

**Studies on Peroxymonosulfuric Acid Treatment for
Totally Chlorine-free Bleaching of
Hardwoods Prehydrolysis-kraft Pulps**

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**Studies on Peroxymonosulfuric Acid Treatment for
Totally Chlorine-free Bleaching of
Hardwoods Prehydrolysis-kraft Pulps**

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Abbreviation

Abbreviation	Description
AOX	Adsorbable Organic Halogen
BOD	Biochemical Oxygen Demand
BSN	National Standardization Agency of Indonesia
COD	Chemical Oxygen Demand
cP	Centipoise
D	Chlorine Dioxide
DP	Dissolving Pulp
E	Extraction
ECF	Elementary Chlorine-Free
E _p	Extraction with Hydrogen Peroxide
HexA	Hexenuronic Acid
HPLC	High Performance Liquid Chromatography
IC	Ion Chromatography
KP	Kraft Pulp
LOKP	Hardwood Oxygen-bleached Kraft Pulp
mPa.s	Millipascal second
Nm ³	Normal cubic meter (25°C and 1 atm)
O	Oxygen
PC	Pulp Consistency
Ph	Prehydrolysis
PHL	Prehydrolysis Liquor / Prehydrolyzate
P _{sa}	Peroxymonosulfuric Acid / H ₂ SO ₅

SNI	Indonesian National Standard
TCF	Totally Chlorine-Free
TSS	Total Suspended Solid
UV	Ultra Violet
Z	Ozone

Chapter 1 Introduction

1.1 Indonesian pulp and paper industry

The pulp and paper industry is one of Indonesia's major industries. The Indonesian pulp and paper industry has grown rapidly since the late 1980s, and Indonesia has emerged as one of the top three pulp and paper producers in Asia and one of the top ten pulp and paper producers in the world.¹⁾ Global consumption of dissolving pulp has doubled from its nadir in 2000, reaching 6 million tons in 2012.²⁾ Meanwhile, in Indonesia, dissolving pulp is still an imported commodity; Toba Pulp Lestari (Indo Barat Rayon, APRIL Group) and South Pacific Viscose (Lenzing, Austria) are the only two dissolving pulp production companies in this country.³⁻⁵⁾ This situation is likely to change in the future, as Indonesia has plans to increase their dissolving pulp production.^{6,7)} Indonesia has several advantages over other pulp and paper producing countries, including its location near the equator, where the sun shines year-round and the harvesting times are shorter. Indonesia is also conveniently surrounded by numerous economically developing Asian countries, creating the potential for the future emergence of a very large new market for pulp and paper products. Relative to its competitors, Indonesia also has more land space for growth and development, especially for the expansion of industrial forest plantations, which serve as sources of raw materials.

During the production process, all Indonesian pulp and paper mills still use the elementary chlorine-free (ECF) method as the main bleaching process. The Indonesian government has developed standards for pulp and paper products, which have been authorized as the Indonesian National Standard (SNI) and officially approved by the National Standardization Agency of Indonesia (BSN). Some standards related to dissolving pulp⁸⁾ are listed in **Table 1.1**.⁸⁾ Per these standards, the quality requirements for dissolving pulp are 88% ISO for brightness, 6.2 mPa.s for viscosity, and 94% α -cellulose.

1.2 Indonesia's environmental policies regarding the pulp and paper industry

As a developing country whose pulp and paper sector has potential for growth, Indonesia needs environmental laws, regulations, standards, and requirements to control the industrial sector and preserve the environment, which should remain capable of sustaining humans and other organisms. The development of Indonesian environmental laws began in the Dutch colonial period, or possibly earlier, and has continued since then. After Indonesia gained independence, the idea of national environmental legislation was first proposed in 1972, coinciding with the Stockholm Convention. An environmental regulation plan was proposed in 1976 and later confirmed in 1982. Since then, environmental regulations have been continuously reviewed and evaluated and updated periodically.

The Indonesian government has issued some regulations concerning the pulp and paper industry to control pollution, including wastewater regulation, which was last updated in 2014 by ministerial regulation No. 5/2014, replacing the previous ministerial decree, No. 51/1995 (**Tables 1.2 and 1.3**).⁹⁾ Meanwhile, air emission regulations have been developed in accordance with ministerial decree No. 13/1995 (**Table 1.4**).¹⁰⁾ Regarding steam boilers, ministerial decree No. 13/1995 (attachment number V-B) was updated in 2007 by ministerial regulation No. 7/2007 (**Table 1.5**).¹¹⁾ Meanwhile, ambient air pollution is controlled by regulation No. 41/1999 (**Table 1.6**).¹²⁾ Ministerial regulation No. 51/1995 (**Table 1.2**) restricted the wastewater discharge by the dissolving pulp industry to no more than 95 m³/tons, while the cap for bleached kraft pulp discharge is 85 m³/tons. According to this standard, wastewater discharged by the dissolving pulp industry can contain no more than 100 mg/L biochemical oxygen demand (BOD₅), 300 mg/L chemical oxygen demand (COD), and 100 mg/L total suspended solids (TSS), while the corresponding values for the bleached kraft industry are 100 mg/L BOD₅, 350 mg/L COD, and 100 mg/L TSS. **Table 1.2** also shows that the maximum wastewater loads are 9.5 kg/ton BOD₅, 28.5 kg/ton COD, and 9.5

kg/ton TSS for the dissolving pulp industry and 8.5 kg/ton BOD₅, 29.75 kg/ton COD, and 8.5 kg/ton TSS for bleached kraft pulp. Meanwhile, for the rayon industry, the maximum discharge is 130 m³/tons, while the maximum wastewater contents are 60 mg/L BOD₅, 150 mg/L COD, and 100 mg/L TSS (**Table 1.3**).

Furthermore, air emission quality standards restrict the bleach plants used in the pulp and paper industry to a maximum emission load of 10 mg/m³ of chlorine gas and/or 125 mg/m³ of chlorine dioxide (**Table 1.4**). As observed in this table, there is no maximum emission load provided for chloroform. To control the ambient air quality, the Indonesian government also limited the chlorine and chlorine dioxide concentrations in the ambient air to 150 µg/(N.m³) over a 24 h measurement period (**Table 1.6**).

In general, bleaching processes can be classified as chlorine, ECF, or totally chlorine-free (TCF). A safer alternative is available on the market for the chemical facilities used by the pulp and paper industry, allowing this industry to reduce or even eliminate unnecessary risks for workers and local communities in terms of intentional or accidental chemical release. By reducing the chemical dosage used in ECF bleaching or by shifting from ECF to TCF bleaching, the pulp and paper industry implements the 3 R's (reuse, reduce and recycle), a concept of environmental management that is often used to improve the environmental performance and competitiveness of numerous industries in parallel. This dosage reduction can also reduce potential hazards to workers and improve the bleaching process by reducing or eliminating the use of toxic, volatile, and flammable chemicals. Furthermore, it can improve the environmental performance of chemical and waste treatment facilities. The utilization of hazardous chemicals in the bleaching process often generates toxic byproducts or pollutants. Although the transition process may require initial capital investment, the reduction in operational costs (especially for the handling of hazardous materials and

wastewater treatment) provided by this technology will eventually prove to be advantageous.^{13,14)}

Table1.1 Indonesian quality standards for dissolving pulp⁸⁾

Parameter	Standard
α -Cellulose	Min 94%
S ₁₈ (Solubility)	Max 4.9%
S ₁₀ (Solubility)	Max 7.9%
Extractive content (dichloromethane)	Max 0.2%
Ash content	Max 0.15%
Acid insoluble ash	Max 80 mg/kg
Calcium content (Ca)	Max 150 mg/kg
Fe content	Max 8 mg/kg
Viscosity (intrinsic)	Min 400 mL/g
Viscosity (cupric ethylenediamine)	Min 6.2 mPa.s (cP)
Brightness	Min 88% ISO
Water content	Max 11%

Table 1.2 Indonesian quality standards for wastewater from pulp dan paper industry⁹⁾

