

**OXYGEN DELIGNIFICATION PROCESS CHEMISTRY FOR  
ACACIA**

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# **OXYGEN DELIGNIFICATION PROCESS CHEMISTRY FOR ACACIA**

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# TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS .....	iii
LIST OF TABLES .....	vii
LIST OF FIGURES .....	ix
SUMMARY .....	xiii
CHAPTER 1 INTRODUCTION .....	1
CHAPTER 2 LITERATURE REVIEW .....	3
2.1. Acacia .....	3
2.1.1. The plantation .....	3
2.1.2. The chemistry .....	7
2.1.3. Fiber and sheet properties .....	11
2.2. Kraft pulping .....	12
2.3. Oxygen delignification .....	19
2.3.1. Lignin reactions .....	21
2.3.2. Carbohydrate reaction .....	22
2.3.3. Process fundamental .....	24
2.3.3.1. Alkali charge .....	26
2.3.3.2. Time and temperature .....	28
2.3.3.3. Consistency .....	30
2.3.3.4. Oxygen pressure .....	30
2.3.3.5. Mechanical processing .....	31
CHAPTER 3 EXPERIMENTAL .....	33

3.1. Chemicals .....	33
3.2. Pre O <sub>2</sub> <i>Acacia mangium</i> kraft pulp .....	33
3.3. Oxygen delignification .....	35
3.4. Mechanical pretreatment .....	36
3.5. Handsheet making .....	38
3.6. Pulp testing .....	39
3.6.1. Physical properties .....	39
3.6.2. Fiber Quality Analyzer .....	39
3.6.3. Kappa number .....	40
3.6.4. Viscosity .....	41
3.6.5. Extractives .....	42
3.6.6. Celluloses .....	42
3.6.7. Hexenuronic acid .....	43
3.6.8. Total charge .....	44
3.7. Experimental error .....	46
 CHAPTER 4 RESULTS AND DISCUSSIONS .....	 47
4.1. Mill's pulp properties .....	47
4.2. The effect of oxygen delignification process on the pulp strength .....	48
4.3. The effect of oxygen delignification process on fiber structures .....	53
4.4. The effect of oxygen delignification process on cellulose degradation .....	55
4.5. The effect of oxygen delignification process on DCM extractive and total fiber charge .....	57
4.6. The effect of oxygen delignification process on Kappa number and hexenuronic acid content .....	59

4.7. The importance of oxygen delignification process parameters on mechanically pretreated pulp .....	60
4.8. Selectivity improvement and extractive removal by various pretreatment methods prior to oxygen delignification .....	64
CHAPTER 5 CONCLUSIONS .....	74
CHAPTER 6 FUTURE WORKS .....	76
APPENDIX A: EXPERIMENTAL ERROR CALCULATIONS .....	77
APPENDIX B: SUMMARY OF TEST RESULTS .....	92
REFERENCES .....	94

## LIST OF TABLES

	Page
Table 1: Chemical composition of <i>Acacia mangium</i> wood [21] .....	8
Table 2: Compositions of hardwoods and unbleached kraft pulp [23] .....	9
Table 3: Fiber dimensions, fiber kink and fiber coarseness for unrefined bleached hardwood kraft pulps [30] .....	11
Table 4: Result of microscopy measurement of cross sectional dimensions of unrefined bleached hardwood kraft pulps [30] .....	12
Table 5: Kraft pulping conditions, <sup>a</sup> pulp yield, and ClO <sub>2</sub> consumption during bleaching by a chlorine dioxide based sequence (DEDED) [23] .....	15
Table 6: Unbleached kraft pulp properties of <i>Acacia mangium</i> from eastern Thailand [8] .....	16
Table 7: Pilot scale kraft cooking results of <i>Acacia mangium</i> [32] .....	18
Table 8: Physical properties of unbleached kraft pulp of three <i>Acacia</i> species [33] .....	18
Table 9: Commercial oxygen delignification operating conditions for <i>Acacia</i> and mixed tropical hardwood (MHW) [35] .....	19
Table 10: Physical properties of hardwood brownstock kraft pulp and oxygen delignified pulp [38] .....	26
Table 11: Effect of alkali addition in oxygen delignification of hardwood kraft pulp on kappa number and viscosity of oxygen delignified* pulps [44] .....	27
Table 12: Effect of reaction temperature on the oxygen delignified* hardwood kraft pulp strength properties [44] .....	29
Table 13: Effect of consistency of oxygen delignification* on hardwood kraft pulp properties [44] .....	30
Table 14: Effect of oxygen delignification* pressure on hardwood kraft pulp properties [44] .....	31
Table 15: Fiber curl and wall dislocation of <i>Pine radiata</i> bleached kraft pulp after treatment by medium consistency laboratory mixer [46] .....	32
Table 16: Pre O <sub>2</sub> and post O <sub>2</sub> <i>Acacia mangium</i> kraft pulp properties .....	34

Table 17: Metal profile of pre O <sub>2</sub> <i>Acacia mangium</i> kraft pulp .....	34
Table 18: Oxygen delignification experimental conditions .....	35
Table 19: Oxygen delignification experimental condition for Yates' algorithm analysis [68] .....	36
Table 20: Summary of standard deviation experimental errors .....	46
Table 21: Yates' algorithm analysis [68] for DZSTS, t=reaction time in minutes, T=reaction temperature in °C, C=NaOH addition in g/kg of pulp, pulp consistency 12 %, oxygen pressure 1,034 kPa .....	60
Table 22: Yates' algorithm analysis [68] for WZSTS, t=reaction time in minutes, T=reaction temperature in °C, C=NaOH addition in g/kg of pulp, pulp consistency 12 %, oxygen pressure 1,034 kPa .....	61
Table 23: Yates' algorithm analysis [68] for Kappa number, t=reaction time in minutes, T=reaction temperature in °C, C=NaOH addition in g/kg of pulp, pulp consistency 12 %, oxygen pressure 1,034 kPa .....	61
Table 24: Metal profile of pre O <sub>2</sub> <i>Acacia mangium</i> and MHW (mixed hardwood) kraft pulp .....	64



## LIST OF FIGURES

	Page
Figure 1: Mean daily tree sap flow (Qwt) against the sapwood area of <i>Acacia mangium</i> tree [10] .....	4
Figure 2: Structure of polyphenols found in <i>Acacia mangium</i> [27] .....	10
Figure 3: Molar percentages of syringyl (S), guaiacyl (G), and p-hydroxyphenyl (H) units (determined by $^{13}\text{C}$ NMR spectroscopy) in (top) wood and (bottom) pulp lignins [23] .....	11
Figure 4: Formation of reactive intermediates during the stepwise reduction of oxygen to water [34] .....	20
Figure 5: Examples of the oxidative reactions of phenolic lignin structures during oxygen delignification [34] .....	22
Figure 6: Cleavage of glycosidic bonds in polysaccharide chains during oxygen delignification [34] .....	23
Figure 7: Oxidation of ketol structures along polysaccharide chains during oxygen delignification [34] .....	23
Figure 8: Single stage medium consistency oxygen delignification (Ahlstrom) [34] ...	24
Figure 9: Two stages medium consistency oxygen delignification (Kvaerner) [34] .....	25
Figure 10: Effect of reaction time and temperature on Kappa number of oxygen delignified hardwood kraft pulp [44]. Oxygen delignification was performed at 10 % consistency, 2 % alkali charge and an oxygen pressure of 0.6 MPa .....	28
Figure 11: Effect of reaction time and temperature on viscosity of oxygen delignified hardwood kraft pulp [44]. Oxygen delignification was performed at 10 % consistency, 2 % alkali charge and an oxygen pressure of 0.6 MPa .....	29
Figure 12: Laboratory inclined Parr reactor .....	37
Figure 13: Laboratory Quantum mixer .....	37
Figure 14: Sheet preparation equipment .....	38

- Figure 15: A conductometric titration curve, with (a) representing neutralization of HCl by titrant (NaOH), (b) representing the point in the titration in which conductivity does not change (ion exchange with fiber acid groups), and (c) representing increases in conductivity as excess NaOH is added ..... 45
- Figure 16: DZSTS, WZSTS and tensile index of oxygen delignified *Acacia mangium* kraft pulp after different oxygen delignification process conditions (a) reaction time, (b) NaOH charge, (c) reaction temperature and (d) mechanical pretreatment mixing time. Oxygen delignification condition is described in Table 18 p.35 ..... 49
- Figure 17: Tear index and burst index of oxygen delignified *Acacia mangium* kraft pulp after different process conditions (a) reaction time, (b) NaOH charge, (c) reaction temperature and (d) mechanical pretreatment mixing time. Oxygen delignification condition is described in Table 18 p.35..... 50
- Figure 18: WZSTS loss of pulp after mechanical pretreatment and mechanical pretreatment followed by oxygen delignification. Oxygen delignification was performed at reaction temperature 90 °C, reaction time 90 min, NaOH charge 20.00 g/kg, consistency 12 % and oxygen pressure 1,034 kPa ..... 51
- Figure 19: DZSTS loss of pulp after mechanical pretreatment and mechanical pretreatment followed by oxygen delignification. Oxygen delignification was performed at reaction temperature 90 °C, reaction time 90 min, NaOH charge 20.00 g/kg, consistency 12 % and oxygen pressure 1,034 kPa ..... 51
- Figure 20: Tensile index of pulp after mechanical pretreatment and mechanical pretreatment followed by oxygen delignification. Oxygen delignification was performed at reaction temperature 90 °C, reaction time 90 min, NaOH charge 20.00 g/kg, consistency 12 % and oxygen pressure 1,034 kPa ..... 52
- Figure 21: Viscosity and brightness of pulp after different oxygen delignification process conditions (a) reaction time, (b) NaOH charge, (c) reaction temperature and (d) mechanical pretreatment mixing time. Oxygen delignification condition is described in Table 18 p.35 ..... 53
- Figure 22: Fines, length, kink index and curl of fiber after different oxygen delignification process conditions (a) reaction time, (b) NaOH charge, (c) reaction temperature and (d) mechanical pretreatment mixing time. Oxygen delignification condition is described in Table 18 p.35 ..... 54
- Figure 23: Alpha-, beta- and gamma-cellulose of pulp after different oxygen delignification process conditions (a) reaction time, (b) NaOH charge, (c) reaction temperature and (d) mechanical pretreatment mixing time. Oxygen delignification condition is described in Table 18 p.35 ..... 56
- Figure 24: Percentage of cellulose and hemicelluloses of pulp after mechanical pretreatment followed by oxygen delignification. Oxygen delignification was

performed at reaction temperature 90 °C, reaction time 90 min, NaOH charge 20.00 g/kg, consistency 12 % and oxygen pressure 1,034 kPa .....	57
Figure 25: Total charge and DCM extractive of pulp after different oxygen delignification process conditions (a) reaction time, (b) NaOH charge, (c) reaction temperature and (d) mechanical pretreatment mixing time. Oxygen delignification condition is described in Table 18 p.35 .....	58
Figure 26: Kappa number and hexenuronic acid content of pulp after different oxygen delignification process conditions (a) reaction time, (b) NaOH charge, (c) reaction temperature and (d) mechanical pretreatment mixing time. Oxygen delignification condition is described in Table 18 p.35 .....	59
Figure 27: Oxygen delignification selectivity ( $\Delta Kappa/\Delta viscosity$ ) of <i>Acacia mangium</i> kraft pulp at various NaOH charge. Oxygen delignification reaction was performed at 12 % consistency, oxygen pressure of 1,034 kPa, temperature of 90 °C, and reaction time of 90 minutes .....	62
Figure 28: Correlation between selectivity ( $\Delta Kappa/\Delta Viscosity$ ) and NaOH addition of oxygen delignified pulp at consistency 12 %, time 120 minutes, temperature 90 °C, and O <sub>2</sub> pressure 1034 KPa. The pulp was mechanically pretreated with Quantum mixer for 15 seconds prior to oxygen delignification reaction ...	63
Figure 29: Relationship between pulp viscosity and DZSTS of oxygen delignified pulp from Yates' algorithm analysis. Oxygen delignification condition is described in Table 19 p.36 .....	63
Figure 30: DCM extractives content of pre O <sub>2</sub> and oxygen delignified <i>A. mangium</i> (A) and MHW (M) pulps. P1 denotes original pre O <sub>2</sub> pulp, P2 denotes pre O <sub>2</sub> pulp after ultrasonic pretreatment followed by filtering and washing, while C, 1, 2, 3, 4 are as described in the detail pretreatment methods (p.65) .....	67
Figure 31: Viscosity of pre O <sub>2</sub> and oxygen delignified <i>A. mangium</i> (A) and MHW (M) pulps. P1 denotes original pre O <sub>2</sub> pulp, P2 denotes pre O <sub>2</sub> pulp after ultrasonic pretreatment followed by filtering and washing, while C, 1, 2, 3, 4 are as described in the detail pretreatment methods (p.65) .....	68
Figure 32: Kappa number of pre O <sub>2</sub> and oxygen delignified <i>A. mangium</i> (A) and MHW (M) pulps. The code C, 1, 2, 3, 4 is as described in the detail pretreatment methods (p.65) .....	69
Figure 33: Selectivity ( $\Delta Kappa / \Delta viscosity$ ) of oxygen delignified <i>A. mangium</i> (A) and MHW (M) pulps. The code C, 1, 2, 3, 4 is as described in the detail pretreatment methods (p.65) .....	70
Figure 34: Fines content of pre O <sub>2</sub> <i>A. mangium</i> (A) and MHW (M) pulps. P1 denotes original pre O <sub>2</sub> pulp, P3 denotes ultrasonic pretreatment of pre O <sub>2</sub> pulp, and	

P4 denotes mechanical pretreatment of pre O <sub>2</sub> pulp. Detail pretreatment methods are described in p.65 .....	71
Figure 35: Fiber length of pre O <sub>2</sub> <i>A. mangium</i> (A) and MHW (M) pulps. P1 denotes original pre O <sub>2</sub> pulp, P3 denotes ultrasonic pretreatment of pre O <sub>2</sub> pulp, and P4 denotes mechanical pretreatment of pre O <sub>2</sub> pulp. Detail pretreatment methods are described in p.65 .....	71

## SUMMARY

Oxygen delignification has been widely used for lignin removal before bleaching and has become one of the dominant post-kraft pulping delignification technologies. Oxygen delignification has become an increasingly important delignification technology for extending kraft pulping because environmental regulatory pressures have come to the fore over the past decade. A series of laboratory oxygen delignification were performed in this study at constant oxygen pressure and consistency to study the response of the pulp to the different process parameters, i.e. reaction temperature, reaction time, soda addition, and mechanical pretreatment, to the zero span tensile strength loss. A pre O<sub>2</sub> *Acacia mangium* kraft pulp was used in this study. The basic chemistry of the oxygen delignified pulps was under study including fiber charge, celluloses/hemicelluloses, and hexenuronic acid. The fiber structure such as curl, kink, fines, and fiber length were also discussed. Mechanically pretreated pulp followed by oxygen delignification was found to increase pulp dry zero span tensile strength and tensile index. Applying mechanical pretreatment for 10 seconds followed by oxygen delignification increased tensile index and dry zero span tensile strength by 6 and 14 % respectively, at conditions described in this study. Oxygen delignification selectivity was observed to decrease by increasing the soda charge. The pulp viscosity and wet zero span tensile index decreased by applying mechanical pretreatment prior to oxygen delignification.

Another series of oxygen delignification were performed to study how the process parameters including reaction time, temperature and soda charge affected to dry zero span tensile strength, tensile index and Kappa number of mechanically pretreated pulp. A

Yates' algorithm was used to analyze the results. Oxygen delignification reaction temperature and soda charge were found to significantly affect to pulp dry zero span tensile strength and tensile index. On the other hand, Kappa number reduction was affected mainly by reaction temperature. These results suggested that oxygen delignification soda charge can be reduced to maintain Kappa number reduction at certain level while improving pulp zero span tensile strength and tensile index. NaOH charge can be reduced as much as 50 % by applying mechanical pretreatment to obtain the same level of selectivity at the oxygen delignification conditions described in this study.

A new *Acacia mangium* and mixed hardwood (MHW) kraft pulps of recent production were studied to evaluate different pretreatment methods prior to oxygen delignification on the selectivity improvement and extractive removal. Four different pretreatment methods were used: applying ultrasonic energy, hot water soaking, soda addition-preheating, and applying mechanical shear. 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<sub>2</sub> 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 the best extractive removal among the other three methods. Ultrasonic and mechanical pretreatments did not create fines formation.

# CHAPTER 1

## INTRODUCTION

Oxygen delignification has been widely used in current production of bleached kraft pulps. The increasing environmental pressure on the pulp industry to decrease the use of chlorine containing bleaching agent is one of the reasons why the pulp industry took the benefit of the oxygen delignification [1]. The economic benefits of oxygen delignification include lower cost of effluent treatment, recovery of heat from the burning of materials removed from the pulp, lower refining energy requirements of oxygen delignified pulps and lower cost of oxygen compared to equivalent amounts of chlorine [2]. The benefit of oxygen delignification for the production of bleached kraft pulps have been recognized for well over four decades. Research studies over this period have examined many applied and fundamental components of oxygen delignification and were generally directed at improving the selectivity of oxygen delignification and /or improving the overall environment performance of kraft bleaching operations via oxygen delignification [3]. As environmental issues have now been addressed, research has returned to the performance of this proven technology.

There are couple factors controlling oxygen delignification operation and one of the ultimate aims of the oxygen delignification process is on how to retain the pulp strength. The pulp strength loss during oxygen delignification is caused by cellulose chain cleavage resulting from attack by oxygen based radicals generated through reaction with lignin [4]. Previous study has found that the zero span tensile loss during oxygen delignification on acacia kraft pulp was about twice as much to those of other kraft pulps [70]. In this study, pre-oxygen delignified *Acacia mangium* kraft pulp was used and a series of oxygen delignification were performed with different process parameter including reaction time, soda charge, reaction temperature and mechanical pretreatment

to understand how those parameters impact on the fiber strength. The fiber strength is evaluated by the zero span tensile strength. The basic chemistry of the pulp is also studied including total fiber charge, hexenuronic acid, lignin, and cellulose/hemicelluloses content. The other basic physical properties including tear index, burst index, tensile index, brightness, fiber length, fines, fiber curl and fiber kink index were also evaluated.

Another series of oxygen delignification were performed to evaluate what process parameters affected most on the fiber strength during oxygen delignification on the mechanically pretreated pulp. A Yates' algorithm analysis was used to quantify the effect of every process variables. The pulp testing results were presented with a standard deviation error's percentage on each measurement.

An evaluation of different pretreatment methods prior to oxygen delignification was performed to study the effect on the selectivity and extractive removal. A recent production of *Acacia mangium* and mixed hardwood (MHW) kraft pulps were used in this experiment. Four different pretreatment methods were used: applying ultrasonic energy, hot water soaking, soda addition-preheating, and applying mechanical shear. The result was compared to those without pretreatment. The effect of pretreatment methods on the fiber structures including fiber length, fiber curl, fiber kink and fines were discussed.



## CHAPTER 2

### LITERATURE REVIEW

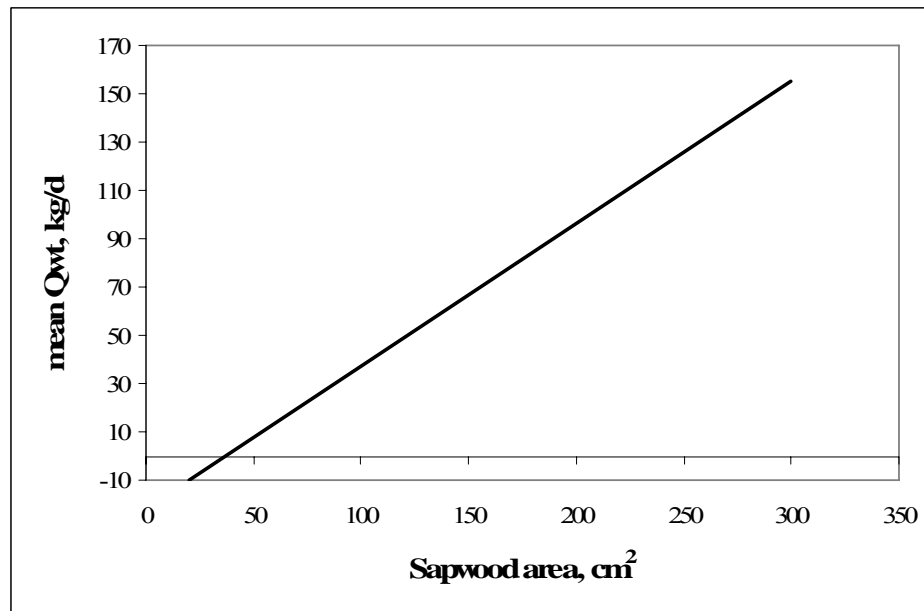
#### 2.1. *Acacia*

##### 2.1.1. The plantation

*Acacia mangium* Willd. is a fast-growing dicotyledonous tree, native to northern Australia and Southeast Asia [5], where it has been planted because of its high silvicultural performance and its ability to grow in degraded soils [6]. *Acacia mangium* is a well-known nitrogen-fixing tree, being used for land rehabilitation, particularly in eroded and nitrogen-deficient soils. As reported by Udarbe [7], the general pattern of growth is evaluated with Mean Annual Increment in the range of 10 - 29 m<sup>3</sup>/ha/yr. The basic density of 8 years old *Acacia mangium* plantation is 409 kg/m<sup>3</sup> [8] which yields an annual wood production of 4 to 12 tons/ha/year. Tree form is relatively good, but there is a tendency for persistent branching which affects wood quality if pruning is not done at an early age. Grown at an initial espacement of 3 m by 3 m the stand closes canopy in 2 to 3 years with the height at about 8 m. When grown for pulp logs on a rotation of 5 to 7 years, pruning and thinning are not necessary. Planting espacement may be reduced to 2.5 m by 2.5 m to take advantage of the fast initial growth. For saw log production the rotation is estimated to be between 12 to 15 years. *Acacia mangium* forms a symbiotic relationship with bacteria *Rhizobium* that fixes nitrogen to enhance the tree growth [9].

*Acacia mangium* is also a fast-transpiring tree species with high daily water consumption. A study on the water consumption of *Acacia mangium* in the Malaysian

state of Sabah, Borneo was reported by Cienciala [10] to vary from 10 to 130 kg/day depending on the sapwood area. The soil in the area of this study consisted of two main types and several intermediate forms. The two main types were Haplic Acrisol with clayish topsoil and Gleyic Podzol with sandy topsoil. Both soil types formed on frequently inter-layered dark shale, siltstones and sandstones. The air temperature was mostly between 22 and 32 °C and daily average around 26 °C. Air humidity fluctuated from 100 to less than 60 % and daily mean was mostly above 80 %. The mean daily transpiration (tree sap flow and tree transpiration can be considered equal on daily basis under non-limiting soil water condition) was a function of sapwood area as shown in Fig 1.



