viscosity) of oxygen delignified *A. mangium* (A) and MHW (M) pulps

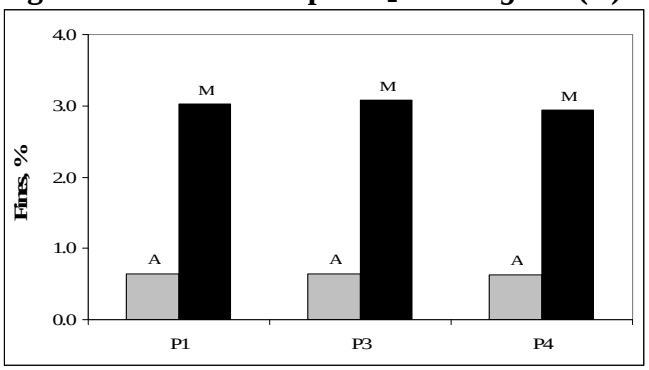


Note: The code C, 1, 2, 3, 4 is as described in the experimental section

The selectivity of oxygen delignification was of interest to see. Figure 4 shows the selectivity of oxygen delignified *A. mangium* and MHW pulps. It was obvious that mechanical pretreatment of the pulp, prior to oxygen delignification, obtained the best selectivity among the other pretreatments. There was an increase on oxygen delignification selectivity of 50 % and 300 % for *A. mangium* and MHW pulp, respectively. This was probably due to a better mixing of added $MgSO_4$ with the pulp prior to an O-stage. This is in accord with the reports by Yang et al [22] and Liden et al [23]. The greater oxygen delignification selectivity on MHW pulp was probably due to less Mg/Mn mole ratio compared to those of *A. mangium* pulp, i.e. 33 and 40, respectively, so that additional $MgSO_4$ was less important to MHW pulp [22, 23]. The other pulp pretreatments did not show a selectivity improvement, as shown in Figure 4.

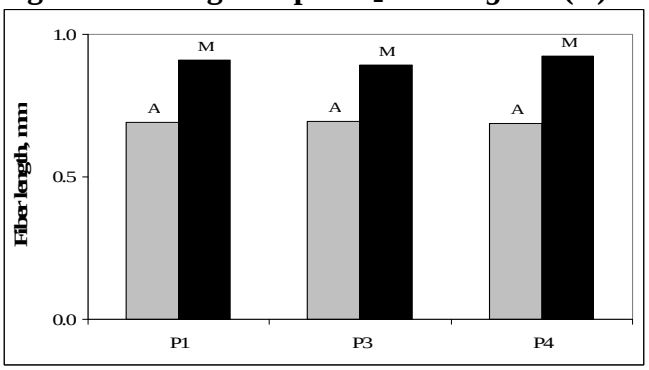
The fines formation due to mechanical and ultrasonic pretreatments of the pulp was also studied. Figure 5 summarized the fines content of pre O_2 *A. mangium* and MHW pulps with and without pretreatment. It was shown that ultrasonic pretreatment of the pulp (pulp sample labeled P3) did not induce fines formation, as suggested by Thompson et al [21]. Figure 5 also shows that mechanical pretreatment of pulp for 5 seconds did not lead to fines formation. Figure 6 confirmed that both ultrasonic and mechanical pretreatment did not physically damage the fiber, as the fiber length remains similar to those of without pretreatment (pulp sample labeled P1).

Fig.5. Fines content of pre O_2 *A. mangium* (A) and MHW (M) pulps



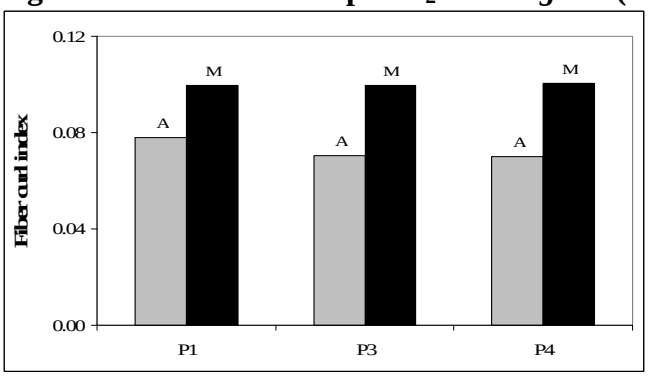
Note: P1 denotes original pre O_2 pulp, P3 denotes ultrasonic pretreatment of pre O_2 pulp, and P4 denotes mechanical pretreatment of pre O_2 pulp

Fig.6. Fiber length of pre O_2 *A. mangium* (A) and MHW (M) pulps



Note: P1 denotes original pre O_2 pulp, P3 denotes ultrasonic pretreatment of pre O_2 pulp, and P4 denotes mechanical pretreatment of pre O_2 pulp

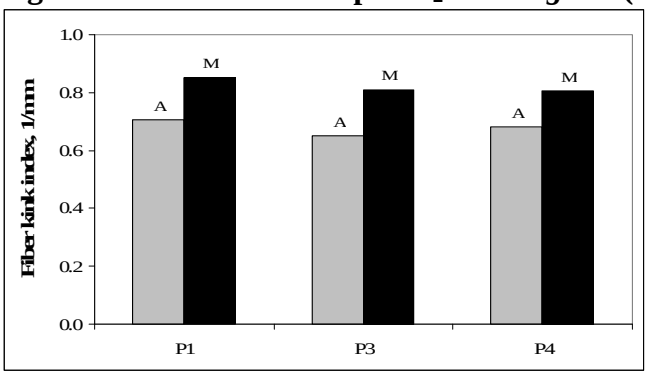
Fig.7. Fiber curl index of pre O_2 *A. mangium* (A) and MHW (M) pulps



Note: P1 denotes original pre O_2 pulp, P3 denotes ultrasonic pretreatment of pre O_2 pulp, and P4 denotes mechanical pretreatment of pre O_2 pulp

On the other hand, the effect of ultrasonic and mechanical pretreatments was found to reduce the fiber curl and kink. Ultrasonic and mechanical pretreatments probably gave 'refining' effect to release reversible curl and kink as reported by Mohlin et al [24]. Figure 7 and 8 summarize the fiber curl and kink of pre O_2 *A. mangium* and MHW pulps.

Fig.8. Fiber kink index of pre O_2 *A. mangium* (A) and MHW (M) pulps



Note: P1 denotes original pre O_2 pulp, P3 denotes ultrasonic pretreatment of pre O_2 pulp, and P4 denotes mechanical pretreatment of pre O_2 pulp

CONCLUSIONS

1. The selectivity of oxygen delignification was improved by applying mechanical pretreatment prior to oxygen delignification reaction for both *A. mangium* and MHW kraft pulps, i.e. 50 and 300 %, respectively.
2. 92 % of *A. mangium* kraft pulp extractives can be removed by ultrasonic pretreatment followed by oxygen delignification with conditions described in this study.
3. Only 33 % of MHW kraft pulp extractives can be removed by ultrasonic pretreatment followed by oxygen delignification with conditions described in this study. This lower result compared to those of *A. mangium* pulp was probably due to a low extractives content of MHW kraft pulp to begin with.
4. Ultrasonic and mechanical pretreatments did not induce fines formation and fiber length degradation for both *A. mangium* and MHW kraft pulps.
5. Ultrasonic and mechanical pretreatments reduced fiber curl and kink for *Acacia mangium* pulp. However MHW fiber kink was improved, but fiber curl did not show a reduction.

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