Process/ Product	Parameters						
	Discharge (m ³ /ton)	BOD ₅		COD		TSS	
		Max content (mg/L)	Max load (kg/ton)	Max content (mg/L)	Max load (kg/ton)	Max content (mg/L)	Max load (kg/ton)
A. Pulp							
Bleached kraft	85	100	8.5	350	29.75	100	8.5
Dissolving pulp	95	100	9.5	300	28.5	100	9.5
Unbleached kraft	50	75	3.75	200	10.0	60	3.0
CMP and Grounwood	60	50	3.0	120	7.2	75	4.5
Semi- chemical	70	100	7.0	200	14.0	100	7.0
Alkaline pulp	80	100	8.0	300	24.0	100	8.0
De-ink pulp	60	100	6.0	300	18.0	100	6.0

Table 1.3 Indonesian quality standards for wastewater from rayon industry⁹⁾

Parameter	Maximum level
pH	6-9
BOD	60 mg/L
COD	150 mg/L
TSS	100 mg/L
Sulfide	0.3 mg/L
Zn	5 mg/L
Maximum quantity wastewater	130 m ³ /ton product of rayon fiber

Table 1.4 Indonesian quality standards for emission from pulp and paper industry ¹⁰⁾

Source	Parameters	Max load (mg/m ³)
Recovery furnace	Total particle	230
	Total reduced sulfur (TRS)	10
Lime Kiln	Total particle	350
	Total reduced sulfur (TRS)	28
Smelt dissolving tank	Total particle	260
	Total reduced sulfur (TRS)	28
Digester	Total reduced sulfur (TRS)	10
Bleach plant	Chlorine (Cl ₂)	10
	Chlorine dioxide (ClO ₂)	125
Power boiler	Total particle	230
	Sulfur dioxide (SO ₂)	800
	Nitrogen oxide (NO ₂)	1000
All	Opacity	35%

Table 1.5 Indonesian quality standards for steam boiler emission from industry¹¹⁾

Parameter	Fuel		
	Coal	Oil	Gas
Particulate	230 mg/m ³	200 mg/m ³	-
Sulfur dioxide	750 mg/m ³	700 mg/m ³	150 mg/m ³
Nitrogen oxide	825 mg/m ³	700 mg/m ³	650 mg/m ³
Opacity	20 %	15 %	-

Table 1.6 Indonesian quality standards for ambient air ¹²⁾

Parameter	Measurement time ^a	Standard
SO ₂	1 hour	900 µg/Nm ³
	24 hours	365 µg/Nm ³
	1 year	60 µg/Nm ³
CO	1 hour	30,000 µg/Nm ³
	24 hours	10,000 µg/Nm ³
NO ₂	1 hour	400 µg/Nm ³
	24 hours	150 µg/Nm ³
	1 year	100 µg/Nm ³
Oxidant	1 hour	235 µg/Nm ³
	1 year	50 µg/Nm ³
HC (Hydrocarbon)	3 hours	160 µg/Nm ³
PM ₁₀ (Particle<10mm)	24 hours	150 µg/Nm ³
PM _{2.5} (Particle<2.5mm)	24 hours	65 µg/Nm ³
	1 year	15 µg/Nm ³
TSP (Dust)	24 hours	230 µg/Nm ³
	1 year	90 µg/Nm ³
Pb	24 hours	2 µg/Nm ³
	1 year	1 µg/Nm ³
Dust fall	30 days	10 Tons/km ² /month
Total fluorides (as F)	24 hours	3 µg/Nm ³
	90 days	0.5 µg/Nm ³
Fluor index	30 days	40 µg/100cm ²
Chlorine & chlorine dioxide	24 hours	150 µg/Nm ³
Sulfate index	30 days	1 mg SO ₃ /100 cm ³

^aMeasured at 25°C and 1 atm

1.3 Bleaching process

1.3.1 Oxygen bleaching

The oxygen bleaching process dates back to 1867, with the first patent involving the flow of hot air through pulp.¹⁵⁾ In this technique, the pulp viscosity decreases sharply at the beginning of the oxygen delignification step. The disadvantage of this bleaching process was later ameliorated by the addition of magnesium salts.¹⁶⁾

The main benefit of the oxygen bleaching process is its environment-friendliness. The application of oxygen bleaching in ECF bleaching chemicals could reduce the demand for chlorine dioxide in the subsequent process, which may in turn reduce the concentration of chlorinated organic products in the wastewater. The oxygen bleaching process has also been found to substantially decrease the BOD, COD, and wastewater color.¹⁷⁾

1.3.2 Chlorine dioxide bleaching

Chlorine dioxide bleaching has stronger selectivity compared to other bleaching processes. Chlorine dioxide readily reacts with lignin and does not have a significant effect on carbohydrate degradation. The first patent on the chlorine dioxide bleaching process was published in 1854.^{18,19)} However, chlorine dioxide bleaching still discharges organochlorine compounds in the form of chloroform from the bleaching and wastewater treatment processes.^{20,21)} In addition, organochlorine species are still present in the solid waste that accumulates in the activated sludge during wastewater treatment.

With a boiling point of 11°C, chlorine dioxide is a volatile liquid with similar hazards level to chlorine. Chlorine dioxide is flammable (as a gas) and combustible (as a liquid). In the case of accidental exposure or deliberate release, the potential hazards of chlorine dioxide include eye, nose, and throat irritation; coughing; wheezing; bronchitis; pulmonary edema; and chronic bronchitis.²²⁾

1.3.3 Ozone bleaching

The first patent on the ozone bleaching process was published in 1889.²³⁾ Meanwhile, the optimal conditions for ozone bleaching were first identified in 1949.²⁴⁾ Although the potential of ozone bleaching was recognized between 1960-1970, its commercial application is still far lower than that of chlorine dioxide bleaching. The main reasons are the low selectivity and higher cost of ozone bleaching relative to chlorine bleaching. The low selectivity of the ozone bleaching process is caused by the formation of radicals, which react with either lignin or carbohydrates.²⁵⁾ Ozone is a highly reactive gas that reacts explosively with easily oxidized substances and reducing agents.²⁶⁾ Recently, it was found that implementing an acid stage before the ozone bleaching stage has a positive impact on the degree of polymerization.²⁷⁾

1.3.4 Alkaline extraction

The role of alkaline extraction is to remove the lignin that has reacted in the previous acid oxidation stage and become potentially soluble. The alkaline extraction process also allows the pulp to undergo further oxidation. In contrast, the acidic oxidation process modifies the molecular structure of lignin and creates blocking groups that prevent further oxidation. The blocking groups can be broken down under alkaline conditions.²⁸⁾

1.3.5 Peroxymonosulfuric acid bleaching

Peroxymonosulfuric acid (H_2SO_5 ; P_{sa}) is a promising alternative reagent for wood delignification and chemical bleaching. P_{sa} has long been recognized as a strong oxidant, having an oxidation potential of +1.44 V.²⁹⁾ Although P_{sa} contains sulfur and oxygen, the formation of SO_x is limited by the energy requirement of this endothermic reaction.

The first monopersulfate synthesis method was patented in 1957 by Stephanou and Lewiston.³⁰⁾ The use of P_{sa} or its salts in pulp bleaching has been studied extensively and was first patented in 1983.³¹⁾ In 1988, Springer and McSweeney³²⁾ patented a pulp bleaching process using P_{sa} generated *in situ*. In the field of delignification, Minor and Springer³³⁾ have reported a peroxymonosulfate-based delignification process conducted under mild conditions using aspen and oak wood that can produce pulp with good properties for use in linerboard, corrugating medium, and printing paper. Springer³⁴⁾ also reported that at very low pH (below 2) and 22°C, peroxymonosulfate is a much more powerful oxidizing agent than hydrogen peroxide.

In particular, P_{sa} is predicted to be highly compatible with the oxygen bleaching process. Springer and McSweeney³⁵⁾ concluded that the effectiveness of peroxymonosulfate treatment on spruce kraft pulp and commercial pine pulp prior to oxygen delignification is similar to that of chlorine pretreatment. Allison and McGrouther³⁶⁾ have reported the application of P_{sa} using an interstage with an O- P_{sa} -O sequence to improve the oxygen delignification process. Moreover, Troughton *et al.*³⁷⁾ patented the bleaching process of chemical pulp using a O- P_{sa} -P sequence in the United States. This patent covered treatment with P_{sa} at 75-100°C for 70-150 min using a pulp consistency (PC) of 12-25%. Bouchard *et al.*³⁸⁾ have reported that peroxymonosulfate powder can be added directly at the end of the oxygen stage (O- P_{sa}) in an ECF bleaching sequence. Jafari *et al.*³⁹⁾ have reported the application of peroxymonosulfate in the multistage oxygen delignification of high-kappa-number pine kraft pulp using an O- P_{sa} -O- P_{sa} -O sequence, achieving 76% kappa number reduction.