**Fig.1. Mean daily tree sap flow (Qwt) against the sapwood area of *Acacia mangium* tree [10].**

A study by Mackensen at PT.IHM (Perusahaan Terbatas Indonesia Hutani Manunggal) in East Kalimantan, Indonesia, showed that fertilization costs for *Eucalyptus deglupta* were generally higher than for *Acacia mangium*, i.e. 13 – 32 % and 9 – 16 % of overall investment costs, respectively [11]. Those range covered from low-, medium- to high-impact management which depended on nutrient losses due to burning of residual phytomass, leaching below root deep, erosion and harvesting techniques. The soil pH in this area was 4.5 - 4.8 and characterized by sand, silt and clay sediment.

A study by Cole [12] on the growth of twelve *Acacia* species on acid soil in Hawaii showed that *Acacia mangium* ranked the best in the growth rate among the others at both low and high soil fertility level. The species under the study were *A. mangium*, *A. crassicarpa*, *A. cincinnate*, *A. leiocalyx*, *A. leptocarpa*, *A. auriculiformis*, *A. orites*, *A. implexa*, *A. angustissima*, *A. polystachya*, and *A. koa*. The low fertility is defined as 14-14-14 plus micronutrient 143 kg/ha, while high fertility is 14-14-14 plus micronutrient 143 kg/ha, lime 8 Mg/ha, P 200 kg/ha, K 77 kg/ha.

*Acacia mangium* has been tested and found suitable for furniture making, general purpose industrial timber (not exposed to the weather), plywood and other panel products, pulp and paper and other related products, charcoal and wood pellets [7]. In recent years, this hardwood species has been recognized as an excellent source of short cellulose fibers for papermaking [13-16]. Extensive plantations are now growing in Southeast Asia, particularly Indonesia, supplying wood to the pulp and paper industry [17]. In Indonesia, *Acacia mangium* has become the dominating plantation pulpwood during the last ten years because *Eucalyptus* plantations have not been successful [8]. Many large scale pulp mills have been built in Indonesia based on *Acacia* plantations.

*Acacia* pulp is very interesting from a quality point of view and fairly similar to *Eucalyptus camadulensis* in terms of fiber morphology. Environmentally *Acacia* species are attractive because of their ability to fix nitrogen from air to improve soil fertility. *Acacia* species have been studied and used for pulpwood in many countries like Australia, Brazil, South Africa, Indonesia, Vietnam, and Malaysia [18]. The interesting properties of *Acacia mangium* fibers together with its easy adaptation to tropical humid climates [5] suggest that extensive *Acacia mangium* plantations soon will spread to other regions of the world such as South America, competing seriously with other tropical hardwood fiber sources.

In terms of species numbers *Acacia*, as currently defined, is the second largest genus in the *Pea* family, i.e. the *Leguminosae* (*Astragalus* is the largest) [19]. This genus contains in excess of 1380 species. This is a conservative number as it does not include many of the undescribed taxa (an estimated 100+ species in Australia and 20 species in America). *Acacias* grow in tropical, subtropical and warm temperate parts of the world and are found in the African region (144 species), Asia (89 species), the Americas (about 185 species) and the Australian region (993 species) [19].

As reported by FAO 2001, the global forest plantation distribution is described as follows: Asia-Pacific 61 %, North & Central America 17 %, South America 9 %, Europe 6 %, Africa 4 %, and Western Asia 3 % [20]. Forest in Asia-Pacific region covers approximately 699 million hectares. Of this area, some 113.2 million hectares are forest plantations, or 16 % of the total forest resource. This is considerably higher than the global average of plantations, which stand at around 5 %. The five countries that from Asia rank among the top ten plantation countries in the world: China (46.7 million

hectares), India (32.6 million hectares), Japan (10.7 million hectares), Indonesia (9.9 million hectares), and Thailand (4.9 million hectares). The distribution of species in Asia-Pacific: *Tectona* 5 %, *Acacia* 7 %, *Hevea* 8 %, *Eucalyptus* 10 %, Unspecified 13 %, *Pinus* 14 %, other coniferous 18 %, and other broad leaved 25 % [20].

*Acacia mangium* is a very promising hardwood plantation species which can grow in degraded soil and can be used for land rehabilitation due to its ability to fix the nitrogen. *Acacia mangium* growth rate is the fastest among the other acacia species in both low and high fertility. In term of overall investment costs, *Acacia mangium* is better than *Eucalyptus deglupta* [11]. *Acacia mangium* wood has been found suitable for many different applications, and thus becoming dominant plantation species.

### **2.1.2. The chemistry**

*Acacia mangium* wood, a prominent fast-growing plantation species used in the pulp and paper industry, has been studied to quantify and structurally characterize the lignin, xylan and cellulose by Pinto [21]. Table 1 summarized the general chemical composition of *Acacia mangium* wood.

The lignin content of *Acacia mangium* wood was shown to be 27.6 %, a value above the range of lignin contents typically found in hardwoods, 20 – 26 % [22], and was found similar to *Eucalyptus urograndis* (see Table 2) [23]. This can be explained, at least partially, by the presence of polyphenolic extractives (see Fig 2) that were not removed by ethanol/toluene extraction of wood [21].

**Table 1. Chemical composition of *Acacia mangium* wood [21]**

	Relative abundance, % dry wood <sup>a</sup>
Ashes	0.22
Extractives	
Ethanol/Toluene	4.46
Dichloromethane	1.32
Methanol/water	4.05
Lignin	
Klason lignin	27.1
Acid soluble lignin	0.54
Holocellulose	70.9
Cellulose (Kurschner-Hoffer)	46.5 <sup>b</sup>
Pentosans	13.3
Neutral monosaccharides <sup>c</sup>	
Rhamnose	0.3
Arabinose	0.2
Xylose	10.9
Mannose	1.0
Galactose	0.6
Glucose	48.0
Uronic acids	7.6

<sup>a</sup> Extractive-free wood, except for extractive content, <sup>b</sup> Corrected for pentosans content,

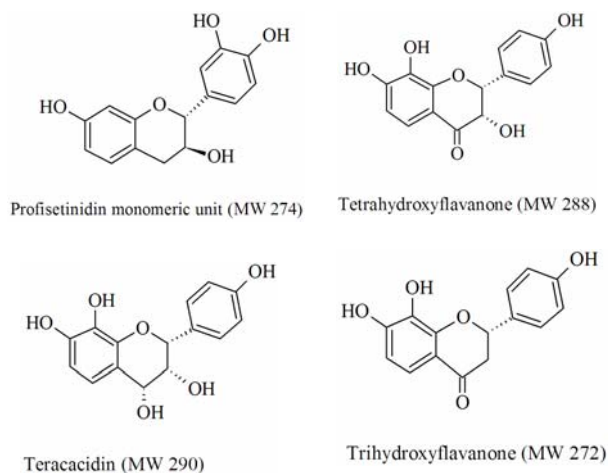
<sup>c</sup> Determined as anhydrous monosaccharide.

The high lignin/polyphenolic extractives content of *Acacia mangium* wood contributes to the high chemical consumption required to chemically delignify this wood and to the low pulp yield, when compared to those of other hardwoods [24] (see section 2.2). Hardwood lignin is a complex macromolecule composed of dehydropolymerized units derived from syringylpropane (S) guaiacylpropane (G), and p-hydrophenylpropane (H). The relative proportions of S, G, and H units and the nature and relative abundance of linkages between them are highly variable, influencing the reactivity of lignin during pulping and bleaching processes [25, 26]. The S/G/H proportion of several hardwoods and unbleached kraft pulp residual lignin is summarized in Fig 3 [23].

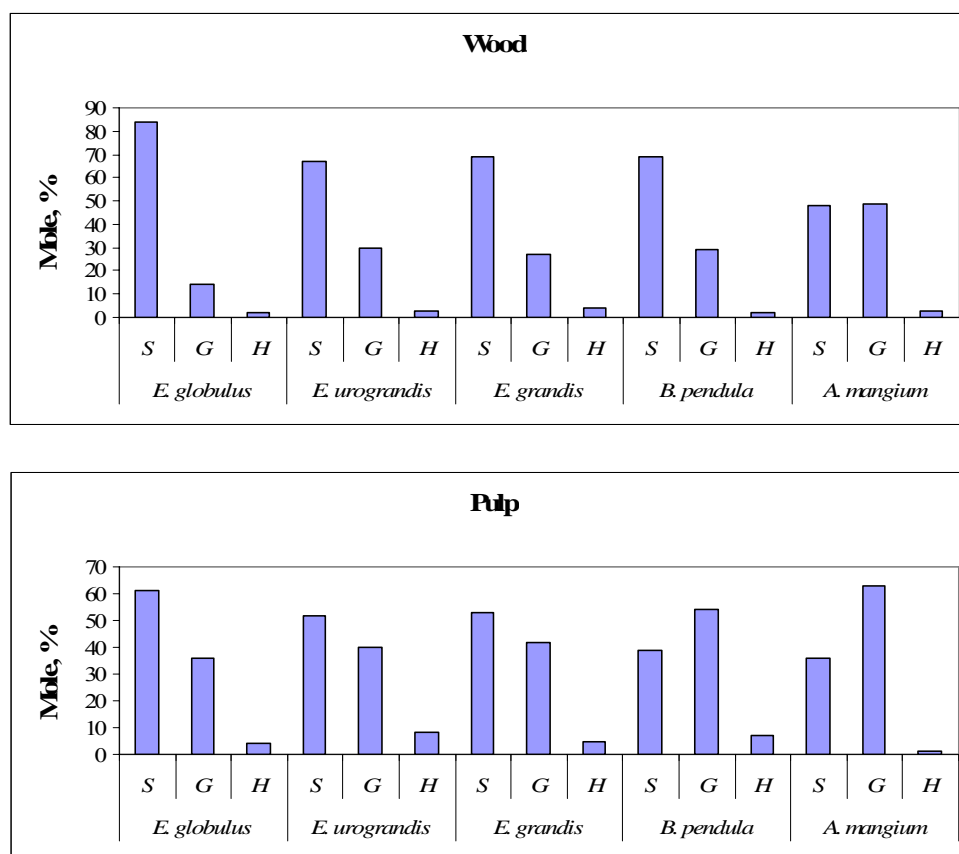
**Table 2. Compositions of hardwoods and unbleached kraft pulp [23]**

Species	<i>E. globulus</i>	<i>E. urograndis</i>	<i>E. grandis</i>	<i>B. pendula</i>	<i>A. mangium</i>
Wood composition, %					
Lignin (Klason)*	22.1	27.9	26.7	21.5	27.6
Glucomanan	53.4	52.1	50.9	44.5	51.6
Xylan	14.2	11.4	12.4	23.6	11.9
Rhamnose	0.3	0.2	0.3	0.8	0.3
Arabinose	0.4	0.4	0.4	0.7	0.2
Mannose	1.1	0.7	0.7	2.1	1.0
Galactomanan	1.5	1.2	1.0	0.8	0.6
Unbleached pulp composition, % (wood basis)					
Lignin (Klason)*	1.3	1.0	1.2	1.3	1.2
Glucomanan	45.0	40.2	40.5	38.8	42.2
Xylan	10.6	6.8	6.6	12.4	6.7
Rhamnose	0.1	0.2	0.2	0.1	0.2
Arabinose	0.1	0.1	0.0	0.1	0.0
Mannose	0.1	0.1	0.1	0.3	0.2
Galactomanan	0.4	0.1	0.1	0.1	0.0

\* Uncorrected for polyphenolics content



**Fig.2. Structure of polyphenols found in *Acacia mangium* [27]**



**Fig.3. Molar percentages of syringyl (S), guaiacyl (G), and p-hydroxyphenyl (H) units (determined by  $^{13}\text{C}$  NMR spectroscopy) in (top) wood and (bottom) pulp lignins [23]**



*Acacia mangium* had a highest surface coverage (24 %) of extractives compared to those of *Betula pendula*, *Eucalyptus globulus*, *Eucalyptus urograndis* and *Eucalyptus grandis* that had 10, 7, 6 and 5 %, respectively [28]. The main component of the extractive was saturated fatty acids (docosanoic, tetracosanoic, hexacosanoic and octacosanoic acids) that were very stable under the condition of ECF bleaching [29].

### 2.1.3. Fiber and sheet properties

Three bleached hardwood kraft pulps have been studied on the fiber and sheet properties by Mohlin [30] i.e. one *Acacia mangium* (Indonesia origin), and two *Eucalyptuses* of Brazillian (A) and Iberian (B) origin. The main difference between the *Acacia* and the *Eucalyptus* was that the *Acacia* had thinner fiber walls and fewer defects (kink) as shown in Table 3 and Table 4.

**Table 3. Fiber dimensions, fiber kink and fiber coarseness for unrefined bleached hardwood kraft pulps [30]**

Pulp	Fiber length, mm	Fiber width, $\mu\text{m}$	Fiber kink, #/fiber	Fiber coarseness, mg/m
<i>Acacia</i>	0.65	14.1	0.22	0.46
<sup>a</sup> <i>Eucalyptus</i> A	0.74	14.9	0.53	0.60
<sup>b</sup> <i>Eucalyptus</i> B	0.71	15.1	0.47	0.59

<sup>a</sup>*Eucalyptus* A: Brazillian origin, <sup>b</sup>*Eucalyptus* B: Iberian origin

**Table 4. Result of microscopy measurement of cross sectional dimensions of unrefined bleached hardwood kraft pulps [30]**

Pulp	Wall thickness, $\mu\text{m}$	Wall perimeter, $\mu\text{m}$	Lumen perimeter, $\mu\text{m}$	Wall area, $\mu\text{m}^2$
<i>Acacia</i>	2.0	38.5	23.0	53.7
<sup>a</sup> <i>Eucalyptus</i> A	2.7	39.4	18.0	70.4
<sup>b</sup> <i>Eucalyptus</i> B	2.5	38.9	19.1	66.5

<sup>a</sup>*Eucalyptus* A: Brazillian origin, <sup>b</sup>*Eucalyptus* B: Iberian origin

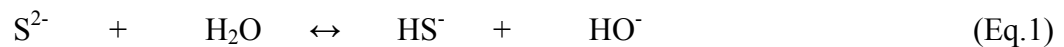
## 2.2. Kraft pulping

In 1879, Dahl, a German chemist, used sodium sulfate as a makeup chemical for soda pulping to regenerate NaOH; actually Na<sub>2</sub>S was formed and, unexpectedly, gave much faster delignification and stronger pulps, since shorter cooking times are used resulting in less carbohydrate degradation. This led to the kraft (or sulfate) process, which is now the dominant process. Although related work on the process had been done earlier, Dahl discovered the kraft chemical recovery process, which is perhaps more important than the kraft cooking process [31]. The first kraft mill went into operation in 1890 in Sweden because the German papermaking industry did not accept this new process. The process developed and grew quickly from 1915 to 1930, especially in the southern U.S. where the resinous pine species did not pulp well by the sulfite process with calcium base.

Kraft pulping is a chemical pulping method using sodium hydroxide and sodium sulfide at pH above 12, at 160-180 °C, corresponding to about 800 kPa steam pressure, for 0.5 - 3.0 hours to dissolve much of the lignin of wood fibers [31]. The disadvantages of kraft pulping are the difficulty with which the pulps are bleached compared to sulfite pulps, low yields due to carbohydrate losses, and sulfur in its reduced form provides emissions that are extremely odiferous. Important variables during kraft cooking are:

1. Wood species (though all species can be pulped) and chip geometry
2. Ratio of effective alkali to wood weight
3. Concentration of effective alkali and liquor:wood
4. Sulfidity
5. H-factor (which, in turn, is a function of cooking time and temperature)

In modern pulping chemistry weight units of NaOH are often replaced by molar units, e.g., moles of effective alkali per liter of solution or kilogram of wood. The charge of effective alkali (NaOH) applied is usually 4 - 5 moles or 16 - 20 % of wood [25]. The following equilibriums are involved in the aqueous solutions containing sodium sulfide and sodium hydroxide [25]:



The equilibrium constants for these reactions are [25]:

$$K1 = [HS^-] [HO^-] / [S^{2-}]$$

$$K2 = [H_2S] [HO^-] / [HS^-]$$

Since  $K1 \sim 10$  and  $K2 \sim 10^{-7}$ , the equilibrium in equation (1-2) strongly favors the presence of hydrogen sulfide ions and for all practical purposes, sulfide ions ( $S^{2-}$ ) can be considered to be absent. The concentration of hydrogen sulfide becomes significant below pH 8 and needs to be considered only in modified kraft pulping processes involving pretreatment at low pH.

*Acacia mangium* can be readily pulped by either the kraft or NSSC (Neutral Sulphite Semi-Chemical) process to produce good quality pulp for fine papers or packaging materials respectively [7]. Test of *Acacia mangium* cooking by CSIRO (Commonwealth Scientific and Industrial Research Organization) has shown that yields of screened pulp of over 50 % can be obtained by the kraft process and as high as 75 % by the neutral sulphite process [18]. Subsequent tests by CSIRO have shown that kraft pulping and papermaking properties of *Acacia mangium* compared very favorably with those of plantation-grown *Gmelina arborea* and *Eucalyptus deglupta* [7]. *Acacia dealbata* and *Acacia melanoxylon* were also reported to exhibit better kraft pulping performance than *Eucalyptus globulus* [71]. An added advantage is the higher basic density of *Acacia mangium* wood.

Due to chemical composition and structure of lignin and extractive (see section 2.1.2.), *Acacia mangium* required the most drastic pulping conditions to get a similar Kappa number and also consumed the most amount of chlorine dioxide during bleaching stages to get a similar brightness compared to those other four hardwoods as shown in Table 5 [23].

**Table 5. Kraft pulping conditions, <sup>a</sup> pulp yield, and ClO<sub>2</sub> consumption during bleaching by a chlorine dioxide based sequence (DEDED) <sup>b</sup> [23]**

Wood species	active alkali % Na <sub>2</sub> O/wood	unbleached pulp Kappa number	unbleached pulp yield, %/wood	ClO <sub>2</sub> consumption %/pulp
<i>E. globulus</i>	16	18.9	55.6	4.4
<i>E. urograndis</i>	20	18.4	49.6	5.3
<i>E. grandis</i>	19	16.1	50.6	5.4
<i>B. pendula</i>	18	18.5	49.8	7.2
<i>A. mangium</i>	24	16.0	51.1	7.4

<sup>a</sup>Kappa number 16-19

<sup>b</sup>Final brightness 90 %

A study by Malinen et al [8] on the cooking of different age of *Acacia mangium* from eastern Thailand showed that the yield decreased rapidly when age of wood increases as shown in Table 6. At Kappa number 20, the pulp yield dropped from 52 to 50 % and the pulp viscosity dropped from 1,200 to 1,000 ml/g along with increasing age.

**Table 6. Unbleached kraft pulp properties of *Acacia mangium* from eastern Thailand [8]**

Species age	Effective alkali, %	Kappa number	Screened yield, %	Viscosity, ml/g	HexA, meq/kg
4 year	16	24.6	53.5	1269	57.7
	18	18.2	51.4	1072	62.6
	19	18.2	52.7	1121	60.6
	20	16.5	51.3	955	47.8
	21	14.9	50.8	904	40.2
	22	17.1	50.9	927	43.4
	23	12.8	49.7	713	24.8
6 year	16	27.3	53.3	1264	64.5
	18	20.3	51.9	1096	64.6
	19	20.5	52.4	1212	68.1
	20	18.6	49.9	992	48.9
	21	16.7	50.1	965	46.8
	22	17.6	49.9	1059	51.0
	23	15.1	48.8	818	34.4
7 year	16	29.0	53.3	1274	57.0
	18	20.1	50.9	1058	60.4
	19	18.2	50.4	1035	58.3
	20	17.3	48.4	913	46.0
	22	18.6	48.2	883	39.0
	23	16.9	49.5	878	39.9
8 year	16	29.0	53.4	1218	-
	18	19.7	50.2	1029	-
	20	19.0	48.0	928	-
	22	16.3	47.5	784	-
	23	15.3	47.7	808	-

The kraft cooking condition was as follows: sulfidity 35 %, liquor to wood ratio 4, time from room temperature to 80 °C 15 minutes, cooking temperature 165 °C, time from 80 to 165 °C 60 minutes, time at 165 °C 80 minutes, and various effective alkali from 16 to 23 % as NaOH. *Acacia mangium* of seven and eight year old had clearly lower yield, probably because of heart rot in the wood as indicated by its high 1 % NaOH solubility, 8.2, 13.7, and 16.7 % for four, seven, and eight year old, respectively. The contents of hexenuronic acids (HexA) in unbleached kraft pulps dropped rapidly with lowering kappa number [8].

A pilot scale pulping study on seven year old *Acacia mangium* by Bahar et al [32] was performed. The pulps were bleached according to CEHH sequence. The results showed that optimum physical properties of bleached *Acacia mangium* pulp obtained at 15.0 % active alkali, 22.5 % sulfidity, 165 °C, and cooking time for 1.5 + 2.0 hours. The cooking results were shown in Table 7.

A kraft cooking study on three different *Acacia* species of six and nine year old was performed by Guo [33] and found that *Acacias* were easily pulped using the conventional kraft process with acceptable pulp yields, i.e. 50 % total yield with Kappa number of 20. The kraft cooking condition was as follows: active alkali 15.0 % (as Na<sub>2</sub>O of oven dry chip), wood to liquor ratio of 1:4, sulfidity 25.0 %, maximum temperature 170 °C, and time at temperature 50 minutes. The physical properties of unbleached kraft pulp were show in Table 8. In general, the physical properties of six year old *Acacia* were better than nine year old *Acacia*.

**Table 7. Pilot scale kraft cooking results of *Acacia mangium* [32]**

Active alkali, %	Max. temp., °C	Screened yield, %	Kappa number
17.0	170	41.2	11.3
15.0	170	48.3	14.4
13.0	170	44.5	17.6
17.0	165	47.5	12.7
15.0	165	42.1	15.3
13.0	165	41.3	21.0

Note: liquor to wood ratio 4, time to reach maximum temperature 1.5 hours, time at maximum temperature 2.0 hours, sulfidity 22.5 %

**Table 8. Physical properties of unbleached kraft pulp of three *Acacia* species [33]**

Species	Age	Tensile Index	Burst Index	Tear Index
	(year)	(Nm/g)	(kPa.m <sup>2</sup> /g)	(mN.m <sup>2</sup> /g)
<i>A. mangium</i>	6	61.1	6.4	10.7
	9	63.4	6.0	8.8
<i>A. crassicarpa</i>	6	58.1	6.1	9.8
	9	62.2	5.8	8.7
<i>A. auriculiformis</i>	6	61.8	6.5	11.2
	9	62.7	6.2	10.5



### 2.3. Oxygen delignification

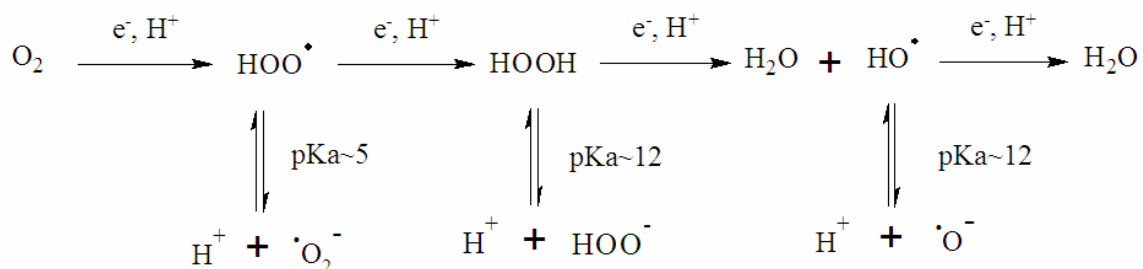
Oxygen delignification is a well established technique in industrial application for delignifying unbleached pulps during the last decade [34]. The main benefit of this process is environmental. Currently most systems installed are based on the medium consistency (10 - 14 %) process. The oxygen delignification reaction is usually conducted for 15 to 90 minutes under pressure of 400 to 1000 kPa and at the temperature of 90 – 110 °C [4, 34]. Due to the severe carbohydrates degradation at higher degree of delignification, the delignification degree for conventional kraft pulp is normally in the range of 35 – 50 % [34]. The typical conditions of oxygen delignification for Acacia and mixed hardwood (MHW) are shown in Table 9.