P_{sa} can also be used for the delignification of non-wood materials, such as maize stem or bagasse. RunCang *et al.*^{40,41)} have reported the delignification of maize stem using P_{sa} with water pretreatment. The results showed that peroxymonosulfuric acid has a significant

delignification effect under acid condition. Abou-Yousef *et al.*⁴²⁾ have also reported the delignification of bagasse using NaOH-P_{sa} and NaOH-P_{sa}-NaOH sequences.

It has been recently shown that P_{sa} can decompose hexenuronic acid (HexA). Petitbreuilh *et al.*⁴³⁾ have reported on the removal of HexA from oxygen-predelignified *Eucalyptus globulus* pulp using P_{sa} followed by treatment with the DED sequence of ECF bleaching. Kuwabara *et al.*^{44,45)} have also reported on the decomposition of HexA by the application of P_{sa} in the filtrate from bleached pulp. Hexenuronic acid is one of the compounds that cause pulp yellowing.

The application of P_{sa} bleaching at the mill has also been reported. Yoshida and Koshitsuka⁴⁶⁾ have described processes for the on-site production of P_{sa} installed in Japanese kraft pulp bleaching plants, which have continuously produced stable P_{sa} at approximately 80% yield based on hydrogen peroxide. Tomoda and Uchida^{47,48)} have reported that the application of P_{sa} to ECF bleaching has been successfully implemented via the conversion of the acid bleaching stage by some Japanese bleached pulp mills.

Table 1.7 Oxidation potential of oxidants²⁹⁾

Oxidants		Oxidation potential (e°, V)
$\text{O}_3 + 2\text{H}^+ + 2\text{e}^-$	$\rightarrow \text{O}_2 + \text{H}_2\text{O}$	2.07
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^-$	$\rightarrow 2\text{H}_2\text{O}$	1.78
$\text{HClO}_2 + 3\text{H}^+ + 4\text{e}^-$	$\rightarrow \text{Cl}^- + 2\text{H}_2\text{O}$	1.56
$\text{HSO}_5^- + 2\text{H}^+ + 2\text{e}^-$	$\rightarrow \text{HSO}_4^- + \text{H}_2\text{O}$	1.44
$\text{Cl}_2 + 2\text{e}^-$	$\rightarrow 2\text{Cl}^-$	1.36
$\text{ClO}_2 + \text{H}^+ + \text{e}^-$	$\rightarrow \text{HClO}_2$	1.15
$\text{CH}_3\text{CO}_3\text{H} + 2\text{H}^+ + 2\text{e}^-$	$\rightarrow \text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{O}$	1.06
$\text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^-$	$\rightarrow \text{Cl}^- + 2\text{OH}^-$	0.90
$\text{HOO}^- + \text{H}_2\text{O} + 2\text{e}^-$	$\rightarrow 3\text{OH}^-$	0.87
$\text{ClO}_2^- + 2\text{H}_2\text{O} + 4\text{e}^-$	$\rightarrow \text{Cl}^- + 4\text{OH}^-$	0.78
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$	$\rightarrow 4\text{OH}^-$	0.40

Table 1.8 Comparison between peroxymonosulfuric acid, chlorine dioxide, and ozone^{27, 50-52)}

	H₂SO₅ (P_{sa})	ClO₂ (D)	O₃ (Z)
Form	Liquid	Liquid	Gas
Hazard	Hazardous liquid (oxidant, strong acid, combustible)	Volatile hazardous liquid (oxidant, flammable, combustible)	Hazardous gas, (pressurized, highly reactive oxidant and potentially explosive)
Toxicity	LD ₅₀ 2,140 mg/kg LC ₅₀ (4h) 0.375 mg/L (rat) LC ₅₀ (96h) 16 mg/L (fish)	LD ₅₀ 292 mg/kg LC ₅₀ (4h) 32 mg/L (rat) LC ₅₀ (96h) 0.02 mg/L (fish)	LC ₅₀ (4h) 4.8 mg/L (rat) LC ₅₀ (96h) 0.0093 mg/L (fish)
Wastewater Effluent	Acidic	Organochlorine	Disinfectant
Emission	SO _x (>212°C)	Chloroform (>60°C)	O ₃ and O ₂
Half live	Stable (liquid) (H ₂ SO ₅ , H ₂ O ₂ , H ₂ SO ₄)	Stable (liquid)	3 d (air) 15 min (water)

1.4 Objective of this study

In this study, a modification to the TCF bleaching method using peroxymonosulfuric acid treatment was conducted on hardwood prehydrolysis-kraft (Ph-kraft) pulp. The goal of this study was to investigate potential alternative sequences in TCF bleaching that minimize the use of ozone bleaching as the main oxidant agent. Although ozone is the strongest oxidant in TCF bleaching, ozone stage is still far less used than chlorine dioxide stage because of its low selectivity, high energy consumption, and high pressure requirement.

The outline of this study is as follows:

In the second chapter, the first objective is to investigate the effect of P_{sa} application on hardwood Ph-kraft pulp in terms of kappa number, brightness, viscosity, and HexA content. The second objective is to confirm the effect of P_{sa} on lignin by analyzing the effect of P_{sa} on a lignin model compound of vanillyl alcohol. The third objective is to clarify the final pulp quality after a full bleaching process (including P_{sa} application) on hardwood Ph-kraft pulp in terms of kappa number, brightness, viscosity, and HexA content. The fourth objective is to analyze the selectivity and effectiveness of ozone and peroxymonosulfuric acid bleaching based on the conditions used in this study.

In the third chapter, the first objective is to propose a new TCF bleaching sequence that includes the application of P_{sa} and excludes the ozone application. The second objective is to improve the proposed new TCF sequence and increase the pulp brightness and viscosity by modifying the pulp consistency, the application of a multistage scheme, and the addition of magnesium sulfate. The third objective is to clarify the potential for P_{sa} applications in ECF bleaching and reduce the dosage of chlorine dioxide.

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Chapter 2 Application of Peroxymonosulfuric Acid as a Modification of the Totally Chlorine-free Bleaching of Acacia Wood Prehydrolysis-kraft Pulp

2.1 Introduction

Indonesia is the ninth largest pulp producer and is the sixth in production of paper and paper board in the world, with the largest volumes generated by two pulp and paper mill groups, Asia Pulp & Paper and Asia Pacific Resources International Limited¹⁾. The pulp production capacity in Indonesia was 8.8 million tons in 2013, and should increase to 10 million tons by 2017. In the production sequence, almost all the Indonesian pulp bleaching mills use chlorine dioxide in elementary chlorine-free (ECF) bleaching.

The switch from chlorine bleaching to ECF bleaching has significantly lowered the quantity of organochlorine substances released in effluent streams and, accordingly, has reduced environmental toxicity. In Japan, the 2007 emissions of adsorbable organic halogen (AOX) or organochlorine substances were reduced to one-fifth of 1997 levels by the switch to ECF bleaching^{2,3)}. However, ECF bleaching still discharges organochlorine compounds in the form of chloroform from the bleaching and wastewater treatment processes^{2,4)}. In addition, organochlorine species are still present in the effluent and accumulate in the activated sludge during wastewater treatment.

In contrast, totally chlorine-free (TCF) bleaching is a process that eliminates the possibility of AOX formation. The interchange of ECF with TCF bleaching will further diminish AOX emissions as well as the amounts of organochlorine substances found in effluents, activated sludge, and the air. However, we must also note that TCF bleaching can produce harmful non-chlorinated environmental pollutants⁵⁾. Furthermore, based on investigations⁶⁾, the TCF bleaching process also has the potential to produce halogenated compounds. Even in low concentrations, chloride ions can be incorporated into halogenated byproducts. In a practical sense, to diminish AOX formation in the system, all processes

should be totally free from supplemental chloride ions, including the closed water system.

Hexenuronic acid (HexA) is considered to cause the brightness reversion (yellowing) of pulp and increases the consumption of bleaching reagents⁷⁻⁹. HexA is an unsaturated molecule that contributes to the consumption of permanganate during the determination of the kappa number, which is proportional to the lignin content, and results in higher values during lignin determinations. It has been reported that the removal of HexA from TCF pulp affects the pulp properties¹⁰.

Peroxymonosulfuric acid (H_2SO_5 ; P_{sa}) has been identified as a promising alternative reagent for the delignification of wood and the bleaching of chemical¹¹⁻¹³. During oxygen delignification the treatment of a chelated pulp with P_{sa} was shown to afford kappa number reduction¹⁴. P_{sa} can improve the brightness of chemical pulp from the perspective of ECF bleaching¹⁵, as well as solubilize lignin¹⁶ and decompose HexA^{17,18}. Recently, it was found that highly stable P_{sa} , as Caro's acid (a mixture of concentrated sulfuric acid and hydrogen peroxide) could be produced on the industrial scale¹⁹, and was successfully incorporated in the bleaching process in Japanese paper mills as a substitute for the acid washing stage during hardwood ECF bleaching²⁰.

In this study, in order to determine a new sequence for TCF bleaching, the application of P_{sa} as a modification of the TCF bleaching process was investigated on hardwood prehydrolysis-kraft pulp.

2.2 Experimental

2.2.1 Materials

Acacia (*Acacia mearnsii*) wood chips obtained from South Africa were used. P_{sa} was synthesized by dropping 95% sulfuric acid (Wako Pure Chemical Industries, Ltd.) into 45% hydrogen peroxide aqueous solution (Mitsubishi Gas Chemical Company, Inc.) at 70°C. The molar ratio of H_2SO_4 to H_2O_2 was 3.0. After mixing, the solution was immediately diluted

with chilled water. The P_{sa} concentration was determined by subtracting the amount of redox titration with cerium (IV) sulfate, which can oxidize residual H_2O_2 , from the total amount of peroxide determined by iodometric titration using $Na_2S_2O_3$. Oxygen-bleached hardwood kraft pulp (LOKP) was prepared from eucalyptus–acacia mixed hardwoods as a non-prehydrolysis-kraft pulp, and was provided by the Niigata Mill, Hokuetsu Kishu Paper Co., Ltd., Japan.

2.2.2 Prehydrolysis and Kraft Cooking

Acacia wood chips were prehydrolyzed at 147°C for 90 min, and kraft-cooked with 18% active alkali and 30% sulfidity at 150°C for 1 to 3 h (H-factor: 165 to 496). The liquor-to-wood ratio was 4 mL/g.

2.2.3 P_{sa} Treatment

Laboratory-prepared pulps and the Niigata mill LOKP were treated with P_{sa} for 70 min at 70°C at a pulp consistency (PC) of 10%. A target amount of P_{sa} solution and aqueous sodium hydroxide to adjust the acidity to pH 3 were added to the pulp suspension.

To determine the required dosage of P_{sa} to the pulp, it was considered that the required molar ratio of P_{sa} to a HexA model compound (hexenuronosyl-xylotriose: Δ -X3) for degradation was about 3.4²¹⁾. When the P_{sa} dosage is 1.0% of the pulp weight, it is estimated that 87.7 mmol P_{sa} is added to 1 kg pulp. It is expected that approximately 26 mmol HexA can be removed from 1 kg pulp.

2.2.4 TCF Bleaching

Pulps were treated under the following conditions:

(1) Oxygen bleaching (O)

PC: 30% (high consistency); oxygen pressure: 0.5 MPa; NaOH dosage: 1%; reaction

temperature and time: 115°C for 60 min.

(2) P_{sa} treatment (P_{sa})

Conditions are as described above.

(3) Ozone bleaching (Z)

PC: 30% (high consistency); pH 3; ozone dosage: 0.5%; reaction temperature and time: 28°C for 15 min.

(4) Alkaline extraction (E) and alkaline extraction with hydrogen peroxide (E_p)

E: PC:10%; NaOH dosage: 1%; reaction temperature and time: 60°C for 60 min.

E_p: PC:10%; H₂O₂ dosage: 1.4%; NaOH dosage: 1%; reaction temperature and time: 70°C for 60 min.

2.2.5 Pulp Testing

Kappa numbers, viscosities and brightness were determined according to TAPPI Test Methods: T236 cm-13, T254 cm-10 and T452 om-08, respectively²²⁾. The brightness (ISO) was measured using a Tokyo-Denshoku Digital Color Meter Model TC-1500 SX. HexA content was determined from 2-furancarboxylic acid and 5-formyl-2-furancarboxylic acid after formic acid hydrolysis at pH 2.5 and 120°C for 3 h, using high performance liquid chromatography with 4:1 acetonitrile-water (pH 2.5) solution as eluent and a detection wavelength of 265 nm²³⁾. A Zorbax ODS column (ϕ4.6 mm x 250 mm) was used. Acid-insoluble lignin was measured using the Klason lignin method (TAPPI Test Method T222 om-11²²⁾), and acid-soluble lignin was determined by UV-Vis spectrophotometry²⁴⁾. The carbohydrate composition of the pulp and the monosaccharide and oligosaccharide contents of the hydrolyzate were determined using a Dionex ICS 3000 ion chromatograph after 4% sulfuric acid hydrolysis at 121°C for 1 h²⁵⁾.

2.2.6 Calculations of Selectivity and Effectiveness

Selectivity was calculated as the kappa number decrease per unit of decreased viscosity ($\Delta\text{kappa number}/\Delta\text{viscosity}$), while effectiveness was calculated as the kappa number decrement per unit chemical dosage ($\Delta\text{kappa number}/\text{unit chemical dosage}$).

2.3 Results and discussion

2.3.1 Characterization of Raw Materials

The prehydrolysis process is an important step for producing dissolving pulp with kraft cooking, which consists of removing part of the hemicelluloses²⁶⁾. As shown in **Table 2.1**, xylan was a major component removed during the prehydrolysis process. The prehydrolysis also removed a very small part of the lignin.

Table 2.2 shows that the kappa number of the Ph-kraft pulp was lower than that of the non-Ph-kraft pulp, indicating lower lignin content. The greater delignification was caused by the removal of the 1.1% xylan during the prehydrolysis reaction. It was reported that holes that are created in the cell walls of the material after the dissolution of amorphous hemicellulose would allow the favorable penetration of chemicals in the subsequent cooking²⁷⁾. In addition, the final conditions of the prehydrolysis treatment are acidic (pH 4.5), which may cause the cleavage of lignin-carbohydrate complex bonds, and thus improve the subsequent alkaline delignification.

Table 2.1 Chemical composition of *Acacia mearnsii* wood, hydrolyzate, and Ph-kraft pulp

Samples	Yield (%) ^a	Acid-insoluble lignin (%) ^a	Acid-soluble lignin (%) ^a	Glucan (%) ^a	Xylan (%) ^a	Other sugars (%) ^a	Ash (%) ^a	Unknown (%) ^a
Wood		20.3	2.9	41.5	17.1	2.1	0.5	15.4
Hydrolyzate	2.6	0.2	0.1	0.1	1.1	0.4	0.1	0.6
Ph-kraft pulp	45.2	0.7	0.4	39.2	4.3	0.8	0.1	0.03

^a % based on wood

2.3.2 Effects of P_{sa} Treatment on Kappa Number and HexA Content

Kuwabara *et al.*⁸⁾ reported on the relationship between P_{sa} dosage and the decomposition of HexA in pulp. A higher dosage of P_{sa} contributes to increased HexA decomposition. The reaction displays a linear correlation in the range of 0.5 to 1.5% P_{sa} dosage for LOKP. This implies that a 1.0% P_{sa} loading contributes to the decomposition of 13 to 15 mmol/kg HexA. If HexA in the pulp could react with P_{sa} with an efficiency similar to that of the HexA model compound Δ -X3, a 1.0% P_{sa} dosage to the pulp would contribute to the decomposition of 26 mmol/kg HexA²¹⁾. In fact, the efficiency of HexA removal from the pulp was almost half that of the model Δ -X3, because the pulp contained other components such as residual lignin which can react with P_{sa} , in addition to the reactions limited to the solid phase of the pulp.