**Table 9. Commercial oxygen delignification operating conditions for *Acacia* and mixed tropical hardwood (MHW) [35]**

	<i>Acacia</i>	MHW
Temperature, °C	87-90	87-90
O <sub>2</sub> charge, kg/ADT	14-17	14-17
NaOH charge, kg/ADT	14-16	16-18
pH	10.8-11.0	10.8-11.0
Consistency, %	12	12
Reaction time, minutes	120	120
Starting Kappa number	12 – 13	13 - 14

Oxygen has a strong tendency to oxidize organic substances under alkaline conditions simultaneously resulting in its stepwise reduction to water by one electron transfer processes [34] as shown in Fig 4. This reaction yields different transients

including hydroperoxyl radicals ( $\text{HOO}^\bullet$ ), hydroperoxide anions ( $\text{HOO}^-$ ), hydroxyl radicals ( $\text{HO}^\bullet$ ), and their anions ( $^\bullet\text{O}^-$ ) [34].



**Fig.4. Formation of reactive intermediates during the stepwise reduction of oxygen to water [34]**

Previous works by Yang et al [36] showed that the level of magnesium was very important to obtain better oxygen delignification selectivity. This report also showed that hardwood kraft pulp contained less magnesium than softwood kraft pulp. On the other hand, hardwood kraft pulp contained more iron and copper than softwood kraft pulp. Iron and copper are harmful for the maintenance of pulp viscosity, thus the addition of magnesium in the hardwood oxygen delignification is more important than in softwood oxygen delignification. It was also indicated in this report that the native magnesium in pulp played a similar role to the added magnesium sulfate during oxygen delignification.

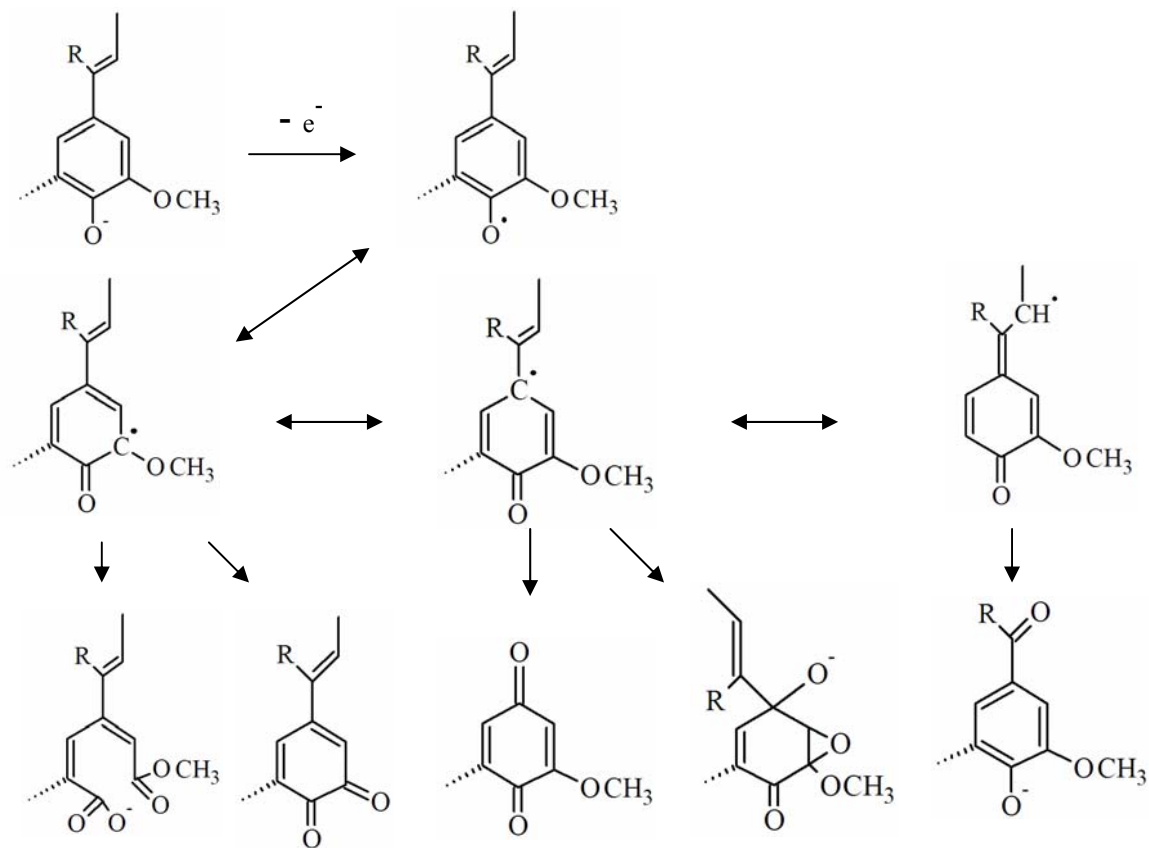
Liden et al [69] reported that  $\text{Mg}^{2+}$  and  $\text{Mn}^{2+}$  can form solid precipitate  $(\text{Mg}, \text{Mn})(\text{OH})_2$  in aqueous solution at certain level of  $\text{Mg}^{2+}$  ion. In this solid state, manganese is redox-stabilized even in highly alkaline environment. This study reported that if the proportion of magnesium in the solid phase is increased by adding more magnesium prior to alkali addition, the concentration of soluble  $\text{Mn}^{2+}$  will be appreciably

decreased. This report suggested that the molar amount of magnesium present during alkaline oxygen delignification should be 20 to 30 times above that of manganese to be effective.

### **2.3.1. Lignin reactions**

Stefan et al [37] reported the impact of the cooking process on oxygen delignification. This study proved that the prehistory of the pulps was a very important factor in determining the response to oxygen delignification. In this study, sulphite pulps showed the greatest yield loss over the oxygen delignification, compared to those of kraft and prehydrolysis kraft pulps. It was also shown that degree of delgnification was not due to different amounts of hexenuronic acid. It was likely that lignin-carbohydrate complexes (LCC) played a very important role in limiting the reaction rate of oxygen delignification. LCC was probably native, and not formed during cooking [37].

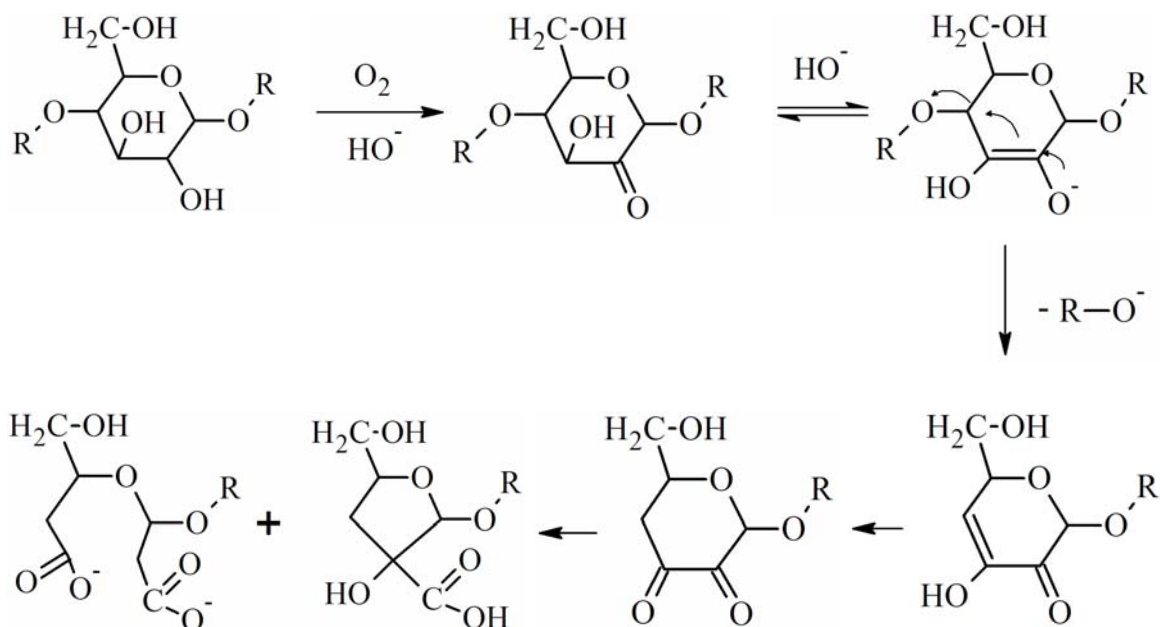
Yang et al [38] reported that the main functional groups contributing to the oxidation of hardwood kraft residual lignin were syringyl, C5 noncondensed guaiacyl units, and stilbene phenolic structures. Shin et al [39] also reported that phenolic hydroxyl units were the most reactive sites of residual lignin under oxygen delignification. Thus the overall performance of oxygen delignification of karft pulp was related to the content and condensed structures of the phenolic units in the residual pulp lignin. Fig 5 illustrates the examples of the primary structures formed during oxidative reactions of phenolic lignin structures [34].



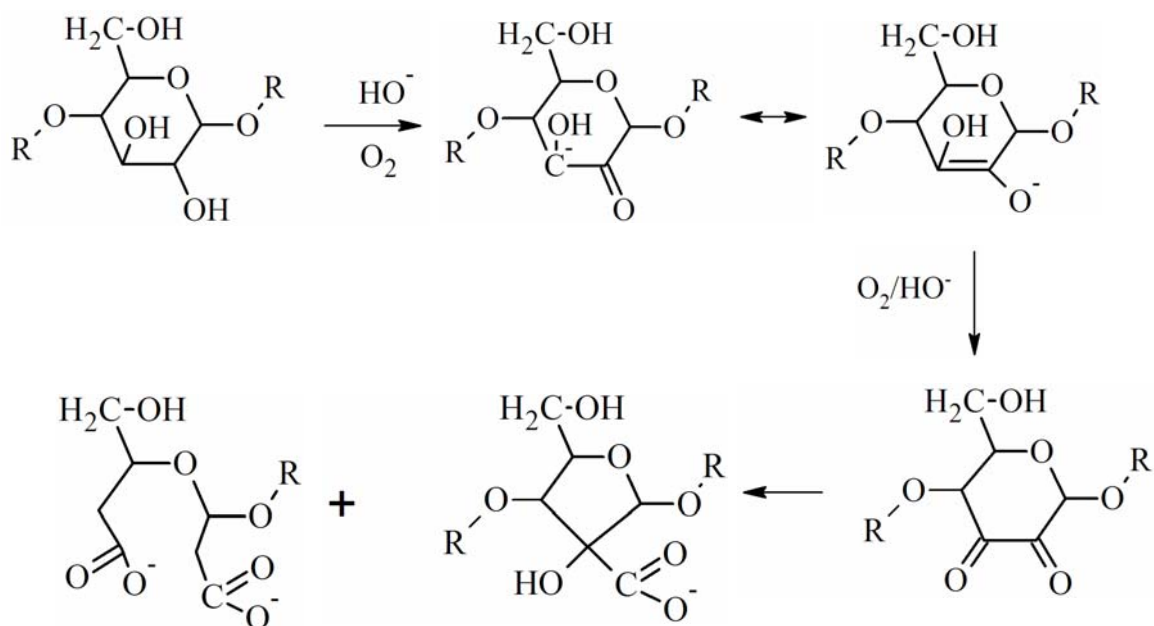
**Fig.5. Examples of the oxidative reactions of phenolic lignin structures during oxygen delignification [34]**

### **2.3.2. Carbohydrate reactions**

The reactions that degrade carbohydrate could be divided into two categories: (1) the cleavage of glycosidic bonds at any point along the polysaccharide chain and (2) the peeling reaction, by which end group units of the chain are successively removed as shown in Fig 6 and Fig 7 [34].



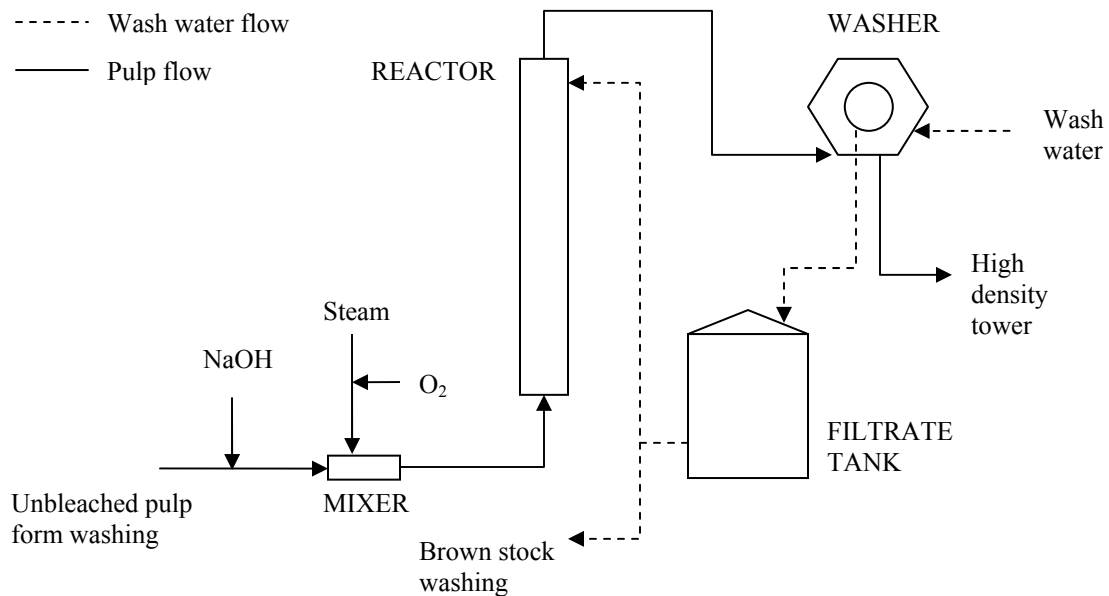
**Fig.6. Cleavage of glycosidic bonds in polysaccharide chains during oxygen delignification [34]**



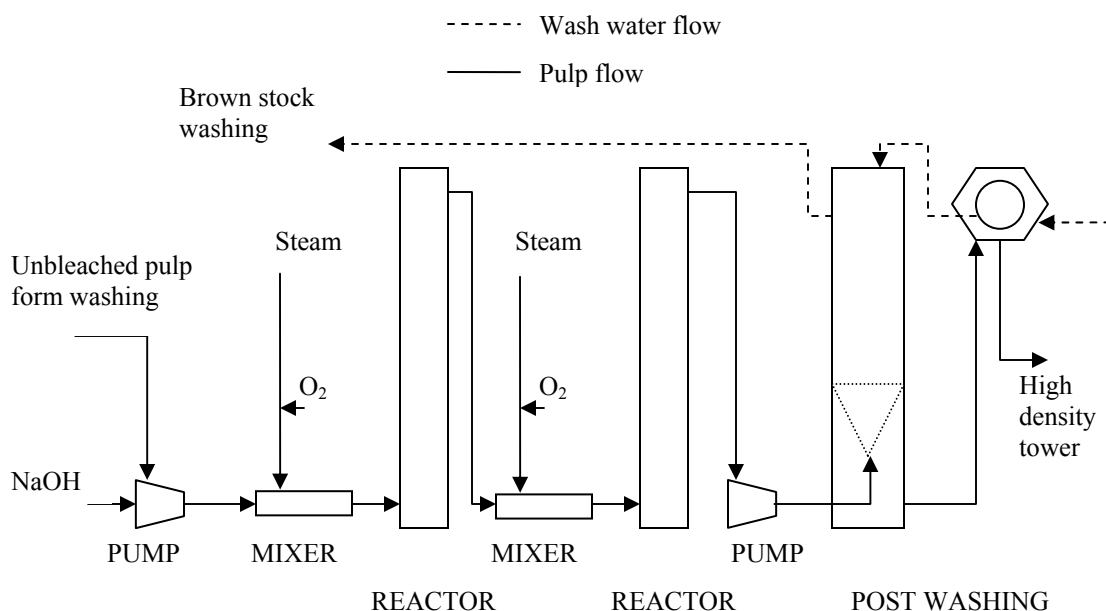
**Fig.7. Oxidation of ketol structures along polysaccharide chains during oxygen delignification [34]**

### 2.3.3. Process Fundamental

The most common single stage industrial oxygen delignification operates at medium consistency (10 – 14 %) with delignification in the range of 30 – 50 % [34] (see Fig 8). The new applications for oxygen delignification involve two oxygen delignification reactors as summarized in Fig 9. These two stages oxygen delignification operation can achieve delignification in the range of 60 – 70 % [34, 40]. An optimization study on two stage oxygen delignification process has been reported by Tran [41]. This report suggested that the temperature of the second reactor should be higher than the first reactor and the oxygen charge split into each reactor. One of the most important factors in the enhanced oxygen delignification is an effective mixing during oxygen reaction.



**Fig.8. Single stage medium consistency oxygen delignification (Ahlstrom) [34]**



**Fig.9. Two stages medium consistency oxygen delignification (Kvaerner) [34]**

An effective washing of the unbleached pulp prior to oxygen delignification reaction is needed for increasing the effect of delignification [34, 42, 43]. However the carry-over of black liquor was reported to hinder delignification only in the first rate period (10 minutes) but had little effect on the second rate period (60 minutes) [43]. The important parameters used to control and optimize an oxygen delignification in a commercial industrial setting are temperature, reaction time, chemical rate, pH, reactor pressure and pulp consistency [34].

### 2.3.3.1. Alkali charge

A study of oxygen bleachability on a hardwood kraft pulps with different kappa numbers has been reported by Yang et al [38]. The results suggested that oxygen bleachability was dependent on the alkali charge and the incoming kappa number of brownstock hardwood kraft pulp. The results indicated that oxygen bleachability decreased as the alkali charge was increased. Table 10 summarized the properties of hardwood brownstock kraft pulp and oxygen delignified pulps.

**Table 10. Physical properties of hardwood brownstock kraft pulp and oxygen delignified pulps [38]**

Sample		1	2	3
Brownstock	Kappa number	29.0	22.9	13.6
	Viscosity, cP	27.8	28.0	24.8
O-delignified <sup>a</sup> (1 % NaOH)	Kappa number	22.4	15.8	8.3
	O-bleachability <sup>b</sup>	6.6	7.1	5.3
	Viscosity, cP	20.3	19.7	16.8
O-delignified <sup>a</sup> (4 % NaOH)	Kappa number	10.8	9.1	7.0
	O-bleachability <sup>b</sup>	4.6	3.4	1.6
	Viscosity, cP	15.0	15.0	12.1

<sup>a</sup>Reaction temperature at 100 °C for 1 h, 10 % consistency, MgSO<sub>4</sub> solution added at 0.05 % w/w. <sup>b</sup>O-bleachability was calculated as  $\Delta\text{kappa}/\text{NaOH charge}$



Nenkova et al [44] reported that a larger alkali addition in oxygen delignification of hardwood kraft pulps resulted in larger cellulose degradation with a small kappa number reduction. This study suggested that a high alkali addition reduced the oxygen delignification selectivity and leads to lower viscosity. Table 11 summarized the effect of alkali addition in oxygen delignification of hardwood kraft pulp on the kappa number and viscosity of oxygen delignified pulps. These results were consistent with previous report by Yang et al [38] as shown in Table 10. This result showed that pulp carbohydrates were significantly degraded when the alkali charge was increased, as the pulp viscosity decreased.

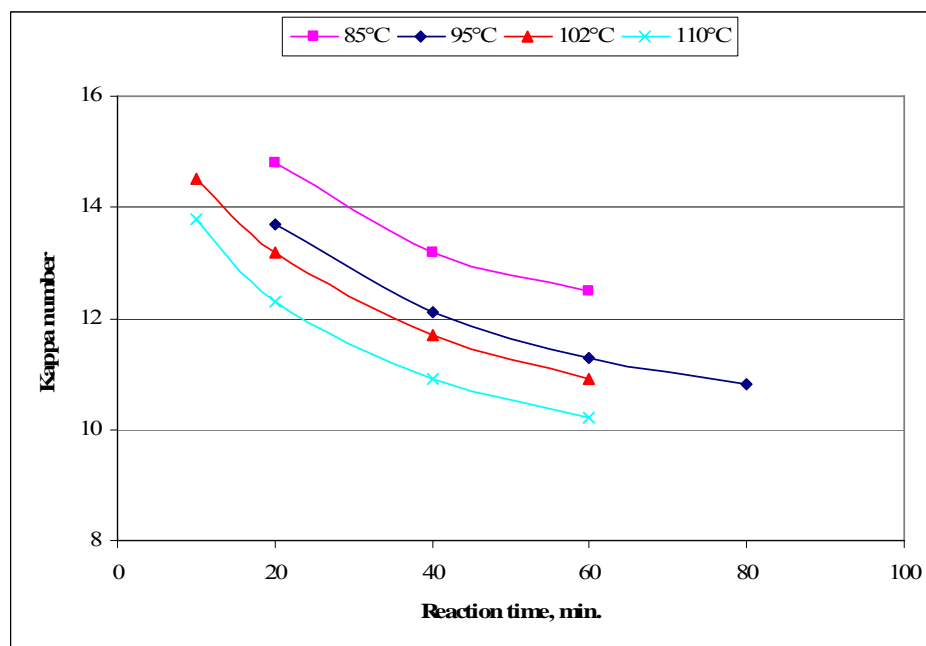
**Table 11. Effect of alkali addition in oxygen delignification of hardwood kraft pulp on kappa number and viscosity of oxygen delignified\* pulps [44]**

NaOH addition, %	Kappa number	Viscosity, dm <sup>3</sup> /kg
2.0	10.7	818
2.5	10.5	787
3.0	10.3	755
3.5	10.0	715

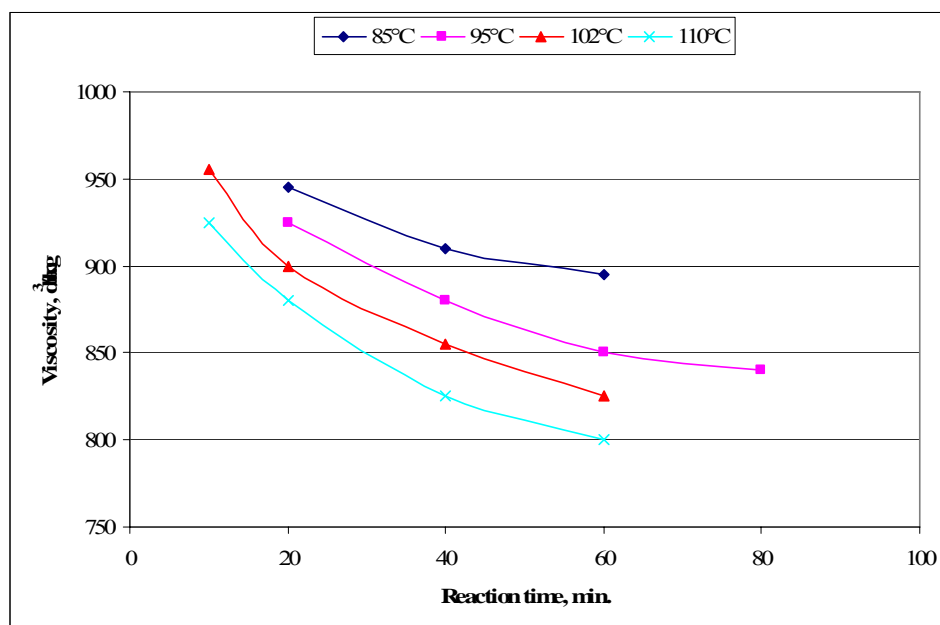
\*Oxygen delignification was performed at 102 °C for 60 min, consistency 10 %, and oxygen pressure 0.6 MPa

### 2.3.3.2. Time and temperature

The effect of reaction time and temperature on oxygen delignification of hardwood kraft pulp was reported by Nenkova et al [44]. The kappa number was decreasing as the reaction time prolonged and the temperature increased as shown in Fig 10. The effect of increasing temperature from 95 to 110 °C is the same as that of doubling the reaction time. The viscosity loss behavior due to increasing reaction time and temperature was reported similar to that of kappa number reduction as shown in Fig 11. It was also reported that an increase in the reaction temperature can considerably accelerate the bleaching process without affecting the pulp strength properties as shown in Table 12.