Ph-kraft pulps with various kappa numbers were treated with P_{sa} before oxygen bleaching. The results showed that the kappa number and HexA content decreased while the brightness increased. Niigata LOKP was also treated at several P_{sa} dosages, resulting in decrements of kappa number and HexA, while the brightness was increased (**Table 2.3**). The experimental data indicated that P_{sa} treatment effectively lowered the kappa number, which is an indicator of lignin removal. Furthermore, the effects were dose-related: a higher dosage of P_{sa} contributed to a larger decrement in the kappa number. Thus, the P_{sa} treatment was able to reduce a part of the residual lignin in the pulp.

Comparing the Ph-kraft pulp and LOKP, the HexA decrement at a 1.0% P_{sa} dosage for the former was in the range 9.0 to 12.0 mmol/kg, whereas that for LOKP was in the range 19.3 to 21.5 mmol/kg. It was found that HexA in the pulp was degraded more easily by P_{sa} treatment when the content was higher.

These experiments showed that the P_{sa} treatment decreased both the kappa number

and HexA content, while increasing the brightness. The application of P_{sa} in TCF bleaching, using the sequence O- P_{sa} -Z-E- E_p , was next investigated.

Table 2.2 Effect of Prehydrolysis on yield, kappa number, and HexA content of pulp

	Yield (%)	Kappa number	HexA (mmol/kg)
Non-Ph-kraft pulp	53.5	24.5	55.0
Ph-kraft pulp	45.2	13.2	18.0
Oxygen-bleached Ph-kraft pulp	-	5.3	19.1

Table 2.3 Effect of P_{sa} dosage on kappa number, HexA content, brightness, and viscosity of pulp

	H ₂ SO ₅ dosage (%)	Kappa number		HexA (mmol/kg pulp)		Brightness (% ISO)		Viscosity (mPa.s)	
		Before	After	Before	After	Before	After	Before	After
Ph- kraft pulp ^a	0.20	21.5	20.7	12.6	10.8	41.4	45.9	85.3	39.3
	0.25	15.7	14.3	15.0	12.3	41.7	46.3	49.0	29.7
	0.30	13.2	11.0	18.0	14.4	41.9	47.9	46.1	27.0
LOKP ^b	0.20	9.1	8.4	60.4	56.1	62.3	66.1	18.2	17.3
	0.40	9.1	7.6	60.4	52.7	62.3	67.0	18.2	15.3
	0.60	9.1	7.1	60.4	47.5	62.3	69.0	18.2	11.7

^a *Acacia mearnsii* pulp by kraft cooking for 1–3 h

^b Eucalyptus–acacia mixed hardwood oxygen-bleached (non-prehydrolyzed) kraft pulp

2.3.3 Effects of P_{sa} Treatment on Kappa Number Determined Using Vanillyl Alcohol

Figure 2.1 (symbol \blacklozenge) shows the relationship between the HexA content and P_{sa} dosage applied to oxygen-bleached Ph-kraft pulp. Application of P_{sa} to the oxygen-bleached Ph-kraft pulp caused the removal of HexA. The 0.5% H_2SO_5 dosage means that 44 mmol H_2SO_5 is added to the 1 kg of pulp during the treatment, and the HexA decrement was 7 mmol/kg at this dosage. Meanwhile, the kappa number decrement as shown in **Figure 2.2** (symbol \blacklozenge) was 3.5. A previous study has shown 1 mol/kg of the HexA decrement corresponds to approximately 0.086 of the kappa number decrement²⁸). The 7 mmol/kg of the decrement indicated 0.6 of the kappa number decrement in this study, and then the difference in 3.5 of the observed decrement and 0.6, which was equal to 2.9, should be caused by the oxidation of residual lignin. To confirm this phenomenon the kappa number decrement using vanillyl alcohol as a free-phenolic lignin model compound was estimated after the P_{sa} treatment.

First, 0.244 mmol (37.5 mg) or 0.061 mmol (9.3 mg) of vanillyl alcohol was mixed with 1 ml (789 mg) of ethanol as a carbohydrate model. Then, 9 ml of water containing 0.044 to 0.132 mmol (0 as control) of H_2SO_5 was added to the mixture. After the P_{sa} treatment for 70 min at 70°C, 400 ml of water, 50 ml of 20% H_2SO_4 and 50 ml of 0.1N $KMnO_4$ were poured into a total mixture, and then the consumed $KMnO_4$ was determined according to TAPPI Test Method T236 cm-13. **Figure 2.2** shows that 0.044 mmol of H_2SO_5 addition contributed to the kappa number decrement by 1.6 to 3.1. It was confirmed that a part of the kappa number decrement observed in the P_{sa} treatment was caused by the lignin oxidation.

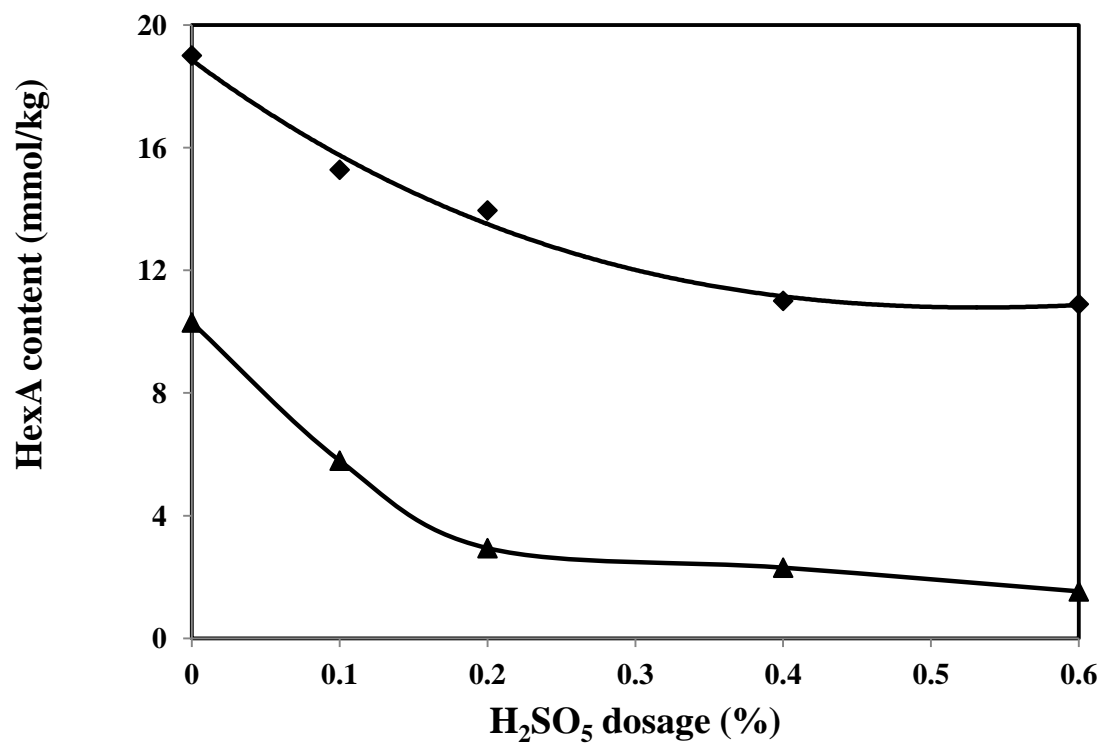


Fig. 2.1 HexA content of the pulp after P_{sa} treatment of oxygen-bleached Ph-kraft pulp, with and without 0.5% ozone application

Legend: ◆: P_{sa} treated; ▲: P_{sa} -Z bleached

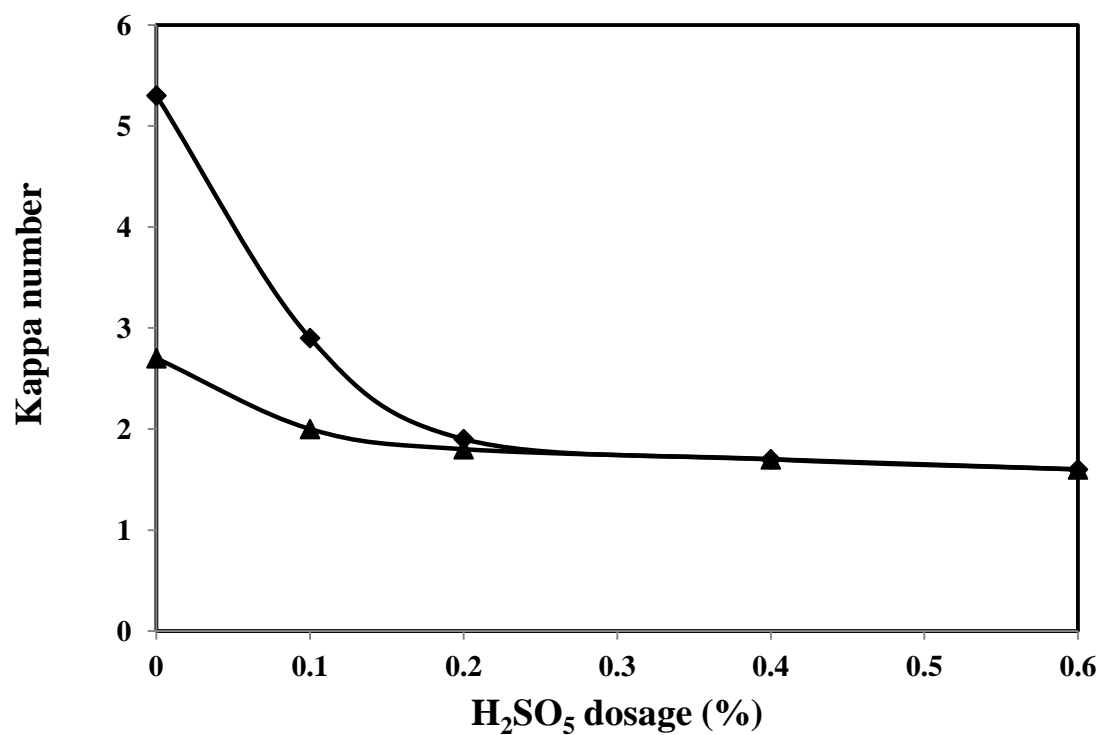


Fig. 2.2 Kappa number of the pulp after P_{sa} treatment of oxygen-bleached Ph-kraft pulp, with and without 0.5% ozone application

Legend: \blacklozenge : P_{sa} treated; \blacktriangle : P_{sa} -Z bleached

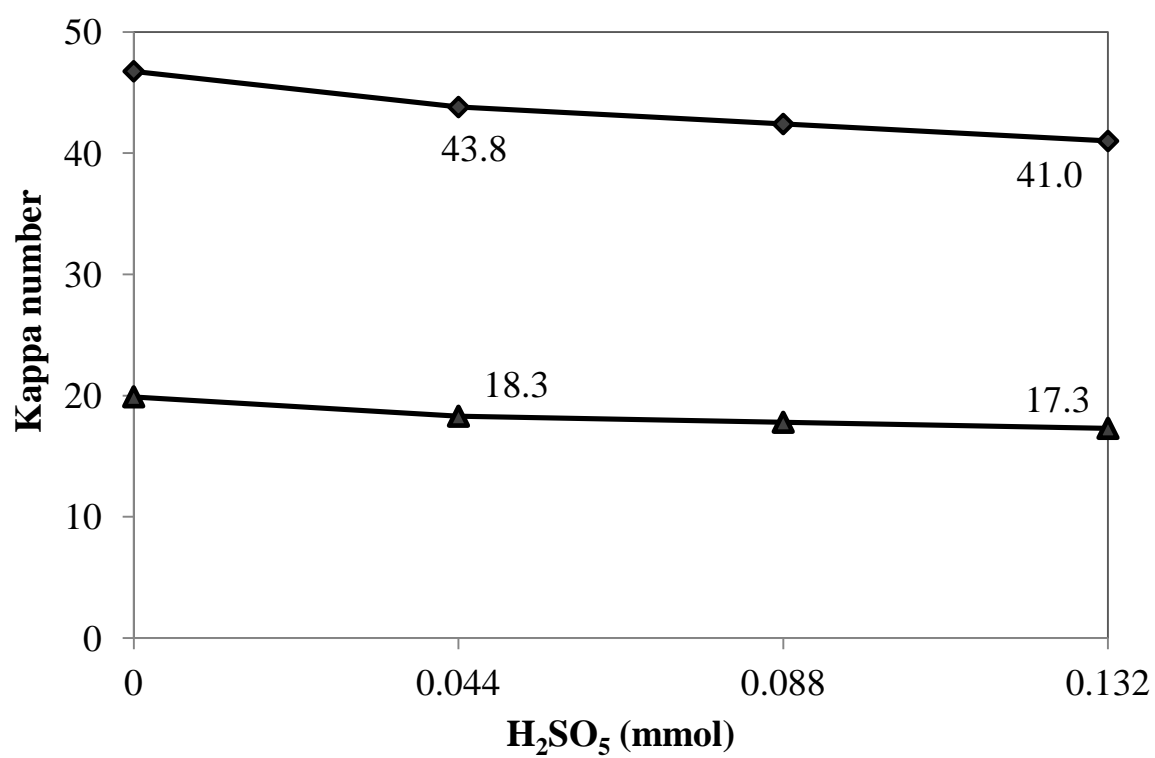


Fig. 2.3 P_{sa} treatment of vanillyl alcohol

Legend: \blacklozenge : 0.244 mmol; \blacktriangle : 0.061 mmol

2.3.4 Application of P_{sa} to TCF Bleaching

2.3.4.1 Effects of P_{sa} on HexA removal from oxygen-bleached Ph-kraft pulp

Figure 2.1 agreed with previous results for LOKP^{8,21)} in which P_{sa} was an effective reagent for reducing HexA. Next, the HexA contents of oxygen-bleached Ph-kraft pulps treated with P_{sa} after ozone bleaching were examined. After ozone bleaching, the HexA content of the P_{sa} -treated pulp was further reduced (**Fig. 2.1**, symbol ▲). HexA increases the consumption of bleaching reagents^{7,8)}. Therefore, the reduction of HexA content would imply that P_{sa} treatment has the potential to reduce ozone consumption in the next stage.

Figure 2.2 shows that after treatment with P_{sa} at a dosage 0.1%, ozone treatment did have an effect on the kappa number decrement. Notably, the ozone treatment showed no significant kappa number decrement after the 0.2 to 0.6% P_{sa} treatment. This was an unexpected result, because the acidic oxidation treatment could lead to modification of the molecular structure of lignin²⁹⁾.

2.3.4.2 Effects of P_{sa} on brightness and viscosity

The relationship between the P_{sa} dosage and brightness showed that a higher dosage of P_{sa} increased pulp brightness. **Figure 2.4** shows that a brightness above 85% ISO was achieved with a P_{sa} dosage above 0.2%. It was found that a P_{sa} dosage of 0.1% could increase the final brightness by 1.0 unit % ISO, while at a 0.6% dosage, brightness was increased by 2.2 unit % ISO.

However, P_{sa} applications from 0.1 to 0.6% decreased pulp viscosity from 21.8 to 15.1 mPa.s (**Fig. 2.5**), which indicates that cellulose is partly degraded. The treatment may have low selectivity due to residual H_2O_2 in the solution. For example, the loss of viscosity during ozone treatment is reportedly due to the reaction between carbohydrates and hydroxyl

and perhydroxyl radicals generated as by-products²⁹⁾. It is presumed that the viscosity loss during P_{sa} treatment would be caused by hydroxyl radicals formed from the residual H_2O_2 . This residual oxidant remains from the synthesis of peroxymonosulfuric acid in which 55% hydrogen peroxide reacts with sulfuric acid at equilibrium. The viscosity loss, as similarly observed during alkaline hydrogen peroxide treatment to improve TCF performance, might be mitigated by the addition of a chelation (Q) stage, but the effects would not be totally identical.