**Fig.10. Effect of reaction time and temperature on Kappa number of oxygen delignified hardwood kraft pulp [44]. Oxygen delignification was performed at 10 % consistency, 2 % alkali charge and an oxygen pressure of 0.6 MPa**



**Fig.11. Effect of reaction time and temperature on viscosity of oxygen delignified hardwood kraft pulp [44]. Oxygen delignification was performed at 10 % consistency, 2 % alkali charge and an oxygen pressure of 0.6 MPa**

**Table 12. Effect of reaction temperature on the oxygen delignified\* hardwood kraft pulp strength properties [44]**

Temperature, °C	Breaking length, m	Tear index, mN.m <sup>2</sup> /g
85	8800	7.6
95	8850	7.7
102	8750	8.0
110	8750	8.1

\*Oxygen delignification was performed at 10 % consistency, 2 % alkali charge, reaction time of 60 minutes, and oxygen pressure of 0.6 MPa

### 2.3.3.3. Consistency

The effect of consistency of oxygen delignification on hardwood kraft pulp was reported to be not significant in Kappa number reduction and brightness improvement [44]. Table 13 summarized the effect of oxygen delignification consistency of 8 to 14 % on the pulp properties. By increasing the consistency from 8 to 14 %, Kappa number increased by 0.2 points, while brightness decreased by 0.6 points.

**Table 13. Effect of consistency of oxygen delignification\* on hardwood kraft pulp properties [44]**

Consistency, %	Kappa number	Brightness, %ISO
8.0	10.5	49.3
10.0	10.5	49.5
12.0	10.7	48.7
14.0	10.7	48.7

\*Oxygen delignification was performed at 102 °C, 2.5 % alkali charge, reaction time of 60 minutes, and oxygen pressure of 0.6 MPa

### 2.3.3.4. Oxygen pressure

The effect of pressure of oxygen delignification on hardwood kraft pulp was studied by Nenkova et al [44]. It was reported that higher oxygen pressure increased the bleaching process only slightly. This was indicated by Kappa number reduction of 0.5

points and viscosity loss 29 dm<sup>3</sup>/kg. There was also no significant pulp strength reduction as shown in Table 14.

**Table 14. Effect of oxygen delignification\* pressure on hardwood kraft pulp properties [44]**

Pressure	Kappa number	Viscosity	Breaking length	Tear index
MPa		dm <sup>3</sup> /kg	m	mN.m <sup>2</sup> /g
0.3	11.0	816	8500	7.5
0.4	10.9	809	8510	7.5
0.5	10.7	799	8520	7.5
0.6	10.5	787	8520	7.5

\*Oxygen delignification was performed at 102 °C, 2.5 % alkali charge, reaction time of 60 minutes, and pulp consistency of 10 %.

#### **2.3.3.5. Mechanical processing**

Oxygen delignification systems are often operated at medium consistency (MC) using MC pumps and mixers [34, 40]. One of the most significant factors to enhance oxygen delignification, as other kinds of bleaching process, is an effective mixing of the chemicals with corresponding pulp [34]. However, as industrial MC pumps and mixers produce excessive floc disruption in intense shear zones, they can also physically damage the pulp fibers. Thus MC pumps and mixers can create fiber deformation [45, 46].

Two types of fiber deformation generally occur: fiber curl and fiber wall dislocations or micro-compressions [46, 47]. The effect of medium consistency laboratory mixer on the value of fiber curl and fiber wall dislocation of *Pine radiata* bleached kraft pulp was reported by Ellis et al [46] as shown in Table 15. Fiber curl influenced the measured zero span tensile index of unrefined pulp as curled fibers are less able to transmit load and contribute to tensile strength [47]. Fiber curl is a reversible effect as it can be removed partially by appropriate pulp refining [48, 71].

**Table 15. Fiber curl and wall dislocation of *Pine radiata* bleached kraft pulp after treatment by medium consistency laboratory mixer [46]**

Mixing time, seconds	Curl Index	Wall Dislocation, #/mm
0	0.22	40.1
1	0.30	43.6
2	0.33	46.5
5	0.30	48.4
10	0.32	-

## **CHAPTER 3**

### **EXPERIMENTAL**

#### **3.1. Chemicals**

All chemicals used in this study were purchased from VWR and Fisher as analytical grade and used as received.

#### **3.2. Pre O<sub>2</sub> *Acacia mangium* kraft pulp**

The pre O<sub>2</sub> *Acacia mangium* kraft pulp was obtained from APRIL's (Asia Pacific Resources Holdings Limited) mill in Sumatra, Indonesia. The post O<sub>2</sub> *Acacia mangium* kraft pulp was also obtained from the same mill for reference. The pulp was kept in the cold room in a wet form (a consistency of 26 % and pH 10.8). The pre O<sub>2</sub> and post O<sub>2</sub> *Acacia mangium* kraft pulp properties are summarized in Table 16.

The metal profile was analyzed by Inductively Coupled Plasma Emission Spectroscopy as shown in Table 17.

**Table 16. Pre O<sub>2</sub> and post O<sub>2</sub> *Acacia mangium* kraft pulp properties**

	Parameter	Unit	Pre O <sub>2</sub>	Post O <sub>2</sub>
1	Kappa number		9.6	4.9
2	Viscosity	cP	23.5	12.4
3	HexA	μmol/g	29.6	23.4
4	Total charge	μeq/g	77.1	64.3
5	DCM extractive	%	1.08	0.49
6	Alpha-cellulose	%	35.2	34.4
7	Gamma-cellulose	%	8.3	8.2
8	Beta-cellulose	%	56.4	57.5
9	Dry z-span	kPa	307	290
10	Wet z-span	kPa	269	248
11	Tear Index	mN.m <sup>2</sup> /g	6.83	8.09
12	Burst Index	kPa.m <sup>2</sup> /g	1.96	2.31
13	Tensile Index	Nm/g	43.7	43.0
14	Brightness	%	41.7	57.9
15	Fines	%	0.66	0.79
16	Fiber length	mm	0.69	0.66
17	Fiber curl		0.072	0.076
18	Kink index	1/mm	1.23	1.37

**Table 17. Metal profile of pre O<sub>2</sub> *Acacia mangium* kraft pulp**

Element	Concentration
	mg/kg
K	1,268
Na	14,300
Ca	494
Mg	71.4
Mn	3.5
Cu	1.1
Fe	7.9
Ni	0.5



### 3.3. Oxygen delignification

The oxygen delignification studies were performed in a laboratory inclined Parr reactor model 4842 (Parr Instrument Company, see Fig 12) at constant oxygen pressure (1,034 kPa) and pulp consistency (12 %). The mixer speed was also kept constant at 20 rpm. The Parr reactor was warmed up to at least 20 °C below the set point. The reactor was then charged with a pulp of an equal amount to 60.00 grams oven dry pulp, the desired amount of NaOH 1.00 N, and de-ionized water so that the final pulp consistency of 12 % was reached. The reactor was secured while heating up continued. The cooling water must run during the reaction. The oxygen pressure (1,034 kPa) was applied after the temperature reached the set point and the timer was started at the same time. When the desired time was reached, 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. A portion of the pulp was used to make a TAPPI hand sheet and the remaining pulp was air dried. For the safety, the side shield protector must be in place during the reaction. The process conditions of oxygen delignification reaction are following the Table 18.

**Table 18. Oxygen delignification experimental conditions**

	a			b			c			d		
Sample code	1	2	3	4	5	6	7	8	9	10	11	12
Reaction time, min	60	90	120	90	90	90	90	90	90	90	90	90
Temperature, °C	90	90	90	90	90	90	85	90	95	90	90	90
NaOH charge, g/kg OD pulp	16.67	16.67	16.67	16.67	20.00	23.33	16.67	16.67	16.67	20.00	20.00	20.00
O <sub>2</sub> pressure, kPa	1,034	1,034	1,034	1,034	1,034	1,034	1,034	1,034	1,034	1,034	1,034	1,034
Consistency, %	12	12	12	12	12	12	12	12	12	12	12	12
Quantum mixer time, sec	0	0	0	0	0	0	0	0	0	5	10	15

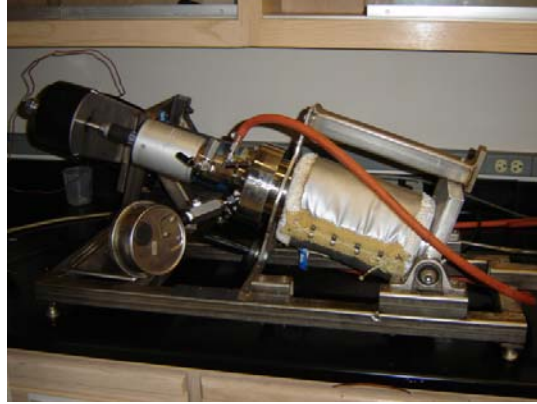
Another series of oxygen delignification were performed to study what is the most pronounced process condition to affect the strength loss on mechanically pretreated pulp. The experimental conditions of oxygen delignification are described in Table 19.

**Table 19. Oxygen delignification experimental condition for Yates' algorithm analysis [68]**

Experiment number	y1	y2	y3	y4	y5	y6	y7	y8
Reaction time, min	60	120	60	120	60	120	60	120
Temperature, °C	70	70	100	100	70	70	100	100
NaOH charge, g/kg OD pulp	10.0	10.0	10.0	10.0	30.0	30.0	30.0	30.0
O <sub>2</sub> pressure, kPa	1,034	1,034	1,034	1,034	1,034	1,034	1,034	1,034
Consistency, %	12	12	12	12	12	12	12	12
Quantum mixer time, sec	15	15	15	15	15	15	15	15

### 3.4. Mechanical pretreatment

A laboratory Quantum mixer was used to simulate the mechanical pretreatment in this study. The consistency was set constant to 10 % and the rotation speed to 2200 rpm. A 10 % consistency pulp of an equal amount to 100.00 grams oven dry pulp was evenly placed in the Quantum mixer chamber and the top of the mixer was then securely locked. The motor timer was set to the desired time at 2200 rpm, and the pulp sample was collected upon completion. For the safety reason, the electric source was shut off during loading and unloading the sample. The laboratory Quantum mixer is shown in Fig 13.



**Fig.12. Laboratory inclined Parr reactor**



**Fig.13. Laboratory Quantum mixer**



**Fig.14. Sheet preparation equipment**

### **3.5. Hand sheet making**

All hand sheets were made according to T205 [49] and restraint-dried in a brass ring at TAPPI standard conditions,  $23.0 \pm 1.0$  °C,  $50.0 \pm 2.0$  % relative humidity, in accordance with T402 [50] prior to physical testing. The sheet preparation equipment is shown in Fig 14.

### **3.6. Pulp testing**

#### **3.6.1. Physical properties**

The physical properties of paper were tested according to TAPPI test method as follows:

Dry zero span tensile strength	T231 [51]
Wet zero span tensile strength	T273 [52]
Tensile strength	T494 [53]
Tearing resistance	T414 [54]
Bursting strength	T403 [55]
Brightness	ISO 2469 [56]

The error analysis is summarized in Table 20 (see page 46).

#### **3.6.2. Fiber Quality Analyzer**

Fiber length, fines, curl and kink were measured with Fiber Quality Analyzer (FQA), OpTest Equipment [57]. FQA uses uniform, diffuse light at an infrared wavelength to illuminate an 80 mm<sup>2</sup> viewing area. Since fibrous materials contain crystalline cellulose, the light can be polarized. A charge coupled device (CCD) camera is used to capture the light that has been polarized, thus capturing images of the fibers.

The fiber contour length, percent fines, and curl are simultaneously analyzed. The curl index is based on a ratio of the contour length to the projected length as indicated by Eq.3 [57].

$$\text{Curl Index} = (l/L) - 1 \quad (\text{Eq.3})$$

Where  $l$  = Contour length, mm

$L$  = Projected length, mm

The error analysis is summarized in Table 20 (see page 46).

### 3.6.3. Kappa number

Kappa number was tested according to T236 [58]. Due to limited pulp samples, a micro Kappa number was used in this experiment. An air-dried sample was weighed to an equal of 2.50 g of oven-dried test specimens and was mixed with 25.00 mL of 4.00 N  $\text{H}_2\text{SO}_4$  and 25.00 mL of 0.10 N  $\text{KMnO}_4$  solutions. The reaction was allowed to proceed for 10 minutes, and then treated with 5.00 mL of 1.00 N KI to stop the reaction. The reaction temperature was recorded at 5 minutes intervals. The reaction was titrated with standard solution 0.10 N  $\text{Na}_2\text{S}_2\text{O}_3$  with starch indicator addition at nearly end of the reaction. The Kappa number was calculated as follows [58]:

$$K = \frac{p f}{w} \left[ 1 + 0.013 (25 - t) \right] \quad (\text{Eq.4})$$

Where K = Kappa number

p = percentage of  $\text{KMnO}_4$  consumed, %

f = correction factor for different of  $\text{KMnO}_4$  consumed

t = reaction temperature,  $^{\circ}\text{C}$

w = amount of moisture-free pulp in the specimen, g

The error analysis is summarized in Table 20 (see page 46).

#### **3.6.4. Viscosity**

Viscosity was tested according to T230 [59]. An air-dried sample was weighed to an equal of 0.25 g of oven-dried test specimen to the nearest  $\pm 0.0001$  g and placed in a bottle. A 25 mL of de-ionized water and 8 to 10 beads were added into bottle and shake for at least 20 minutes until the fibers were completely dispersed. A 25 mL of CED (Cupri Ethylene Diamine) solution was added into the bottle and shake for at least 30 minutes until the fibers were completely dissolved. Viscosity tubes of size number 150 were used in this experiment. The sample solution was transferred into the viscosity tube and the viscosity tube was placed in a water bath at constant temperature  $25.0 \pm 0.1$   $^{\circ}\text{C}$ . The time required for the sample solution to flow from the upper mark to the lower mark of the viscosity tube was recorded and the viscosity was calculated as follows [59]:

$$V = C t d \quad (\text{Eq.5})$$

Where V = viscosity, cP

C = viscometer constant

t = efflux time, s

d = density of the pulp solution, g/cm<sup>3</sup> (=1.052)

The error analysis is summarized in Table 20 (see page 46).

### **3.6.5. Extractives**

Extractives content was tested according to T204 [60]. An air-dried sample was weighed to an equal of about 5 g of oven-dried sample to the nearest 0.1 mg. The sample was placed in the extraction thimble and the extraction thimble was positioned in the Soxhlet apparatus. Dichloromethane was used as a solvent in this experiment. The extraction was allowed to proceed for 5 hours. At the end of the extraction, dichloromethane was recovered and the extractives were transferred to an aluminum pan then evaporated in the hood prior to oven drying. A percent of extractives to the dry pulp sample was calculated. The error analysis is summarized in Table 20 (see page 46).

### **3.6.6. Celluloses**



The alpha-, beta-, and gamma- celluloses were tested according to T203 [61]. An air-dried sample was weighed to an equal of 1.5000 g of oven-dried sample to the nearest 0.1 mg. The pulp sample was extracted consecutively with 17.5 % and 9.45 % NaOH solutions at 25 °C. The soluble fraction, consisting of beta- and gamma-celluloses, is determined volumetrically by oxidation with potassium dichromate, and the alpha-cellulose, as an insoluble fraction, is derived by difference. The error analysis is summarized in Table 20 (see page 46).

### **3.6.7. Hexenuronic acids**

Hexenuronic acid groups in pulp were determined with published method by Chai [62]. A 0.0500 g of air-dried pulp hand sheet with known moisture was weighed to the nearest 0.1 mg. The pulp sample was placed in the 20.00 mL vial containing 10 mL of hydrolysis solutions. The hydrolysis solution consisted of 22.00 mmol/L (0.60 %) mercuric chloride and 0.70 % sodium acetate. The vial was sealed and thoroughly shaken to get good mixing. The vial was then heated for 30 minutes in water bath at 60 - 70 °C. After the solution was cooled to room temperature, the UV absorption of filtered solution was measured in a 10 mm path length silica cell using a Perkin Elmer UV/VIS/NIR Spectrophotometer Lambda 900 at the wavelength of 260 and 290 nm. The hexenuronic acid content in pulp is calculated as follows [62]:

$$C_{\text{HexA}} = 0.287 \times (A_{260} - 1.2 \times A_{290}) \times V / w \quad (\text{Eq.6})$$

Where  $C_{\text{HexA}}$  = Hexenuronic acid concentration, mol/g

$A_{260}$  = Absorption intensity at 260 nm wavelength

$A_{290}$  = Absorption intensity at 290 nm wavelength

$V$  = volume of hydrolysis solution, mL

$W$  = oven-dried weight of sample, g

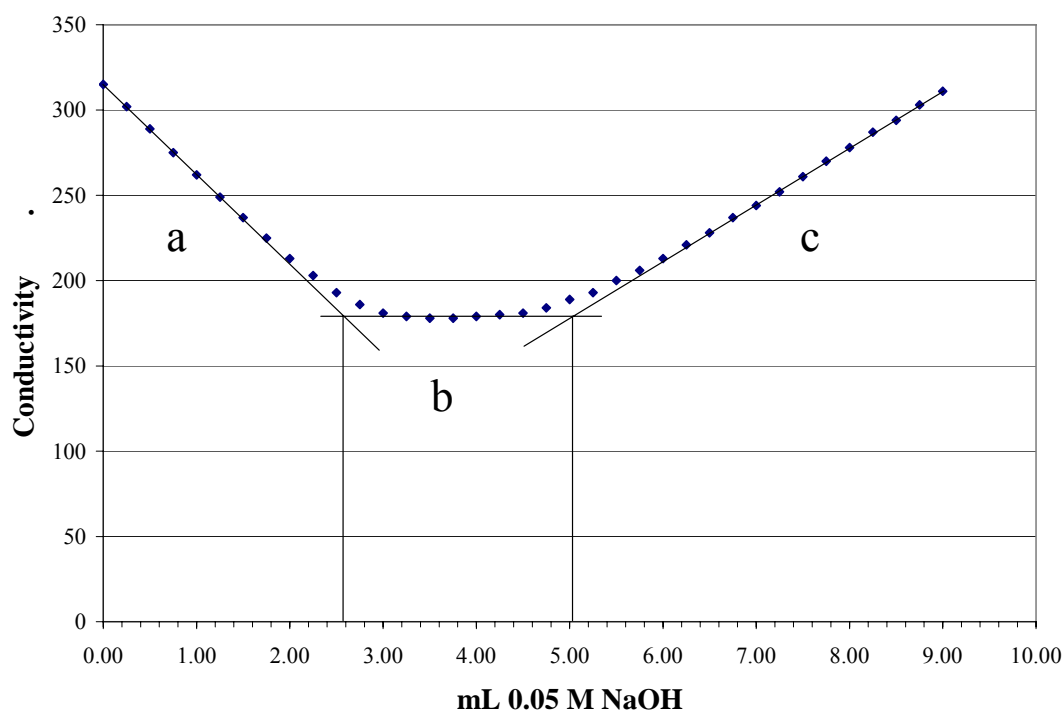
The error analysis is summarized in Table 20 (see page 46).

### **3.6.8. Total charge**

Total charge was measured by using conductometric titration [63]. The acid groups bound to pulp fibers can be in the salt or protonated form. In an electrolyte solution, the bound cation can be exchanged. To perform the conductometric titration, the pulps were stirred with 300.00 mL of 0.10 M HCl to liberate the fibers and convert the pulp to the protonated form. Then, the pulp was washed with deionized water, dispersed in 250 mL of 0.001 M NaCl, and 1.50 mL of 0.10 M HCl was added. Then, the solution was titrated with a standardized 0.05 M NaOH solution while conductivities were measured. The conductivity reading was obtained by dipping the conductivity probe into the solution up and down and side by side to ensure fresh solution in the conductivity probe cell until a stable conductivity value was displayed.

The total acid groups are extrapolated from plots of the titration data as shown in Fig 15. Initial conductometric titration curves indicate a rapid decrease representing the

neutralization of strong acid groups, which is indicated by the portion of the plot tangent to line 'a'. The portion of the plot tangent to line 'b' represents the point in the titration in which conductivity does not change, and the part of the plot tangent to line 'c' represents increases in conductivity as excess titrant is added. The first point in which conductivity stops changing represents weaker acids beginning to dissociate. Carboxylic acids continue to dissociate until all have dissociated, at which point the conductivity again begins to increase, representing increases in conductivity due to excess NaOH [64].



**Fig.15. A conductometric titration curve, with (a) representing neutralization of HCl by titrant (NaOH), (b) representing the point in the titration in which conductivity does not change (ion exchange with fiber acid groups), and (c) representing increases in conductivity as excess NaOH is added**

The error analysis is summarized in Table 20 (see page 46).

### 3.7. Experimental errors

The experimental errors represent the percentage of standard deviation to the average of each measurement. For each set of experiment, the standard deviation and average of the measurement values were calculated [65]. The average of the standard deviation error for each measurement was calculated and summarized in Table 20. The detail calculation of the experimental errors associated with each measurement was described in Appendix A.