The decreasing pulp viscosity is an indicator of carbohydrate degradation in the pulp. According to Brasileiro *et al.*¹⁶⁾, peracids could be applied in the bleaching process without harming pulp strength properties, and could therefore be used in TCF bleaching without reducing pulp quality. As a result, further research is required to investigate pulp strength properties and viscosities after the application of P_{sa} in TCF bleaching. Next, the selectivity of the P_{sa} and ozone treatments is compared based on kappa number and viscosity.

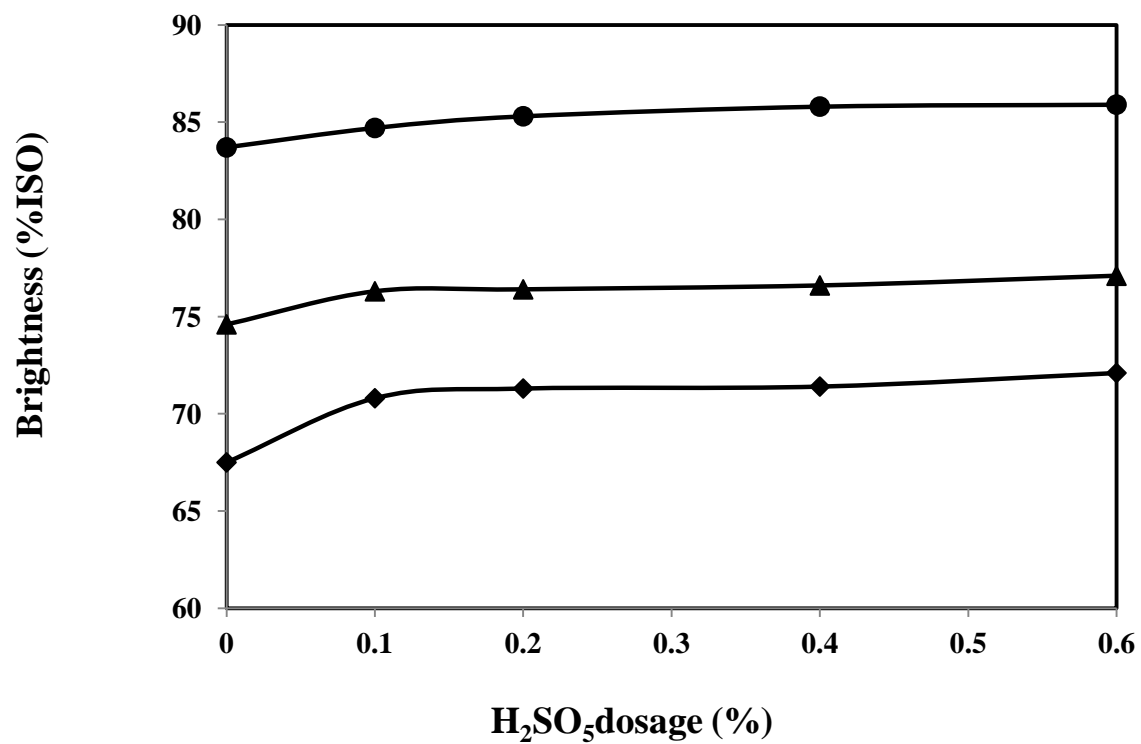


Fig. 2.4 Brightness of pulp produced by modified TCF bleaching with P_{sa} application to oxygen-bleached Ph-kraft pulp

Legend: ◆: P_{sa} treated, ▲: P_{sa}-Z bleached, ●: P_{sa}-Z-E-E_p bleached

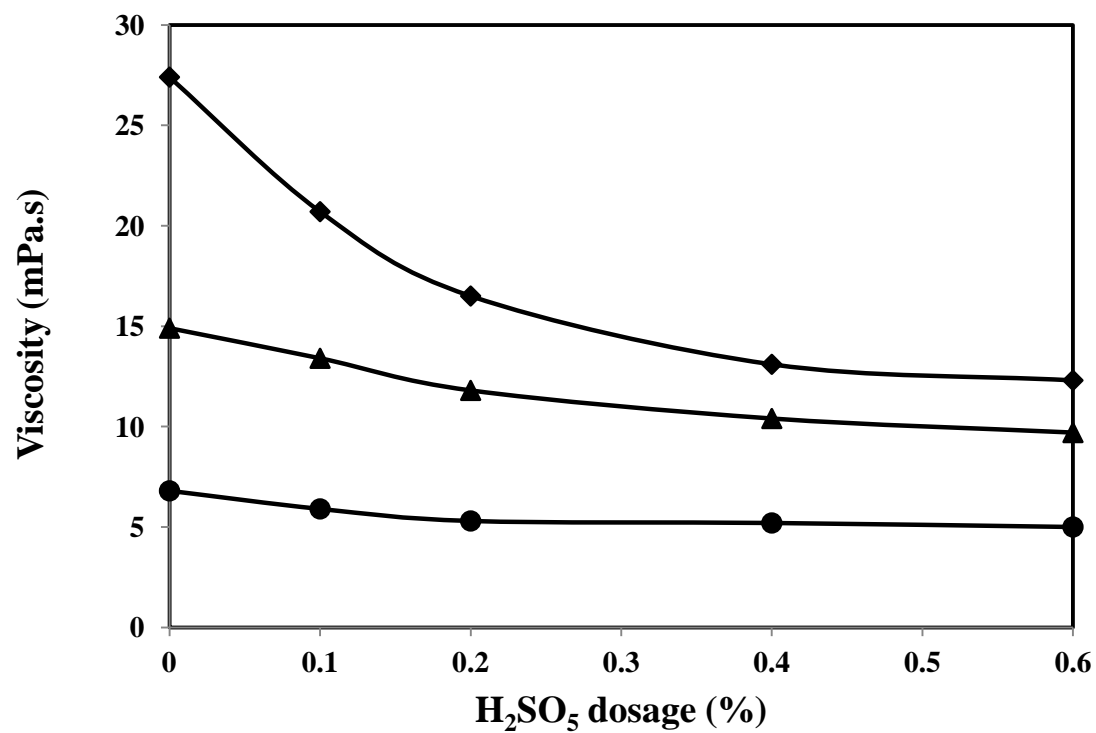


Fig. 2.5 Viscosity of pulp produced by modified TCF bleaching with P_{sa} application to oxygen-bleached Ph-kraft pulp

Legend: ◆: P_{sa} treated, ▲: P_{sa}-Z bleached, ●: P_{sa}-Z-E-E_p bleached

2.3.5 Selectivity and Effectiveness of P_{sa} Based on Kappa Number Decrement

Figures 2.2 and **2.5** show plots of changes in the kappa number and viscosity vs P_{sa} dosage, respectively. A dosage of 0.2% P_{sa} resulted in a kappa number decrease of 3.4 and a 10.9 mPa.s viscosity loss, whereas ozone treatment at a dosage of 0.5% gave a lower decrement of kappa number (2.6) but a higher loss of viscosity (12.5 mPa.s). The selectivity was calculated from the kappa number and viscosity data in **Figs. 2.2** and **2.5**. **Table 2.4** reveals that ozone treatment had a selectivity of 0.21 at a dosage of 0.5%, whereas P_{sa} application exhibited selectivity in the range 0.36 to 0.25 with 0.1 to 0.6% dosages. Thus, P_{sa} demonstrates better selectivity than ozone treatment. The effectiveness as determined from the kappa number decrement, and the chemical dosage of P_{sa} or ozone was calculated on the basis of the data in **Fig. 2.2**. The P_{sa} treatment has a higher effectiveness than ozone: ozone treatment with a 0.5% dosage had an effectiveness of 5.2, whereas P_{sa} treatment had an effectiveness range of 24.0 to 6.2 for P_{sa} dosages of 0.1 to 0.6%. These results suggest a potential benefit the decreased consumption of oxidant in the Z stage. The selectivities calculated for the Z and P_{sa} stages indicate that we may theoretically decrease ozone consumption by increasing the peroxymonosulfuric acid dosage.

Bleaching was conducted using the sequence O- P_{sa} -E- E_p , with a P_{sa} dosage of 0.2%. The final pulp brightness achieved was 82.2% ISO, implying that P_{sa} is a promising alternative reagent for pulp bleaching. However, the application of P_{sa} as a main bleaching agent without ozone treatment is still under further investigation.