**Table 20. Summary of standard deviation experimental errors**

	Properties	% error, avg
1	DZSTS (Dry Zero Span Tensile Strength)	2.8
2	WZSTS (Wet Zero Span Tensile Strength)	3.5
3	Tensile index	4.0
4	Tear index	8.3
5	Burst index	7.4
6	Brightness	0.5
7	Fines	5.3
8	Fiber length	2.3
9	Fiber curl	1.5
10	Fiber kink	2.8
11	Kappa number	1.5
12	Viscosity	0.9
13	Hexenuronic acid	0.8
14	DCM extractive	2.4
15	Total charge	1.4
16	Cellulose/hemicelluloses	2.4

## CHAPTER 4

### RESULTS AND DISCUSSIONS

#### 4.1. Mill's pulp properties

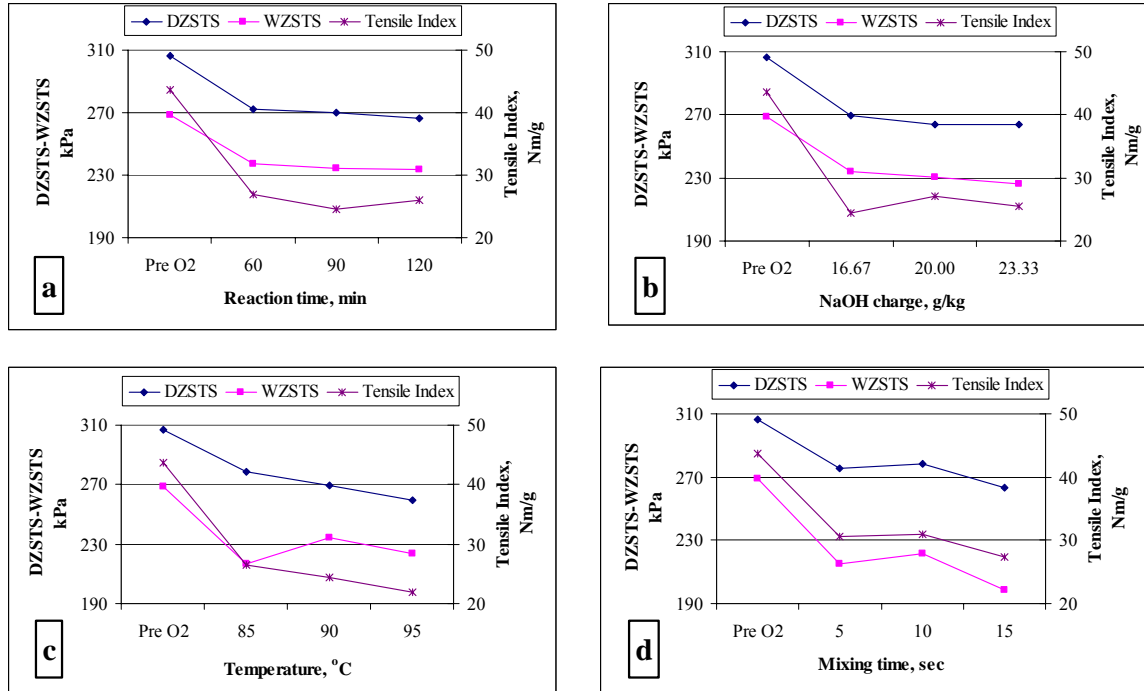
Kappa number reduction (49 %) from mill's pre O<sub>2</sub> to post O<sub>2</sub> *Acacia mangium* kraft pulp showed a typical mill operation target (see Table 16 p.64). Dry zero span tensile strength (DZSTS) loss was found to be only 5 % which differed from prior results, i.e. 21 % and 25 % [70]. Even though the pulp did not indicate a dramatic DZSTS loss, however the pre O<sub>2</sub> kraft pulp was still being used in this study. There was a change in fiber morphology from mill pre O<sub>2</sub> to post O<sub>2</sub>, i.e. fiber became shorter (4 %), more fines (20 %), more curl (5 %) and more kink (11 %). Table 16 summarized the pre O<sub>2</sub> and post O<sub>2</sub> of *Acacia mangium* kraft pulp.

Mill's oxygen delignification operating conditions were shown in Table 9 p.19 and mill was basically operating the oxygen delignification at similar condition for both *Acacia mangium* and MHW (mixed hard woods) kraft pulps. There was a little difference on NaOH addition, i.e. 14-16 and 16-18 kg/ADT for *Acacia mangium* and MHW, respectively. According to Neto et al [28], *Acacia mangium* pulp has a surface coverage of extractive around five times higher than that of other hard wood, i.e. *Betula pendula*, *Eucalyptus globulus*, *Eucalyptus grandis*, *Eucalyptus urograndis*. This significant difference requires a different pulping and bleaching conditions [25]. A series of oxygen

delignification were performed with different conditions to study the response of *Acacia mangium* pulp. The results were discussed in the following sections.

#### **4.2. The effect of oxygen delignification process on the pulp strength**

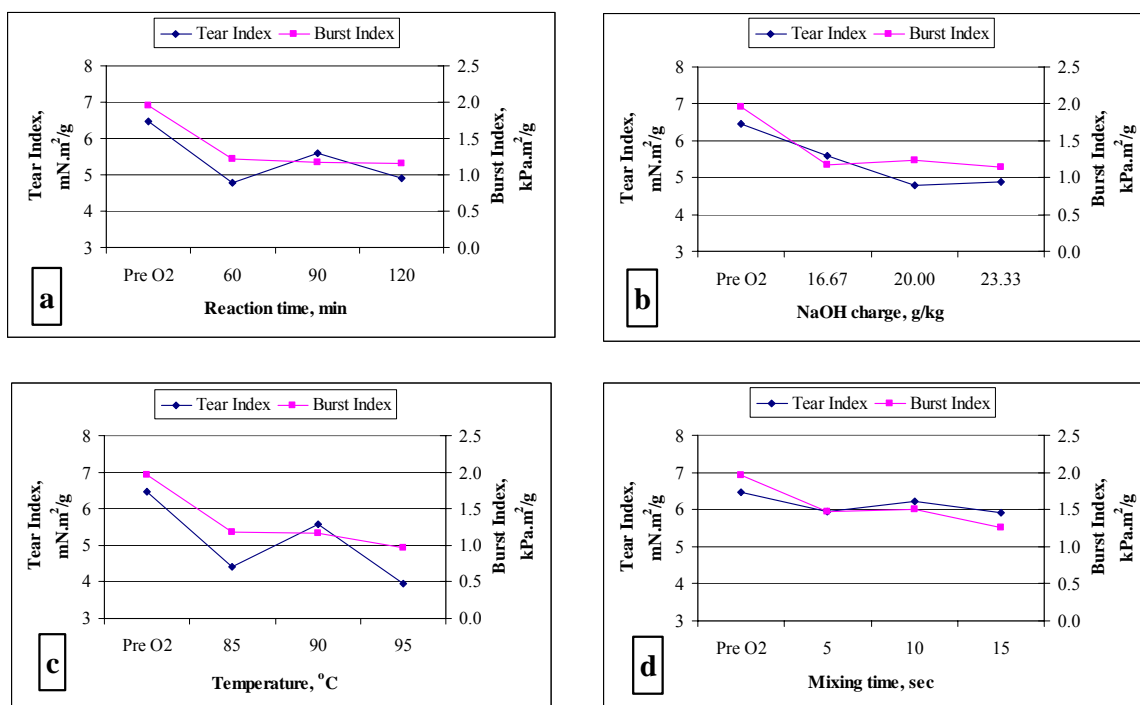
Pre O<sub>2</sub> *Acacia mangium* kraft pulp underwent different oxygen delignification conditions by varying reaction times, NaOH charges, reaction temperatures and mechanical pretreatment times and keeping the rest of the process parameters constant (see Table 18 p.35). The response of the pulp on different process parameters after oxygen delignification reaction with respect to pulp strength was shown in Fig 16. Pre O<sub>2</sub> pulp tensile index was 30 % lower to those reported by Guo et al [33] which was 61.1 and 63.4 Nm/g for six and nine year old *Acacia mangium* kraft pulp respectively. This could be due to a different kraft pulping conditions. It was found that pulp DZSTS decreased by 15 % at NaOH addition of 20.00 g/kg (see Table 18 p.35 for detail oxygen delignification conditions) as shown in Fig 16b. The same 15 % loss in pulp DZSTS was found at oxygen delignification reaction temperature of 95 °C (see Table 18 p.35 for detail oxygen delignification conditions) as shown in Fig 16c. This was in agreement to what reported by Yang et al [38] whereas increasing NaOH addition on oxygen delignification leads to a viscosity loss. Pulp tensile index was found to remain high, at mechanical pretreatment time 5 and 10 seconds followed by oxygen delignification i.e. 30.6 and 30.9 Nm/g, respectively, as shown in Fig 16d. Similar result was also observed in pulp DZSTS at mechanical pretreatment time 5 and 10 seconds followed by oxygen delignification i.e. 275 and 279 kPa, respectively, as shown in Fig 16d.



**Fig.16. DZSTS, WZSTS and tensile index of oxygen delignified *Acacia mangium* kraft pulp after different oxygen delignification process conditions (a) reaction time, (b) NaOH charge, (c) reaction temperature and (d) mechanical pretreatment mixing time. Oxygen delignification condition is described in Table 18 p.35**

The effect of medium consistency mixing on DZSTS and WZSTS was similar to studies by Santos et al [71] on the bleached *Acacia* kraft pulp over the refining revolutions. Pulp WZSTS dropped by 26 % at mechanical pretreatment time of 15 seconds followed by oxygen delignification as shown in Fig 16d. This was the greatest decrease among the oxygen delignification process parameters studied.

Pulp strength properties were also found to follow a similar trend including tear and burst index as shown in Fig 17. Tear and burst index had the highest value even at mechanical pretreatment time 15 seconds, i.e. 5.91 mN.m<sup>2</sup>/g and 1.26 k.Pa.m<sup>2</sup>/g, respectively as shown in Fig 17d.

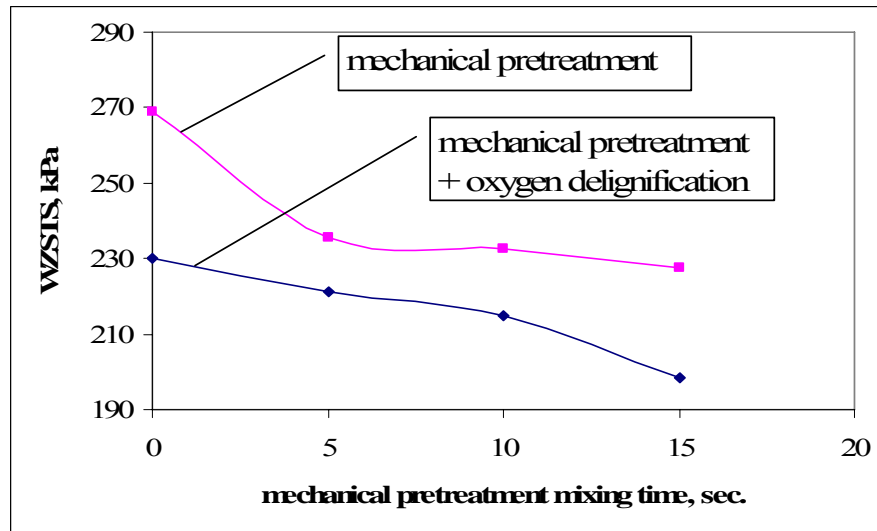


**Fig.17. Tear index and burst index of oxygen delignified *Acacia mangium* kraft pulp after different process conditions (a) reaction time, (b) NaOH charge, (c) reaction temperature and (d) mechanical pretreatment mixing time. Oxygen delignification condition is described in Table 18 p.35**

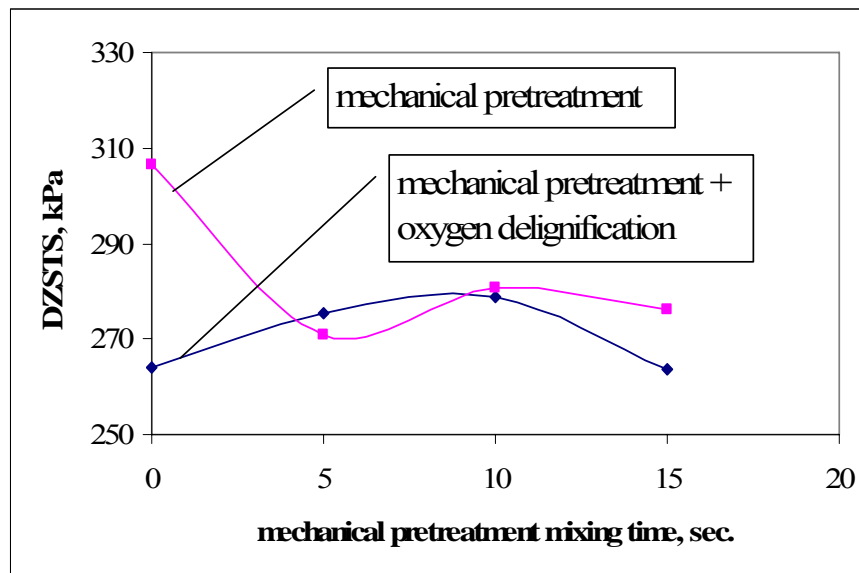
On the other hand, oxygen delignification reaction temperature induced pulp tear and burst index reduction by 40 and 50 %, respectively, at 95 °C as shown in Fig 17c.

The role of the mechanical pretreatment and oxygen delignification on the pulp WZSTS was shown in Fig 18. Pulp WZSTS reduced 14 % by the oxygen delignification alone and there was an additional reduction of 3, 6, and 12 % by applying mechanical pretreatment for 5, 10 and 15 seconds, respectively. A different trend was obtained on pulp DZSTS as shown in Fig 19. Pulp DZSTS increased by 6 % after 10 seconds mechanical pretreatment followed by oxygen delignification.

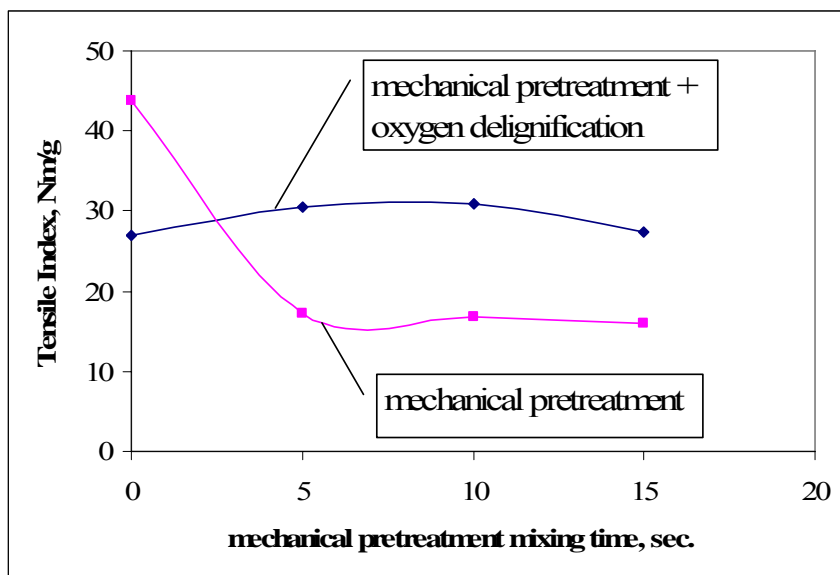




**Fig.18. WZSTS loss of pulp after mechanical pretreatment and mechanical pretreatment followed by oxygen delignification. Oxygen delignification was performed at reaction temperature 90 °C, reaction time 90 min, NaOH charge 20.00 g/kg, consistency 12 % and oxygen pressure 1,034 kPa**



**Fig.19. DZSTS loss of pulp after mechanical pretreatment and mechanical pretreatment followed by oxygen delignification. Oxygen delignification was performed at reaction temperature 90 °C, reaction time 90 min, NaOH charge 20.00 g/kg, consistency 12 % and oxygen pressure 1,034 kPa**

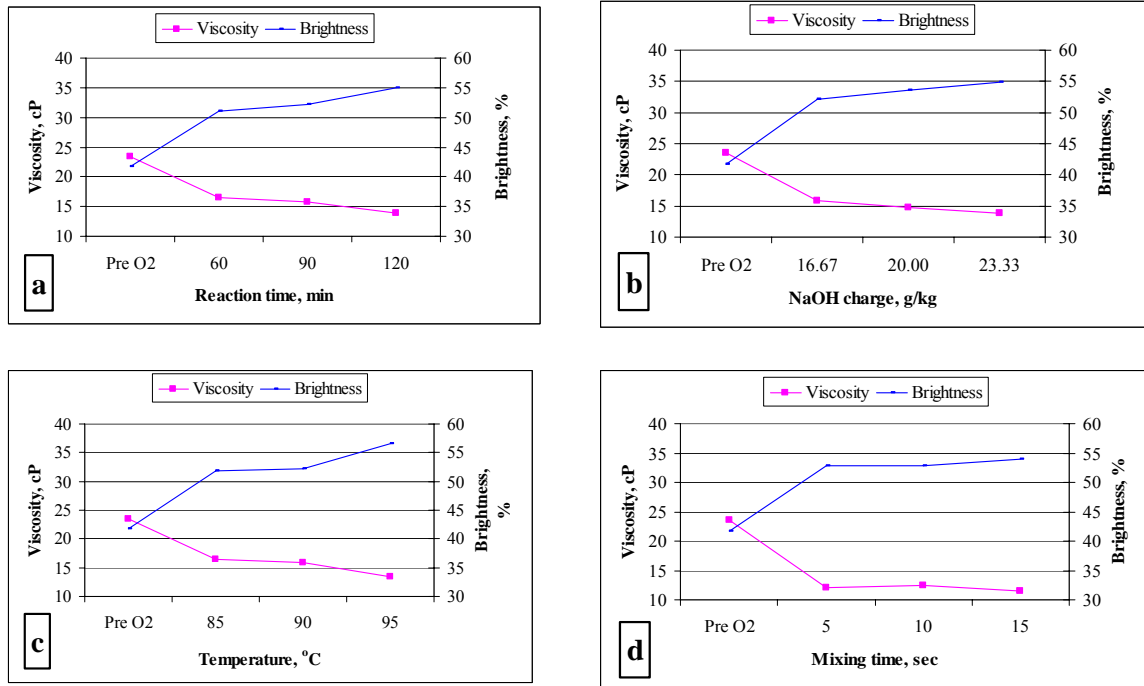


**Fig.20. Tensile index of pulp after mechanical pretreatment and mechanical pretreatment followed by oxygen delignification. Oxygen delignification was performed at reaction temperature 90 °C, reaction time 90 min, NaOH charge 20.00 g/kg, consistency 12 % and oxygen pressure 1,034 kPa**

Pre O<sub>2</sub> pulp tensile index dropped by 60 % by applying mechanical pretreatment for 10 seconds as shown in Fig 20. But after mechanical pretreatment for 10 seconds followed by oxygen delignification, pulp tensile index increased by 14 % compared to those without mechanical pretreatment.

The viscosity loss during different oxygen delignification process conditions is shown in Fig 21. By applying mechanical pretreatment on the pulp for 5 seconds followed by oxygen delignification, pulp viscosity reduced to 12.1 cP. This was 50 % reduction from pre O<sub>2</sub> pulp and comparable to mill post O<sub>2</sub> pulp i.e. 12.4 cP. A similar trend was obtained for pulp brightness as shown in Fig 21a – d. The highest pulp

brightness was reached at oxygen delignification temperature of 95 °C i.e. 56.5 % as shown in Fig 21c.

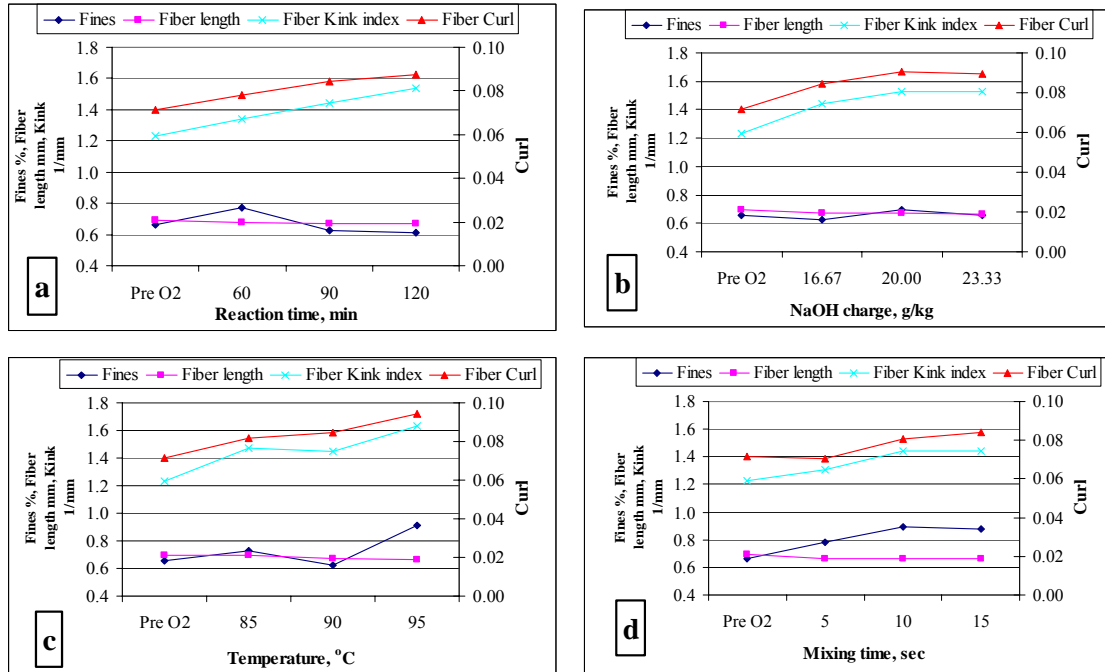


**Fig.21. Viscosity and brightness of pulp after different oxygen delignification process conditions (a) reaction time, (b) NaOH charge, (c) reaction temperature and (d) mechanical pretreatment mixing time. Oxygen delignification condition is described in Table 18 p.35**

#### 4.3. The effect of oxygen delignification process on fiber structures

The changes in fiber length, curl, kink and creation of fines after different oxygen delignification process are shown in Fig 22a-d. Overall fiber length was somewhat longer (3 %) to those reported by Mohlin [30], which was 0.65 mm. On the other hand, the fiber

kink was found four times to those reported by Mohlin [30], which was 0.34/mm. Fiber curl was also found somewhat higher (0.07 – 0.09) than prior report [71] i.e. 0.05 – 0.06 for *Acacia* species. This indicated severe mechanical shear taken place in the mill process equipments [45, 46].



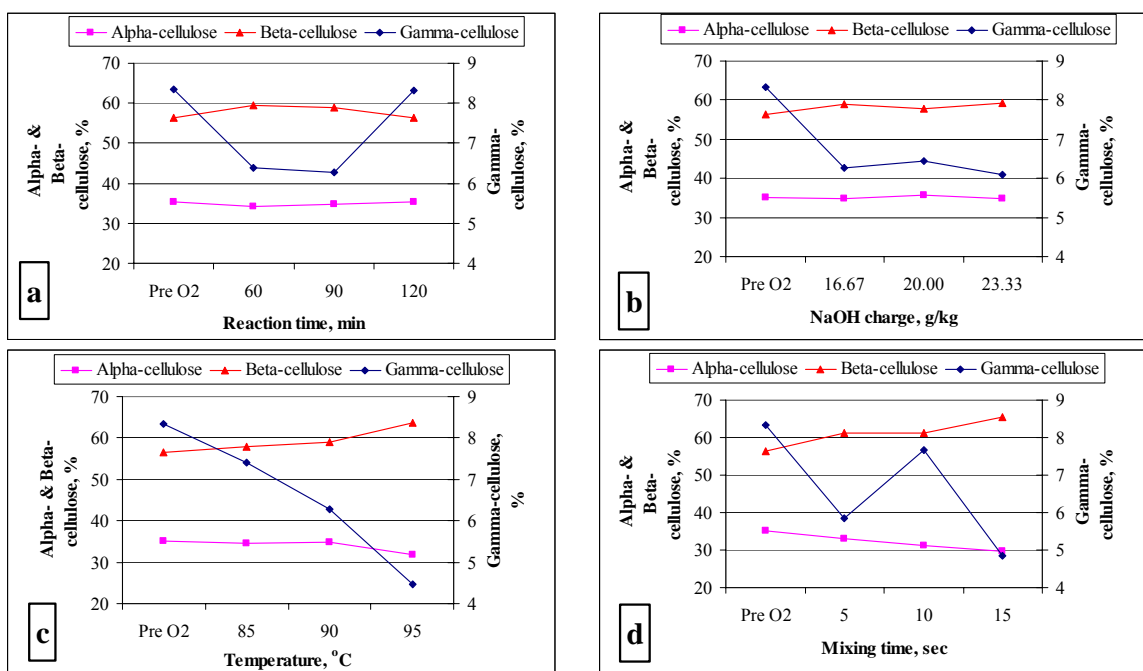
**Fig.22. Fines, length, kink index and curl of fiber after different oxygen delignification process conditions (a) reaction time, (b) NaOH charge, (c) reaction temperature and (d) mechanical pretreatment mixing time. Oxygen delignification condition is described in Table 18 p.35**

Fiber length did not show a significant change ( $0.660 \pm 0.006$  –  $0.698 \pm 0.008$  mm) after different oxygen delignification processes at confidence level 95%. Fiber curl ( $0.070 \pm 0.001$  –  $0.080 \pm 0.001$ ) and kink ( $1.31 \pm 0.09$  –  $1.45 \pm 0.03$ ) did not increase significantly by applying mechanical pretreatment on pulp followed by oxygen

delignification compared to those of oxygen delignification process conditions studied at confidence level 95%. This behavior was reported by Santos et al [71] on bleached *Acacia* kraft pulps whereas refining showed to reduce fiber curl. This explained why the mechanical pretreatment can increase pulp DZSTS, tensile, burst and tear index as mentioned in section 4.2 p.48 [45]. Fiber curl was reported to contribute to pulp strength [48, 71].

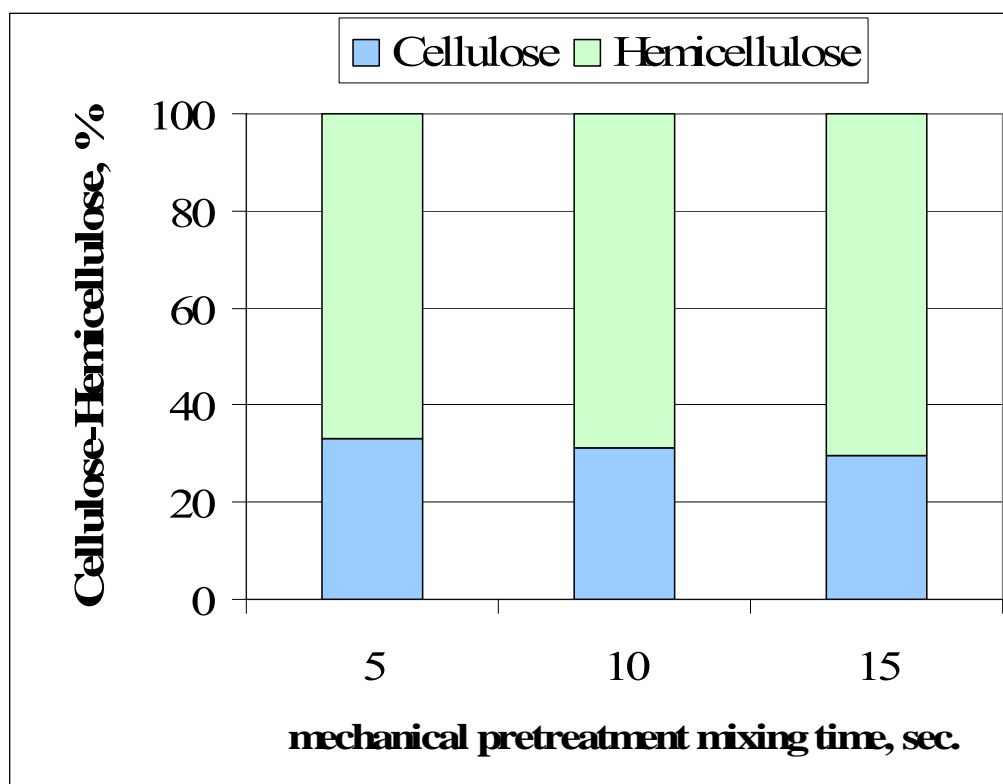
#### **4.4. The effect of oxygen delignification process on cellulose degradation.**

Cellulose degradation during oxygen delignification process was studied. Alpha-, beta-, and gamma-celluloses were determined to explore the changes during oxygen delignification as shown in Fig 23a – d. In general, alpha-cellulose content in this experiment (30 – 36 %) was lower to those reported by Bahar [32], which was 42.2 %. This could be due to different oxygen delignification process conditions. Beta- and gamma-celluloses did not show a good trend, especially at different reaction time (Fig 23a) and pretreatments (Fig 23d). Beta- and gamma-cellulose were categorized as hemicelluloses with DP (degree of polymerization) between 15 and 90, and less than 15, respectively, while alpha-cellulose was long chain cellulose (DP>90) [66]. Fraction of gamma-cellulose was consistently decreased at reaction temperature of 85, 90 and 95 °C, i.e. 7.4, 6.3, 4.5 %, respectively. Overall, alpha-cellulose was degraded to a small degree (0 – 9 %), except by applying mechanical pretreatment for 15 seconds followed by oxygen delignification reaction (15 %).



**Fig.23. Alpha-, beta- and gamma-cellulose of pulp after different oxygen delignification process conditions (a) reaction time, (b) NaOH charge, (c) reaction temperature and (d) mechanical pretreatment mixing time. Oxygen delignification condition is described in Table 18 p.35**

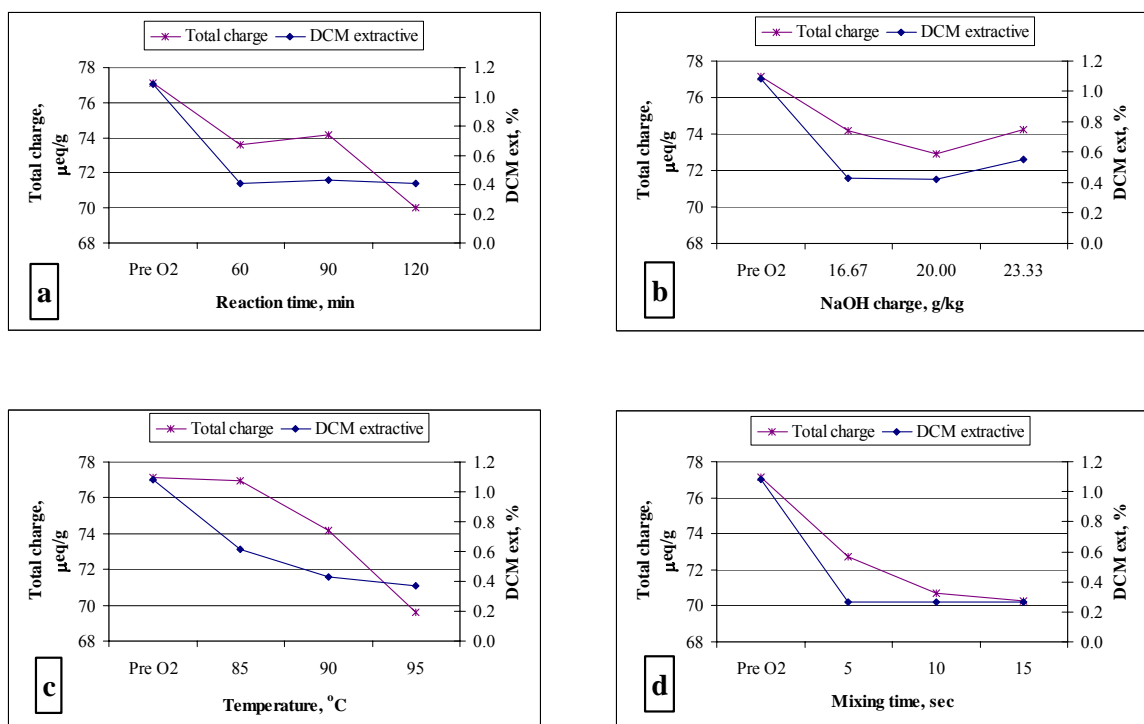
This suggested that mechanical pretreatment induced cellulose degradation as shown in Fig 24. The increase in hemicelluloses content on mechanically pretreated pulp probably contributed to pulp DZSTS and tensile index (see section 4.2 p.48) as shown in Fig 24. This was in agreement to studies by Molin [74] on Norway spruce kraft pulp. Hemicelluloses content increased from 67 to 70 % by applying mechanical pretreatment from 5 to 15 seconds.



**Fig.24. Percentage of cellulose and hemicelluloses of pulp after mechanical pretreatment followed by oxygen delignification. Oxygen delignification was performed at reaction temperature 90 °C, reaction time 90 min, NaOH charge 20.00 g/kg, consistency 12 % and oxygen pressure 1,034 kPa**

#### **4.5. The effect of oxygen delignification process on DCM extractive and total fiber charge**

Total fiber charge and DCM (dichloromethane) extractive were studied as shown in Fig 25. Total charge did not show a good trend as oxygen delignification reaction time and NaOH addition increasing. On the other hand, total charge decreased from  $77.0 \pm 2.8$  to  $69.6 \pm 2.0$   $\mu\text{eq/g}$  by increasing oxygen delignification reaction temperature from 85 to 95 °C as shown in Fig 25c at confidence level 95%.



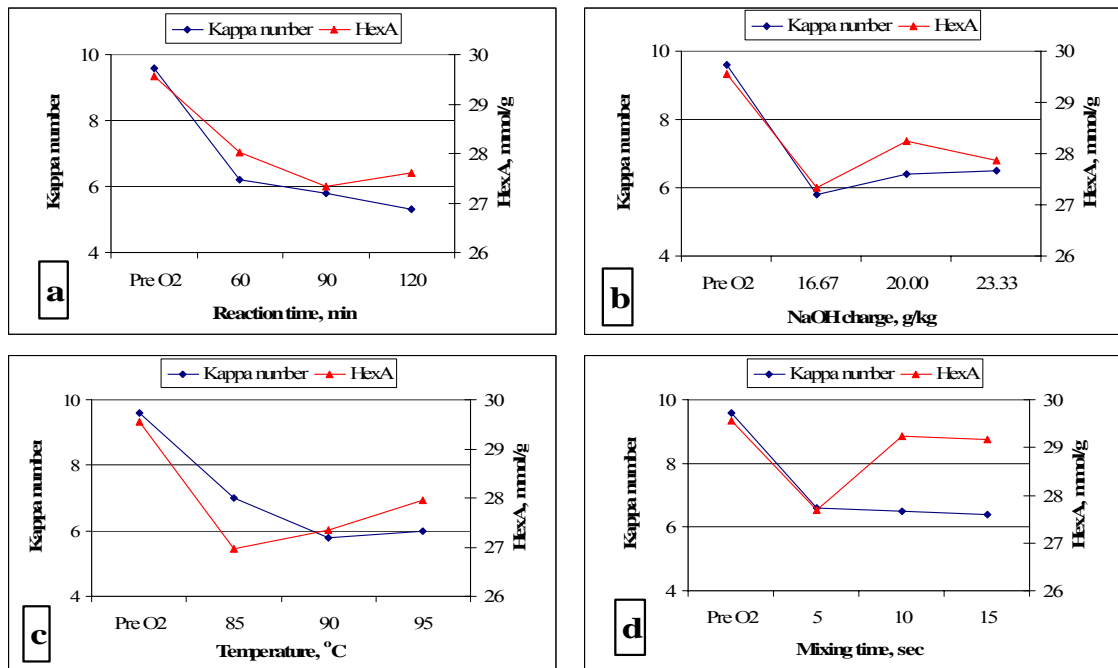
**Fig.25. Total charge and DCM extractive of pulp after different oxygen delignification process conditions (a) reaction time, (b) NaOH charge, (c) reaction temperature and (d) mechanical pretreatment mixing time. Oxygen delignification condition is described in Table 18 p.35**

DCM extractives dropped by 76 % by applying 5 seconds mechanical pretreatment followed by oxygen delignification as shown in Fig 25d. This was probably due to applying filtration on pulp after mechanical pretreatment as suggested by Bouchard et al [72]. Increasing NaOH charge on oxygen delignification to 23.33 g/kg was found to reduce DCM extractives by 50 % which was the lowest DCM extractives reduction among oxygen delignification process parameters studied (>60 %). This result was in agreement to studies by Bouchard et al [72] whereas NaOH addition during oxygen delignification did not improve extractives removal.



#### 4.6. The effect of oxygen delignification process on Kappa number and hexenuronic acid content.

Kappa number and hexenuronic acid content were also studied as shown in Fig 26.



**Fig.26. Kappa number and hexenuronic acid content of pulp after different oxygen delignification process conditions (a) reaction time, (b) NaOH charge, (c) reaction temperature and (d) mechanical pretreatment mixing time. Oxygen delignification condition is described in Table 18 p.35**

Kappa number did not show a good trend as NaOH addition and reaction temperature increasing (see Fig 26b and 26c). Kappa number reduction of 35 to 45 % was obtained by increasing oxygen delignification reaction time from 60 to 120 min as shown in Fig 26a. Hexenuronic acid content showed lower values (23 – 30  $\mu\text{mol/g}$ ) to studies by Malinen

[8] which was 40 – 60  $\mu\text{mol/g}$  on unbleached *Acacia mangium* kraft pulps. This was probably due to different pulping conditions. Overall, hexenuronic acid content did not show a good trend.

#### 4.7. The importance of oxygen delignification process parameters on mechanically pretreated pulp

The importance of oxygen delignification process parameters on mechanically pretreated pulp was investigated. A series of oxygen delignification were performed with different reaction times, temperatures and NaOH additions (see Table 19 p.36). Pulp WZSTS and DZSTS were then analyzed as shown in Table 21 and 22.

**Table 21. Yates' algorithm analysis [68] for pulp DZSTS, t=reaction time in minutes, T=reaction temperature in °C, C=NaOH addition in g/kg of pulp, pulp consistency 12 %, oxygen pressure 1,034 kPa**

Exp.	Variables			DZSTS	Calculations			Estimated effects	
	t	T	C		1	2	3		
y1	60	70	10.0	292	575	1115	2104	Grand average	263
y2	120	70	10.0	284	539	989	-49	t effect	-12.2
y3	60	100	10.0	290	568	-49.0	-183	T effect	-45.8
y4	120	100	10.0	249	421	0.0	-5.1	t T effect	-1.3
y5	60	70	30.0	291	-7.9	-36.0	-126	C effect	-31.4
y6	120	70	30.0	277	-41.1	-147	49.0	t C effect	12.3
y7	60	100	30.0	203	-14.0	-33.2	-111	T C effect	-27.8
y8	120	100	30.0	217	14.1	28.1	61.3	t T C effect	15.3

It is shown in Table 21 and 22 that reaction temperature and NaOH addition were the most pronounced factors affecting pulp DZSTS and WZSTS on mechanically pretreated

pulp (see the shaded rows). Pulp Kappa number was also evaluated to understand how oxygen delignification process parameters affecting lignin removal. Yates' algorithm analysis was shown in Table 23.

**Table 22. Yates' algorithm analysis [68] for pulp WZSTS, t=reaction time in minutes, T=reaction temperature in °C, C=NaOH addition in g/kg of pulp, pulp consistency 12 %, oxygen pressure 1,034 kPa**

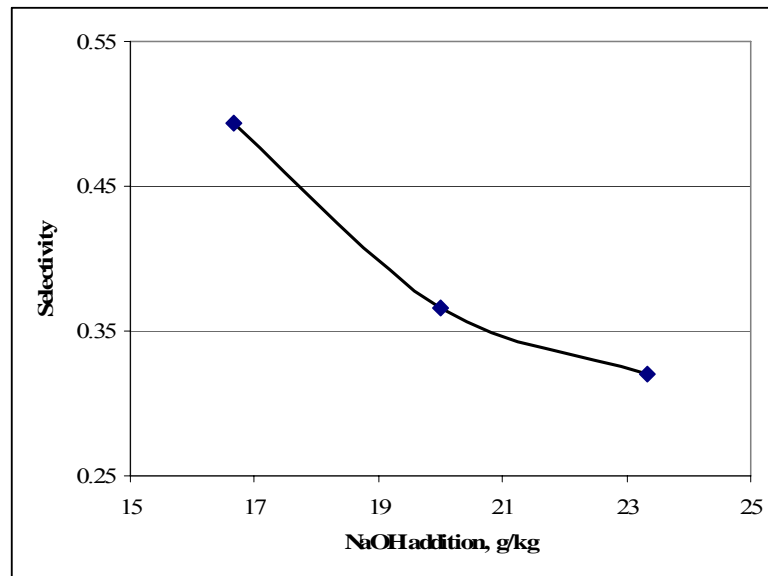
Exp.	Variables			WZSTS	Calculations			Estimated effects	
	t	T	C		1	2	3		
y1	60	70	10.0	242	480	913	1626	Grand average	203
y2	120	70	10.0	238	433	714	-52.4	t effect	-13.1
y3	60	100	10.0	236	410	-42.0	-154	T effect	-38.4
y4	120	100	10.0	198	303	-10.4	-23.0	t T effect	-5.7
y5	60	70	30.0	211	-3.9	-46.3	-199	C effect	-49.8
y6	120	70	30.0	200	-38.1	-107	31.6	t C effect	7.9
y7	60	100	30.0	151	-10.8	-34.3	-61.0	T C effect	-15.3
y8	120	100	30.0	152	0.4	11.3	45.6	t T C effect	11.4

**Table 23. Yates' algorithm analysis [68] for pulp Kappa number, t=reaction time in minutes, T=reaction temperature in °C, C=NaOH addition in g/kg of pulp, pulp consistency 12 %, oxygen pressure 1,034 kPa**

Exp.	Variables			Kappa #	Calculations			Estimated effects	
	t	T	C		1	2	3		
y1	60	70	10.0	8.9	17.0	30.2	58.2	Grand average	7.3
y2	120	70	10.0	8.1	13.2	28.1	-3.0	t effect	-0.7
y3	60	100	10.0	7.3	16.7	-2.2	-9.2	T effect	-2.3
y4	120	100	10.0	5.9	11.4	-0.7	-0.4	t T effect	-0.1
y5	60	70	30.0	8.5	-0.9	-3.8	-2.1	C effect	-0.5
y6	120	70	30.0	8.2	-1.3	-5.3	1.5	t C effect	0.4
y7	60	100	30.0	5.9	-0.4	-0.5	-1.5	T C effect	-0.4
y8	120	100	30.0	5.5	-0.4	0.0	0.5	t T C effect	0.1

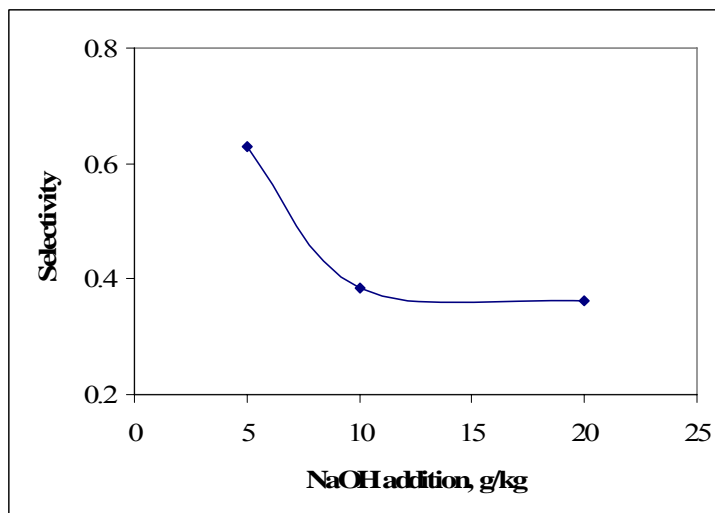
Table 23 showed that reaction temperature was the dominant factor affecting kappa number reduction. Both pulp strength (DZSTS and WZSTS) and Kappa number results

(see Table 21, 22, 23) suggested that NaOH charge could be reduced so as to retain pulp strength when mechanical pretreatment was applied prior to oxygen delignification reaction. This is because reducing NaOH charge improves selectivity as shown in Fig 27.

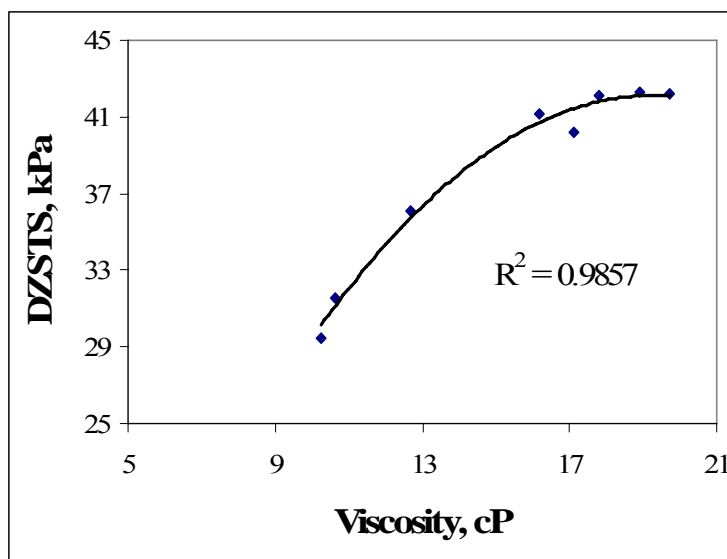


**Fig 27. Oxygen delignification selectivity ( $\Delta Kappa/\Delta viscosity$ ) of *Acacia mangium* kraft pulp at various NaOH charge. Oxygen delignification reaction was performed at 12 % consistency, oxygen pressure of 1,034 kPa, temperature of 90 °C, and reaction time of 90 minutes**

Further study was performed to predict how much NaOH could possibly be reduced by applying mechanical pretreatment on pulp prior to oxygen delignification at the same selectivity of actual mill production. 15 seconds mechanical pretreatment was chosen as a base of the experiment and the results were shown in Fig 28. Mill was operating at 16.67 g/kg NaOH addition and had a selectivity of 0.45 (see Appendix B p.92). Based on Fig 27, NaOH could be reduced by 50 % at the same selectivity.



**Fig.28. Correlation between selectivity ( $\Delta Kappa/\Delta Viscosity$ ) and NaOH addition of oxygen delignified pulp at consistency 12 %, time 120 minutes, temperature 90 °C, and O<sub>2</sub> pressure 1034 KPa. The pulp was mechanically pretreated with Quantum mixer for 15 seconds prior to oxygen delignification reaction**



**Fig.29. Relationship between pulp viscosity and DZSTS of oxygen delignified pulp from Yates' algorithm analysis. Oxygen delignification condition is described in Table 19 p.36**

Pulp viscosity and DZSTS were found to have relatively good relation in this experiment as shown in Fig 29.

#### 4.8. Selectivity improvement and extractive removal by various pretreatment methods followed by oxygen delignification reaction

A recent mill production of *Acacia mangium* and mixed hardwood (MHW) pre O<sub>2</sub> kraft pulps was used in this experiment. These pulps were washed with de-ionized water until the effluent was pH neutral and colorless. These wet pulps (17 % consistency) were stored in cold room. Table 24 summarized metal profile of both pulps. Both pulps underwent different pretreatment methods followed by oxygen delignification.

**Table 24. Metal profile of pre O<sub>2</sub> *Acacia mangium* and MHW (mixed hardwood) kraft pulps**

Metal	<i>A. mangium</i> , 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

Four different pretreatment methods were used: applying ultrasonic energy, hot water soaking, soda addition-preheating, and applying mechanical shear. The detail pretreatment methods are as follows:

1. Pulp of an equal amount to 35 g oven dry were ultrasound for 2 hours at 1 % consistency, temperature of 25 °C, amplitude 40 %, energy 1.0 MJ while 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. Pulp of an equal amount to 60 g oven dry were preheated at 12.8 % consistency and temperature of 70 °C for 2 hours in the water bath. A 0.50 %  $\text{MgSO}_4$  (5.0 % w/w solution) was added prior to preheating. The oxygen delignified pulp sample of this pretreatment was labeled as 2A for *Acacia mangium* pulp and 2M for MHW pulp.
3. Pulp of an equal amount to 60 g oven dry were premixed with 2.0 % NaOH and heated at 12.8 % consistency and temperature of 70 °C for 2 hours in the water bath. A 0.50 %  $\text{MgSO}_4$  (5.0 % w/w solution) was added prior to NaOH addition. The oxygen delignified pulp sample of this pretreatment was labeled as 3A for *Acacia mangium* pulp and 3M for MHW pulp.
4. Pulp of an equal amount to 100 g oven dry underwent mechanical pretreatment in a laboratory Quantum mixer at speed 2200 rpm and 12.8 % consistency for 5 seconds. A 0.50 %  $\text{MgSO}_4$  (5.0 % w/w solution) was added prior to mechanical pretreatment. The oxygen delignified pulp sample of this pretreatment was labeled as 4A for *Acacia mangium* pulp and 4M for MHW pulp.

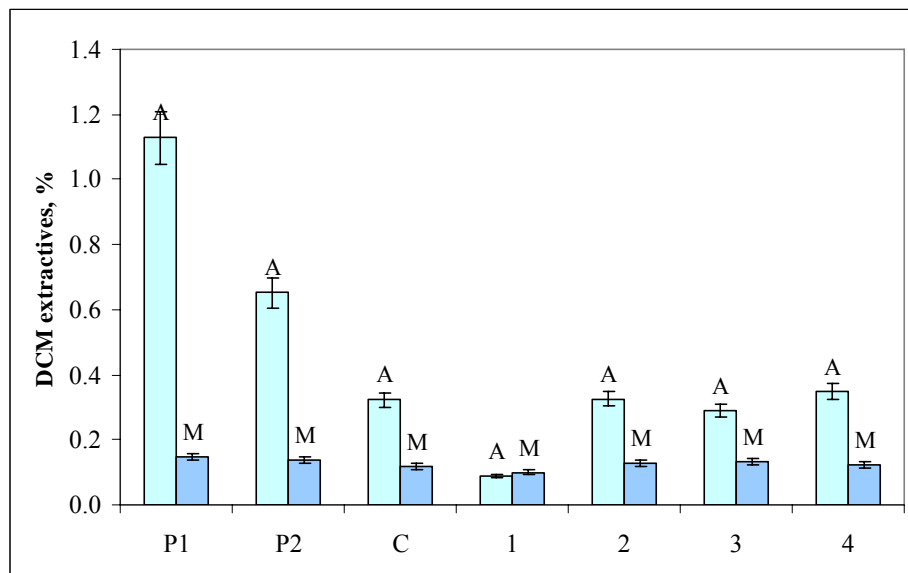
A control pulp samples were made without pretreatment prior to oxygen delignification and labeled as CA for *Acacia mangium* pulp and CM for MHW pulp. The oxygen delignification was performed at 12 % consistency, oxygen pressure 1,034 kPa, reaction

time 60 minutes, reaction temperature 90 °C, MgSO<sub>4</sub> addition 0.50 % (5.0 % w/w solution), and NaOH addition 2.0 % (1.00 N solution).

Oxygen delignification reactions were performed immediately after pretreatment of pulp samples were done. There was no washing and/or filtering between pretreatment and oxygen delignification reaction except for pulp sample labeled number 1 (see p.65 for detail). Thus pre O<sub>2</sub> pulp was filtered and washed after pretreatment number 1 was done. Fig 30 summarized the DCM extractives of pre O<sub>2</sub> and oxygen delignified pulps for each pretreatment method. Pre O<sub>2</sub> *A. mangium* pulp had significantly higher DCM extractives content (eight times) than those of MHW pulp. It is obviously shown in Fig 30 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 [72]. 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 pretreatment methods studied. Similar result was obtained for ultrasonic pretreatment of MHW pulp even though only a total of 33 % extractive removed from pre O<sub>2</sub> MHW pulp. A low extractive content (0.15 %) of pre O<sub>2</sub> MHW pulp was probably one reason why significant extractive removal (33 %) was not observed in this pulp. Further study is needed to prove this hypothesis. Oxygen delignification alone removed extractive content by 51 and 19 % for *A. mangium* and MHW pulps (pulp sample labeled C), see Fig 30. NaOH pretreatment (Fig 30, pulp sample labeled 3) proved to be inefficient to remove extractive [72], i.e. 74 and 14 % for *A. mangium* and MHW pulps, respectively. Efficient



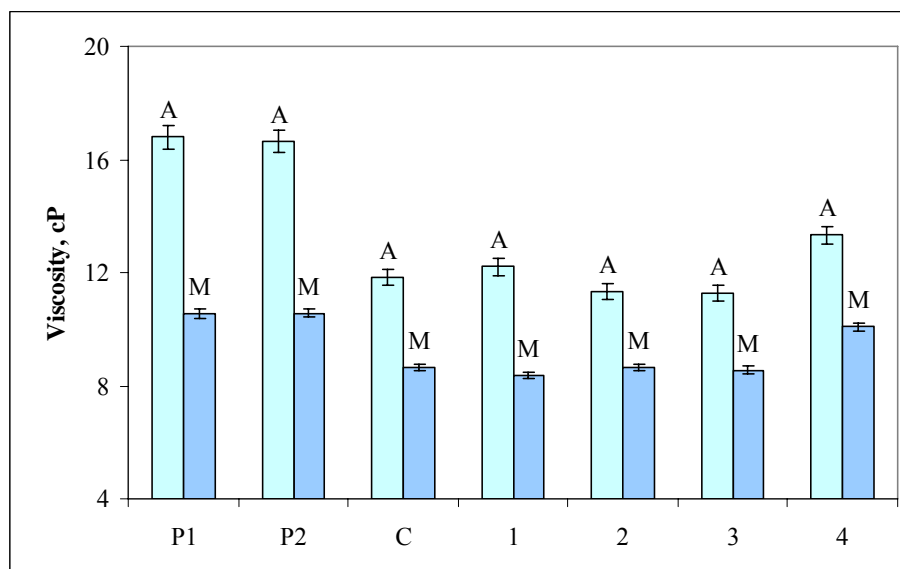
extractive removal was not obtained by hot water pretreatment of pulp (Fig 30, pulp sample labeled 2), i.e. 70 and 14 % for *A. mangium* and MHW pulps, respectively.



**Fig.30. DCM extractives content of pre O<sub>2</sub> and oxygen delignified *A. mangium* (A) and MHW (M) pulps. P1 denotes original pre O<sub>2</sub> pulp, P2 denotes pre O<sub>2</sub> pulp after ultrasonic pretreatment followed by filtering and washing, while C, 1, 2, 3, 4 are as described in the detail pretreatment methods (p.65)**

Pulp viscosity measurement was performed to see how pulp pretreatment followed by oxygen delignification affected cellulose degradation. Fig 31 summarized viscosity of pre O<sub>2</sub> and oxygen delignified *A. mangium* and MHW pulps. Fig 31 showed that most of the pulp pretreatment methods did not induce significant cellulose degradation (2 – 4 % viscosity reduction). A slight viscosity reduction occurred on hot water and NaOH pretreatments (Fig 31, pulp sample labeled 3), i.e. 4 and 0 % for *A. mangium* and MHW pulps, respectively. It was also shown in Fig 31 that ultrasonic pretreatment did not degrade fiber cellulose as viscosity remains the same as before ultrasonic pretreatment, i.e. 16.8 and 10.6 cP for *A. mangium* and MHW pulps,

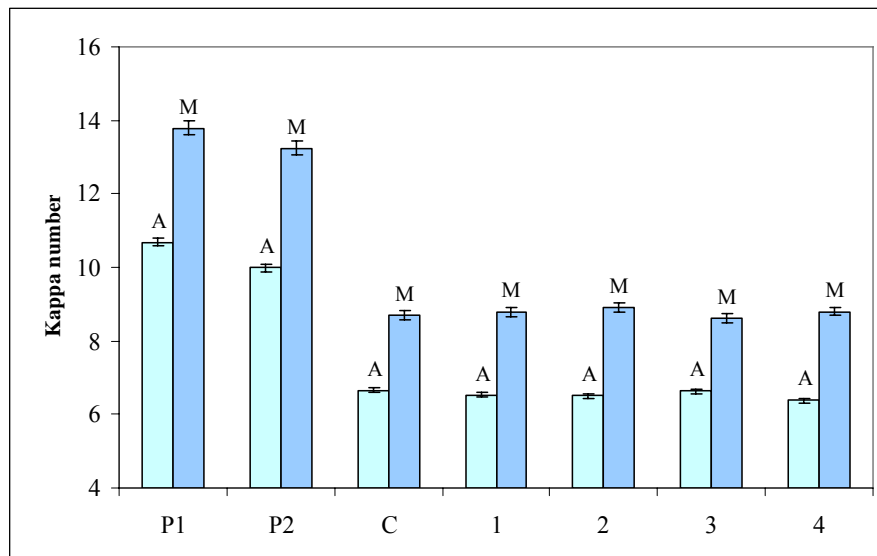
respectively (pulp sample labeled P1 and P2). This was in agreement to studies by Thompson et al [73].



**Fig.31. Viscosity of pre O<sub>2</sub> and oxygen delignified *A. mangium* (A) and MHW (M) pulps. P1 denotes original pre O<sub>2</sub> pulp, P2 denotes pre O<sub>2</sub> pulp after ultrasonic pretreatment followed by filtering and washing, while C, 1, 2, 3, 4 are as described in the detail pretreatment methods (p.65)**

Kappa number of the Pre O<sub>2</sub> and oxygen delignified pulps was determined. Fig 32 summarized pulp Kappa number of pre O<sub>2</sub> and oxygen delignified *A. mangium* and MHW pulps. In general, Kappa number of oxygen delignified pulps with pretreatment was at similar level to those of without pretreatment; maximum difference of 4 and 2 % for *A. mangium* and MHW pulps, respectively. Fig 32 also showed that ultrasonic pretreatment followed by filtering and washing released some residual lignin in pulp (pulp sample labeled P2), i.e. 7 and 4 % Kappa number reduction for *A. mangium* and

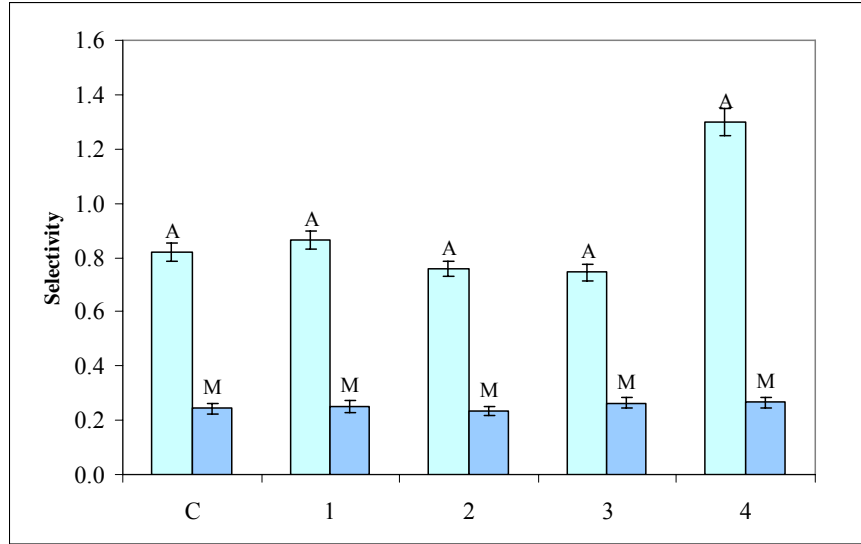
MHW pulps, respectively. Cell wall breakage and pores formation due to ultrasonic effect could be one reason why Kappa number decreased by applying ultrasonic pretreatment followed by filtering and washing [73]. Further study is needed to confirm this hypothesis.



**Fig.32. Kappa number of pre O<sub>2</sub> and oxygen delignified *A. mangium* (A) and MHW (M) pulps. The code C, 1, 2, 3, 4 is as described in the detail pretreatment methods (p.65)**

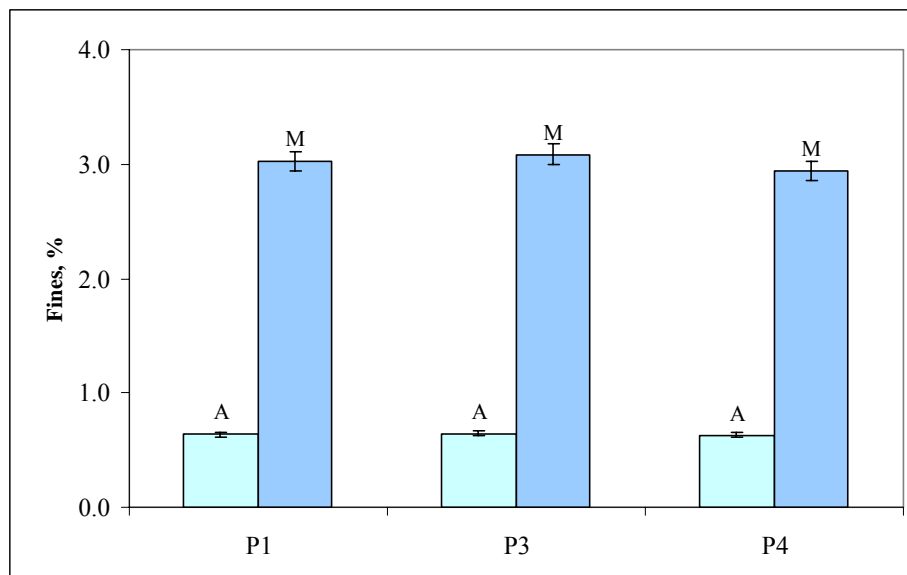
Selectivity of oxygen delignification was quite interesting to see. Fig 33 showed selectivity of oxygen delignified *A. mangium* and MHW pulps. It was obvious that mechanical pretreatment of pulp followed by oxygen delignification obtained the best selectivity among pretreatment methods studied. This was probably due to a better mixing of added MgSO<sub>4</sub> with pulp as suggested by Yang et al [36] and Liden et al [69] so that harmful transition metals (Fe, Mn, Cu) are deactivated. The other pulp pretreatments

(method 1, 2, and 3) did not show significant selectivity improvement, i.e. 1 and 10 % for *A. mangium* and MHW pulps, respectively, as shown in Fig 33.

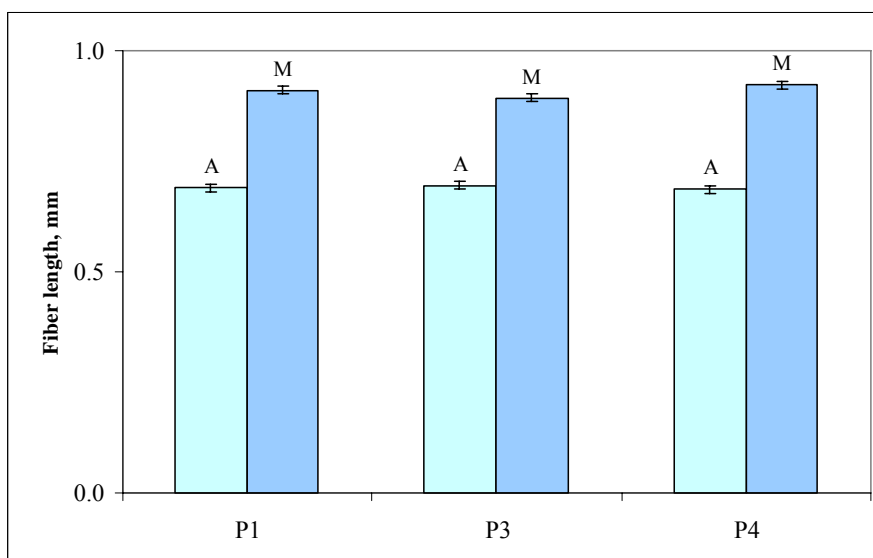


**Fig.33. Selectivity ( $\Delta$  Kappa /  $\Delta$  viscosity) of oxygen delignified *A. mangium* (A) and MHW (M) pulps. The code C, 1, 2, 3, 4 is as described in the detail pretreatment methods (p.65)**

Fines formation due to mechanical and ultrasonic pretreatments of pulp was studied. Fig 34 summarized fines content of pre O<sub>2</sub> *A. mangium* and MHW pulps with and without pretreatment. It was proven that ultrasonic pretreatment of pulp (Fig 34, pulp sample labeled P3) did not induce fines formation as suggested by Thompson et al [73]; fines content difference of 1 and 2 % for *A. mangium* and MHW pulps, respectively. Fig 34 also showed that mechanical pretreatment of pulp for 5 seconds did not lead to fines formation, i.e. 1 and 3 % for *A. mangium* and MHW pulps, respectively.



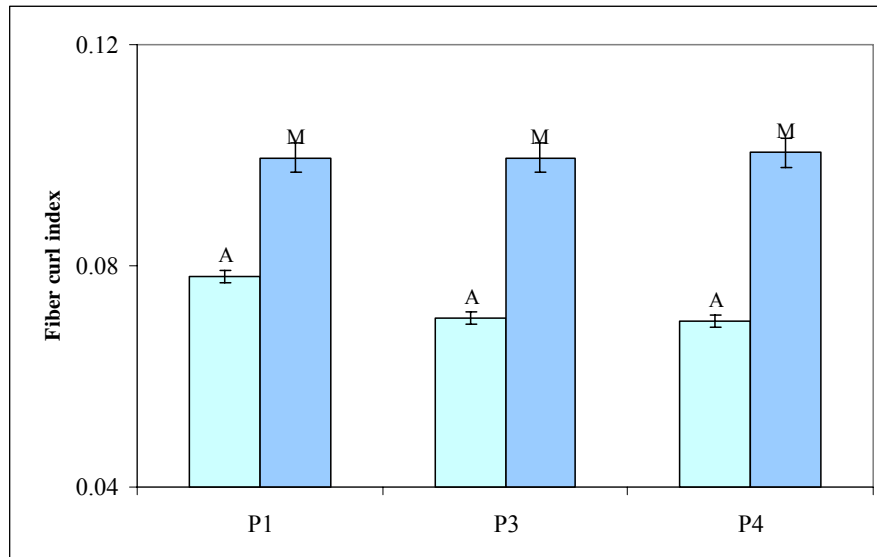
**Fig.34. Fines content of pre O<sub>2</sub> *A. mangium* (A) and MHW (M) pulps. P1 denotes original pre O<sub>2</sub> pulp, P3 denotes ultrasonic pretreatment of pre O<sub>2</sub> pulp, and P4 denotes mechanical pretreatment of pre O<sub>2</sub> pulp. Detail pretreatment methods are described in p.65**



**Fig.33. Fiber length of pre O<sub>2</sub> *A. mangium* (A) and MHW (M) pulps. P1 denotes original pre O<sub>2</sub> pulp, P3 denotes ultrasonic pretreatment of pre O<sub>2</sub> pulp, and P4 denotes mechanical pretreatment of pre O<sub>2</sub> pulp. Detail pretreatment methods are described in p.65**

Fig 35 confirmed that both ultrasonic and mechanical pretreatment did not physically damage fiber as fiber length remains similar to those of without pretreatment (pulp sample labeled P1); maximum fiber length difference of 1 and 2 % for *A. mangium* and MHW pulps, respectively.

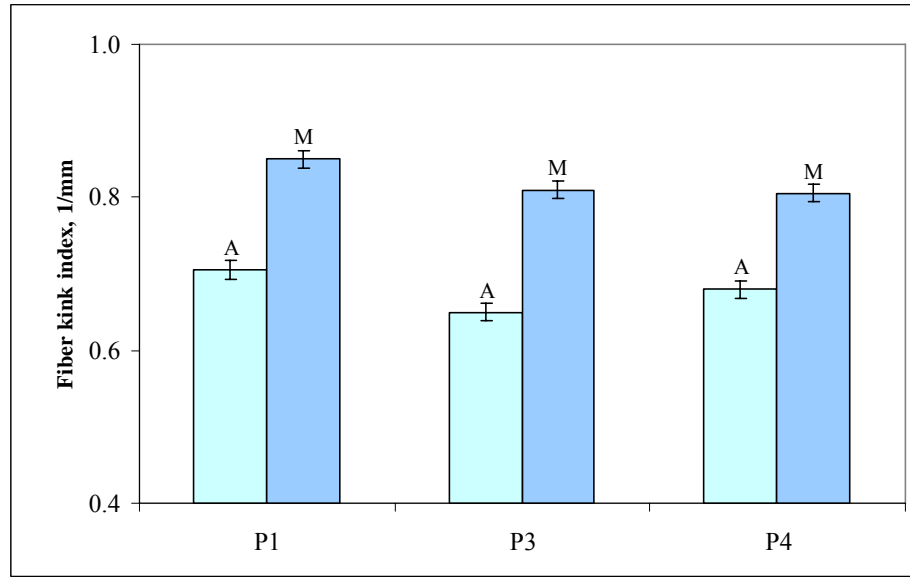
The response of pre O<sub>2</sub> pulp with regard to fiber length, curl, kink and fines were evaluated. Fig 34 and 35 summarized fiber curl and kink of pre O<sub>2</sub> pulp.



**Fig.34. Fiber curl of pre O<sub>2</sub> *A. mangium* (A) and MHW (M) pulps. P1 denotes original pre O<sub>2</sub> pulp, P3 denotes ultrasonic pretreatment of pre O<sub>2</sub> pulp, and P4 denotes mechanical pretreatment of pre O<sub>2</sub> pulp. Detail pretreatment methods are described in p.65**

Ultrasonic and mechanical pretreatments on pulp were found to reduce the fiber curl of *A. mangium* pulp by 13 %, whereas fiber curl of MHW pulp remains the same to those of without pretreatments (see Fig 34). Ultrasonic pretreatment on pulp was observed to reduce fiber kink, i.e. 8 and 5 % for *A. mangium* and MHW pulps,

respectively (see Fig 35). Mechanical pretreatment on pulp was also found to reduce fiber kink by 4 and 5 % for *A. mangium* and MHW pulps, respectively (see Fig 35). Ultrasonic and mechanical pretreatments probably gave ‘refining’ effect to release reversible curl and kink as reported by Mohlin et al [48].



**Fig.35. Fiber kink index of pre O<sub>2</sub> *A. mangium* (A) and MHW (M) pulps. P1 denotes original pre O<sub>2</sub> pulp, P3 denotes ultrasonic pretreatment of pre O<sub>2</sub> pulp, and P4 denotes mechanical pretreatment of pre O<sub>2</sub> pulp. Detail pretreatment methods are described in p.65**

## CHAPTER 5

### CONCLUSIONS

1. Mechanical pretreatment for 10 seconds followed by oxygen delignification was found to increase pulp DZSTS 6% ( $264 \pm 3$  to  $279 \pm 5$ ) and tensile index 14% ( $27.1 \pm 0.7$  to  $30.9 \pm 0.8$ ) at 95% confidence level and at oxygen delignification reaction temperature 90 °C, reaction time 90 min, NaOH charge 20.00 g/kg, consistency 12 %, and oxygen pressure 1,034 kPa. However, pulp WZSTS decreased 4% ( $230 \pm 4$  to  $219 \pm 7$ ) by applying mechanical pretreatment followed by oxygen delignification at the same conditions. The increase in hemicellulose content 6% ( $64.1 \pm 0.4$  to  $68.7 \pm 0.3$ ) at the same mechanical pretreatment and oxygen delignification conditions, probably contributed to this increase on pulp DZSTS and tensile index.
2. Total fiber charge decreased by 4 % ( $77.0 \pm 2.8$  to  $69.6 \pm 2.0$ ) at confidence level 95% with increasing reaction temperature from 85 to 95 °C at oxygen delignification reaction time 90 min, NaOH charge 16.67 g/kg, consistency 12 %, and oxygen pressure 1,034 kPa.
3. Reaction temperature and NaOH addition of oxygen delignification were found to be dominant factors affecting pulp DZSTS and WZSTS on mechanically pretreated pulp (see Table 21 p.60 and Table 22 p.61) at oxygen delignification conditions described in Table 19 p.36. On the other hand, Kappa number was



mainly affected by oxygen delignification reaction temperature (see Table 23 p.61) at the same oxygen delignification conditions.

4. NaOH addition could possibly be reduced by 50 % by applying mechanical pretreatment for 15 seconds followed by oxygen delignification to obtain the same selectivity of mill production at conditions described in this study (see Table 19 p.36 and Fig 28 p.63).
5. The selectivity of oxygen delignification was improved by applying mechanical pretreatment followed by oxygen delignification reaction for both *A. mangium* and MHW kraft pulps, i.e. 50 and 300 %, respectively, at process conditions described in p.65.
6. 92 % of *A. mangium* kraft pulp extractives can be removed by ultrasonic pretreatment followed by oxygen delignification at conditions described in this study (p.65).
7. Only 33 % of MHW kraft pulp extractives can be removed by ultrasonic pretreatment followed by oxygen delignification at conditions described in this study (p.65). This lower result compared to those of *A. mangium* pulp (92 %) was probably due to low extractives content (0.15 %) of MHW kraft pulp to begin with.

## **CHAPTER 6**

### **FUTURE WORKS**

1. An optimization of oxygen delignification process on how to remove extractive while retaining the fiber strength or other desired properties.
2. A study on why mechanical pretreated pulp did not induce substantial fiber curl and kink.
3. A study on the mechanism of extractive removal by ultrasonic pretreatment.

## APPENDIX A

### EXPERIMENTAL ERROR CALCULATIONS

#### 1. Dry zero span tensile strength error calculation

	Pre O <sub>2</sub>	Post O <sub>2</sub>	90	120	60	90	90	90	90	90	90	90	90	90	90	90	90	90
	Reaction time, min		90	120	60	90	90	90	90	90	90	90	90	90	90	90	90	90
	Temperature, °C		90	90	90	90	90	90	90	90	90	90	90	90	90	90	90	90
<b>Oxygen Delignification Condition</b>	NaOH charge, g/kg OD pulp		16.67	16.67	16.67	20.00	23.33	16.67	16.67	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
	O <sub>2</sub> pressure, kPa		1034	1034	1034	1034	1034	1034	1034	1034	1034	1034	1034	1034	1034	1034	1034	1034
	Consistency, %		12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12
	Quantum mixer time, sec		0	0	0	0	0	0	0	0	5	10	10	10	10	15		
<b>DZSTS (corrected)</b>	kPa	306	267	257	279	260	263	281	264	287	273	255						
		303	271	257	262	263	256	271	244	281	286	265						
		306	260	263	265	260	276	291	254	267	283	272						
		297	257	267	275	273	259	278	264	274	270	252						
		303	278	263	265	270	253	271	261	267	276	249						
		310	260	274	275	266	276	285	257	277	280	269						
		300	271	260	272	256	263	271	264	267	286	265						
		300	278	270	279	263	259	288	251	291	290	272						
		317	271	274	272	270	270	278	271	274	276	265						
		313	278	280	279	260	256	271	261	264	283	269						
		317	278			263	270		264	281	263							
	avg	307	270	266	272	264	264	278	260	275	279	264						
	std dev	6.8	7.7	7.9	6.3	5.4	8.2	7.6	7.5	8.9	8.1	8.3						
	% error	2.2	2.9	3.0	2.3	2.0	3.1	2.7	2.9	3.2	2.9	3.2						
	% error avg	2.8																

## 2. Wet zero span tensile strength error calculation

	Pre O <sub>2</sub>	Post O <sub>2</sub>	50 min											
			90	120	60	90	90	90	90	90	90	90	90	
Oxygen Delignification Condition	Reaction time, min		90	120	60	90	90	90	90	90	90	90	90	
	Temperature, °C		90	90	90	90	90	90	85	95	90	90	90	
	NaOH charge, g/kg OD pulp		16.67	16.67	16.67	20.00	23.33	16.67	16.67	20.00	20.00	20.00	20.00	
	O <sub>2</sub> pressure, kPa		1034	1034	1034	1034	1034	1034	1034	1034	1034	1034	1034	
	Consistency, %		12	12	12	12	12	12	12	12	12	12	12	
	Quantum mixer time, sec		0	0	0	0	0	0	0	0	5	10	15	
WZSTS (corrected)	kPa	290	237	227	245	233	229	221	224	230	230	229	229	
		273	233	233	231	226	222	211	224	220	223	196	196	
		273	237	237	231	236	226	201		210	237	202	202	
		249	226	233	242	236	229	204		206	227	205	205	
		262	233	240		236	236	218		219	213	196	196	
		283	240	237		219	215	228		223	210	192	192	
avg std dev % error % error avg		280	233	230		229	226	235		206	243	189	189	
		253	230	230		226	222			206	207	199	199	
		266	237				232			213	220	189	189	
		259	233							213	203	189	189	
		269	234	233	237	230	226	217	224	215	221	199	199	
		13.2	8.6	4.5	7.1	6.3	6.1	12.3	0.0	8.2	13.2	12.1	12.1	
	4.9	3.4	1.9	3.0	2.7	2.7	5.7	0.0	3.8	6.0	6.1	6.1		

### 3. Tensile index error calculation

[illegible]

#### 4. Tear index error calculation

<b>Oxygen Delignification Condition</b>	Reaction time, min	60	70	120	60	100	120	60	120	70	120	60	120
	Temperature, °C	70	10.0	10.0	100	100	100	70	100	30.0	30.0	100	100
	NaOH charge, g/kg OD pulp	10.0	1034	1034	1034	1034	1034	30.0	1034	1034	1034	30.0	30.0
	O <sub>2</sub> pressure, kPa	1034	12	12	12	12	12	12	12	12	12	12	12
	Consistency, %	15	15	15	15	15	15	15	15	15	15	15	15
	Quantum mixer time, sec												
Tear Index	mN.m <sup>2</sup> /g	5.9	5.0	5.0	3.4	2.7	4.6	4.0	2.5	2.1	2.1	2.1	2.1
		5.3	5.7	5.7	3.2	2.4	3.9	3.3	2.0	2.1	2.1	2.1	2.1
		5.2			3.2		3.9						
	avg	5.5	5.4	5.4	3.3	2.6	4.2	3.7	2.3	2.1	2.1	2.1	2.1
	stdev	0.3	0.5	0.5	0.1	0.2	0.4	0.5	0.4	0.0	0.0	0.0	0.0
% error		6.3	9.4	9.4	3.0	7.9	9.6	13.3	17.2	0.0	0.0	0.0	0.0
	% error avg	8.3											

[illegible]



[illegible]



## 7. Fines content error calculation

Oxygen Delignification Condition	Reaction time, min	60	120	60	120	60	120	60	120
	Temperature, °C	70	70	100	100	70	70	100	100
	NaOH charge, g/kg OD pulp	10.0	10.0	10.0	10.0	30.0	30.0	30.0	30.0
	O <sub>2</sub> pressure, kPa	1034	1034	1034	1034	1034	1034	1034	1034
	Consistency, %	12	12	12	12	12	12	12	12
	Quantum mixer time, sec	15	15	15	15	15	15	15	15
Fines - length w.	%	0.75	0.81	0.68	0.86	0.75	0.73	0.73	0.85
avg		0.69	0.75	0.76	0.89	0.66	0.77	0.82	0.85
stdev		0.72	0.78	0.72	0.88	0.71	0.75	0.78	0.85
% error		0.04	0.04	0.06	0.02	0.06	0.03	0.06	0.00
% error avg	5.3	5.9	5.4	7.9	2.4	9.0	3.8	8.2	0.0

## 8. Mean fiber length error calculation

<b>Oxygen Delignification Condition</b>	Reaction time, min	60	120	60	120	60	120	60	120
	Temperature, °C	70	100	70	100	70	100	70	100
	NaOH charge, g/kg OD pulp	10.0	10.0	10.0	10.0	30.0	30.0	30.0	30.0
	O <sub>2</sub> pressure, kPa	1034	1034	1034	1034	1034	1034	1034	1034
	Consistency, %	12	12	12	12	12	12	12	12
	Quantum mixer time, sec	15	15	15	15	15	15	15	15
Mean length - l. w.	mm	0.67	0.68	0.69	0.66	0.67	0.68	0.63	0.67
avg		0.68	0.67	0.67	0.65	0.73	0.70	0.65	0.64
stdev		0.68	0.68	0.68	0.65	0.70	0.69	0.64	0.65
% error		0.01	0.00	0.01	0.01	0.04	0.01	0.01	0.02
% error avg	2.3	<b>0.84</b>	<b>0.63</b>	<b>2.07</b>	<b>2.05</b>	<b>6.36</b>	<b>1.74</b>	<b>1.66</b>	<b>2.82</b>

## 9. Fiber curl error calculation

<b>Oxygen Delignification Condition</b>	Reaction time, min	60	120	60	120	60	120	60	120	60	120
	Temperature, °C	70	70	100	100	70	70	100	100	70	70
	NaOH charge, g/kg OD pulp	10.0	10.0	10.0	10.0	30.0	30.0	30.0	30.0	30.0	30.0
	O <sub>2</sub> pressure, kPa	1034	1034	1034	1034	1034	1034	1034	1034	1034	1034
	Consistency, %	12	12	12	12	12	12	12	12	12	12
	Quantum mixer time, sec	15	15	15	15	15	15	15	15	15	15
Mean curl - l. w.		0.063	0.074	0.079	0.105	0.071	0.078	0.118	0.126		
avg		0.064	0.074	0.076	0.106	0.071	0.073	0.117	0.122		
stdev		0.064	0.074	0.078	0.106	0.071	0.076	0.118	0.124		
% error		0.001	0.000	0.002	0.001	0.000	0.004	0.001	0.003		
% error avg	1.5	1.11	0.00	2.74	0.67	0.00	4.68	0.60	2.28		

## 10. Fiber kink error calculation

<b>Oxygen Delignification Condition</b>	Reaction time, min	60	120	60	120	60	120	60	120	60	120
	Temperature, °C	70	100	100	100	70	100	100	100	70	100
	NaOH charge, g/kg OD pulp	10.0	10.0	10.0	10.0	30.0	30.0	30.0	30.0	30.0	30.0
	O <sub>2</sub> pressure, kPa	1034	1034	1034	1034	1034	1034	1034	1034	1034	1034
	Consistency, %	12	12	12	12	12	12	12	12	12	12
	Quantum mixer time, sec	15	15	15	15	15	15	15	15	15	15
Kink index	1/mm	1.18	1.34	1.37	1.64	1.2	1.34	1.76	1.84		
		1.24	1.4	1.26	1.67	1.28	1.32	1.76	1.76		
avg		1.21	1.37	1.32	1.66	1.24	1.33	1.76	1.80		
stdev		0.04	0.04	0.08	0.02	0.06	0.01	0.00	0.06		
% error		<b>3.5</b>	<b>3.1</b>	<b>5.9</b>	<b>1.3</b>	<b>4.6</b>	<b>1.1</b>	<b>0.0</b>	<b>3.1</b>		
% error avg	<b>2.8</b>										

# 11. Kappa number error calculation

Oxygen Delignification Condition	Reaction time, min	60	120	60	120	60	120	60	120	60	120
	Temperature, °C	70	70	100	100	70	70	100	100	70	70
	NaOH charge, g/kg OD pulp	10.0	10.0	10.0	10.0	30.0	30.0	30.0	30.0	30.0	30.0
	O <sub>2</sub> pressure, kPa	1034	1034	1034	1034	1034	1034	1034	1034	1034	1034
	Consistency, %	12	12	12	12	12	12	12	12	12	12
	Quantum mixer time, sec	15	15	15	15	15	15	15	15	15	15
Kappa		8.9	8.1	7.1	5.9	8.5	8.2	5.7	5.4		
avg		9.0	8.0	7.4	5.9	8.6	8.1	6.0	5.6		
stdev		8.9	8.1	7.3	5.9	8.5	8.2	5.9	5.5		
% error		0.01	0.05	0.18	0.01	0.12	0.11	0.21	0.12		
% error avg	1.5	0.2	0.6	2.5	0.1	1.4	1.4	3.6	2.1		

## 12. Viscosity error calculation

<b>Oxygen Delignification Condition</b>	Reaction time, min	60	120	60	120	60	120	60	120	60	120
	Temperature, °C	70	100	100	100	70	100	100	100	70	100
	NaOH charge, g/kg OD pulp	10.0	10.0	10.0	10.0	30.0	30.0	30.0	30.0	30.0	30.0
	O <sub>2</sub> pressure, kPa	1034	1034	1034	1034	1034	1034	1034	1034	1034	1034
	Consistency, %	12	12	12	12	12	12	12	12	12	12
	Quantum mixer time, sec	15	15	15	15	15	15	15	15	15	15
Viscosity	cP	19.0	16.0	18.0	12.8	19.6	17.0	10.3	10.6		
avg		18.7	16.3	17.7	12.6	19.8	17.3	10.2	10.6		
stdev		18.9	16.2	17.8	12.7	19.7	17.1	10.2	10.6		
% error		0.21	0.24	0.24	0.15	0.08	0.20	0.06	0.03		
% error avg	0.9	1.12	1.49	1.32	1.19	0.39	1.16	0.56	0.25		

### 13. Hexenuronic acids measurement error calculation

<b>Oxygen Delignification Condition</b>	Reaction time, min	90
	Temperature, °C	90
	NaOH charge, g/kg OD pulp	16.67
	O <sub>2</sub> pressure, kPa	1034
	Consistency, %	12
	Quantum mixer time, sec	0
HexA	mmol/g	27.0
		27.3
avg		27.2
stdev		0.22
<b>% error</b>		<b>0.81</b>
<b>% error avg</b>	<b>0.8</b>	

### 14. Cellulose/hemicelluloses measurement error calculation

<b>Oxygen Delignification Condition</b>	Reaction time, min	90	90	90
	Temperature, °C	90	85	90
	NaOH charge, g/kg OD pulp	20.00	16.67	20.00
	O <sub>2</sub> pressure, kPa	1034	1034	1034
	Consistency, %	12	12	12
	Quantum mixer time, sec	0	0	10
Cellulose	%	35.7	38.7	31.1
		36.0	34.6	31.5
avg		35.8	36.6	31.3
stdev		0.26	2.88	0.22
<b>% error</b>		<b>0.73</b>	<b>7.86</b>	<b>0.70</b>
Hemicellulose	%	64.3	61.4	68.9
		64.0	65.4	68.6
avg		64.2	63.4	68.7
stdev		0.26	2.88	0.22
<b>% error</b>		<b>0.41</b>	<b>4.54</b>	<b>0.32</b>
<b>% error avg</b>	<b>2.4</b>			



[illegible]



[illegible]

## APPENDIX B

### SUMMARY OF TEST RESULTS

#### 1. SUMMARY OF OXYGEN DELIGNIFICATION TEST RESULTS

			Pre O <sub>2</sub>	Post O <sub>2</sub>	reaction time, min			NaOH charge, g/kg pulp			reaction temperature, °C			mixing time, sec		
	Parameter	Unit			60	90	120	16.67	20.00	23.33	85	90	95	5	10	15
1	Kappa number		9.6	4.9	6.2	5.8	5.3	5.8	6.4	6.5	7.0	5.8	6.0	6.6	6.5	6.4
2	Viscosity	cP	23.5	12.4	16.6	15.8	14.0	15.8	14.8	13.8	16.4	15.8	13.4	12.1	12.4	11.6
3	HexA	µMol/g	29.6	23.4	28.0	27.3	27.6	27.3	28.2	27.9	27.0	27.3	27.9	27.7	29.2	29.2
4	Total charge	µeq/g	77.1	64.3	73.6	74.2	70.0	74.2	72.9	74.2	77.0	74.2	69.6	72.7	70.7	70.3
5	DCM extractive	%	1.08	0.49	0.41	0.43	0.41	0.43	0.42	0.55	0.61	0.43	0.37	0.26	0.27	0.27
6	Alpha-cellulose	%	35.2	34.4	34.2	34.8	35.3	34.8	35.7	34.8	34.6	34.8	31.8	33.0	31.1	29.6
7	Gamma-cellulose	%	8.3	8.2	6.4	6.3	8.3	6.3	6.4	6.1	7.4	6.3	4.5	5.8	7.7	4.8
8	Beta-cellulose	%	56.4	57.5	59.4	59.0	56.4	59.0	57.9	59.1	58.0	59.0	63.7	61.2	61.2	65.6
9	DZSTS	kPa	307	290	272	270	266	270	264	264	278	270	260	275	279	264
10	WZSTS	kPa	269	248	237	234	233	234	230	226	217	234	224	215	221	199
11	Tear Index	mN.m <sup>2</sup> /g	6.83	8.09	4.75	5.49	4.72	5.49	5.41	5.17	4.35	5.49	4.24	6.22	6.00	6.86
12	Burst Index	kPa.m <sup>2</sup> /g	1.96	2.31	1.22	1.17	1.16	1.17	1.23	1.14	1.19	1.17	0.97	1.47	1.51	1.26
13	Tensile Index	Nm/g	43.7	43.0	26.9	24.5	26.0	24.5	27.1	25.4	26.6	24.5	21.9	30.6	30.9	27.4
14	Brightness	%	41.7	57.9	51.0	52.2	55.0	52.2	53.6	54.9	51.9	52.2	56.5	52.8	52.8	53.9
15	Fines	%	0.66	0.79	0.78	0.63	0.62	0.63	0.70	0.66	0.73	0.63	0.91	0.79	0.89	0.88
16	Fiber length	mm	0.69	0.66	0.68	0.67	0.67	0.67	0.67	0.66	0.70	0.67	0.67	0.66	0.66	0.67
17	Fiber Curl		0.072	0.076	0.078	0.085	0.088	0.085	0.091	0.090	0.082	0.085	0.095	0.071	0.081	0.084
18	Fiber Kink index	1/mm	1.23	1.37	1.34	1.45	1.54	1.45	1.53	1.53	1.48	1.45	1.64	1.31	1.45	1.44

## 2. SUMMARY OF YATES' ALGORITHM TEST RESULTS

	Experiment number	y1	y2	y3	y4	y5	y6	y7	y8
	Reaction time, min	60	120	60	120	60	120	60	120
	Temperature, °C	70	70	100	100	70	70	100	100
<b>Oxygen Delignification Condition</b>	NaOH charge, g/kg OD pulp	10.0	10.0	10.0	10.0	30.0	30.0	30.0	30.0
	O2 pressure, kPa	1034	1034	1034	1034	1034	1034	1034	1034
	Consistency, %	12	12	12	12	12	12	12	12
	Quantum mixer time, sec	15	15	15	15	15	15	15	15
Brightness	%	45.3	47.9	52.6	59.1	47.1	50.0	58.2	60.1
Tensile Index	Nm/g	29.3	27.8	18.8	14.7	23.7	20.4	12.4	11.9
Tear Index	mN.m <sup>2</sup> /g	5.47	5.39	3.26	2.59	4.17	3.70	2.26	2.11
Burst Index	kPa.m <sup>2</sup> /g	1.41	1.38	0.65	0.56	0.96	0.85	0.47	0.43
DZSTS	kPa	292	284	290	249	291	277	203	217
WZSTS	kPa	242	238	236	198	211	200	151	152
Kappa number		8.9	8.1	7.3	5.9	8.5	8.2	5.9	5.5
Fines	%	0.72	0.78	0.72	0.88	0.71	0.75	0.78	0.85
Fiber length	mm	0.68	0.68	0.68	0.65	0.70	0.69	0.64	0.65
Fiber Curl		0.064	0.074	0.078	0.106	0.071	0.076	0.118	0.124
Fiber Kink index	1/mm	1.21	1.37	1.32	1.66	1.24	1.33	1.76	1.80
Viscosity	cP	18.9	16.2	17.8	12.7	19.7	17.1	10.2	10.6
Total charge	µeq/g	80.3	80.4	80.4	76.5	80.5	77.6	76.6	71.8
DCM extractives	%	0.29	0.29	0.44	0.19	0.39	0.34	0.17	0.16

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