Table 2.4 Selectivity and Effectiveness of P_{sa} and Ozone Treatment

H ₂ SO ₅ dosage (%)	Selectivity (Δkappa number/Δviscosity)		Effectiveness (Δkappa number/% chemical used)	
	P _{sa} treated	P _{sa} -Z* bleached	P _{sa} treated	P _{sa} -Z* bleached
0.0	-	0.21	-	5.2
0.1	0.36	0.12	24.0	1.8
0.2	0.31	0.03	17.0	0.2
0.4	0.25	0.00	9.0	0.0
0.6	0.25	0.00	6.2	0.0

* Ozone dosage 0.5%

2.4 Conclusions

1. The application of P_{sa} to the TCF bleaching of *Acacia mearnsii* Ph-kraft pulp using the sequence O- P_{sa} -Z-E- E_p indicated the potential for obtaining high brightness. The experiments resulted in a lower HexA content and a lower kappa number. When the P_{sa} dosage was in the range 0.2 to 0.6%, the brightness reached 85 to 86% ISO.
2. Although the application of P_{sa} in bleaching effectively removed HexA, cellulose was partially depolymerized during the treatment, resulting in a loss of pulp viscosity. The viscosity loss was presumed to result from attack by hydroxyl radicals, which must originate from residual hydrogen peroxide.
3. P_{sa} application also strongly suggested the possibility of decreased ozone consumption. Compared with 0.5% ozone treatment, the application of P_{sa} demonstrated higher selectivity and effectiveness, based on kappa number and viscosity decrements. The preliminary results suggest that P_{sa} can be applied as an alternative to ozone.

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Chapter 3 Peroxymonosulfuric Acid Treatment as an Alternative to Ozone for Totally Chlorine-free and Elementary Chlorine-free Bleaching of Hardwoods Prehydrolysis-kraft Pulp

3.1 Introduction

3.1.1 Present status of the Indonesian pulp and paper industry

The pulp and paper industry is one of the major industries in the world, which is raising environmental concerns over its utilization of vast resources of power, water, and raw materials resulting in large amounts of waste. The Indonesian pulp and paper industry has rapidly expanded since the late 1980s and pushed itself into the group of the largest pulp and paper producers in the world. At the end of 2014, Indonesia was the third largest pulp and paper manufacturer in Asia and the largest ASEAN pulp and paper producer¹⁾.

Around 84 pulp and paper mills contribute to the total pulp production in Indonesia with a total capacity of 8.8 million tons reached in 2013 (**Fig. 3.1**). Most of the produced pulp comes from Asia Pulp and Paper (APP) owned by the Sinar Mas group with its seven subsidiary mills including Tjiwi Kimia, Indah Kiat Pulp & Paper, Pindo Deli Pulp & Papers, Lontar Papyrus Pulp & Paper Industry, Univenus, Ekamas Fortuna, and Purinusa Ekapersada with a total capacity of 2.7 million tons per year. Asia Pacific Resources International Holdings Ltd. (APRIL) owned by the Royal Golden Eagle (RGE) group (including its subsidiary mill Toba Pulp Lestari) comes second with a total capacity of 2.2 million tons per year²⁾.

Compared to other pulp and paper producing countries, Indonesia has some advantages including a location near the equator where the sun shines all year round, and trees grow on average three times faster than in subtropical countries, which means shorter harvesting times. Indonesia is also conveniently situated in the middle of economically developing Asian countries, which can potentially grow into a new giant market for pulp and paper products in the future.

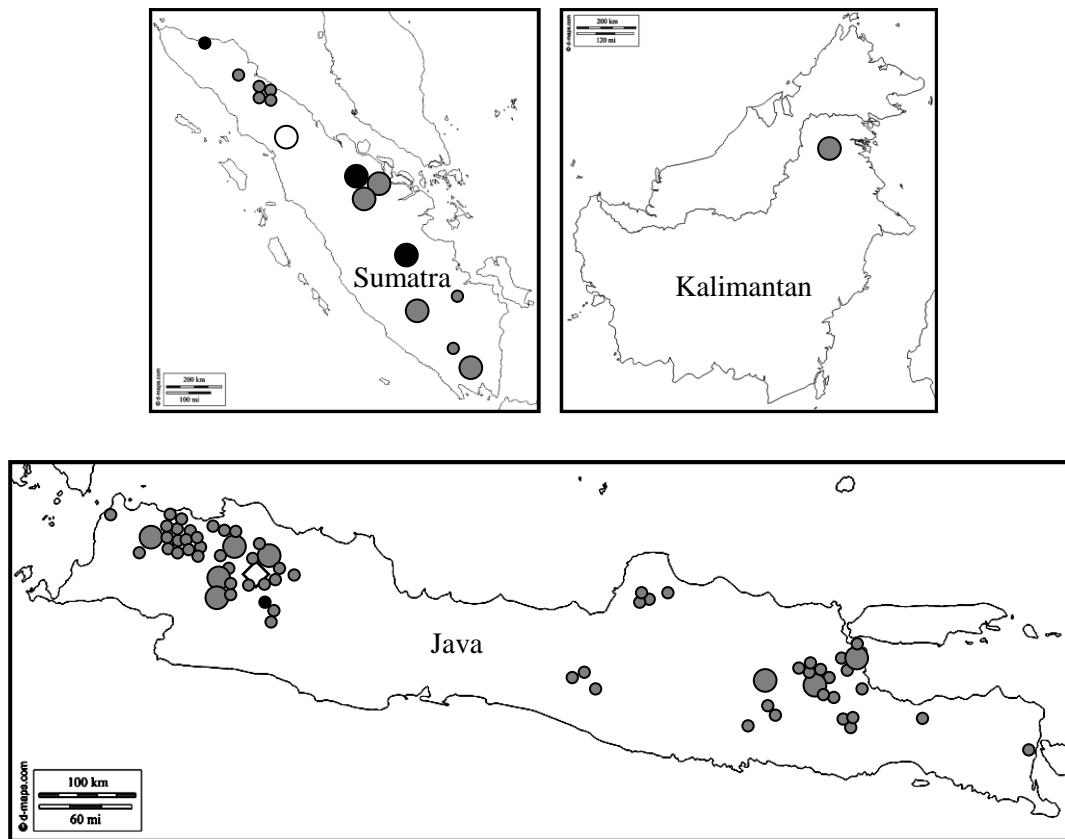


Fig. 3.1 Pulp and paper mills in Indonesia. *Open circle* pulp and dissolving pulp mill; *Open diamond* dissolving pulp mill; *gray filled circle* paper mill; *black filled circle* pulp and paper mill; *large circle/diamond* large mill (>200,000 tons/year); *small circle* small mill (<200,000 tons/year)

Indonesia still has more land space for growth and development under sustainable managements, especially for expansion of industrial forest plantations serving as raw material sources.

Dissolving pulp is still an imported commodity, and Toba Pulp Lestari (Indo Barat Rayon, APRIL-group) along with South Pacific Viscose (Lenzing, Austria) are the only dissolving pulp industries in Indonesia^{2,3}). This situation will likely change in the future as Indonesia is already planning to develop its dissolving pulp production. To maintain high quality, Indonesia has developed pulp and paper standards for products, which have been already authorized as the Indonesian National Standard (SNI) and were officially approved by the National Standardization Agency of Indonesia (BSN). Some standards related to dissolving pulps are listed in **Table A1** of the **Appendix**.

3.1.2 Environmental policy on the pulp and paper industry

As one of the biggest pulp and paper producers, Indonesia is facing circumstances related to environmental pollution caused by pulp and paper wastes, including wastewater and air pollution. Chemical facilities of the pulp and paper industry pose a big threat to the health and safety of its employees and surrounding local communities, especially in the case of accidents or intentional chemical release. As a developing country with a growth potential in the pulp and paper sector, Indonesia needed to develop environmental laws, regulations, standards, and requirements to control the industrial sector and to preserve the environment, which should be able to function properly for humans and other living forms in the world. The development of Indonesian environmental laws started since from the Netherlands' colonial period and has continued ever since. After obtaining independence, the idea of national environmental regulations was first suggested in 1972 and coincided with the Stockholm conference. An environmental regulation plan was launched in 1976 and

confirmed later in 1982 by legalization of Indonesian law on the principal terms of environmental management. The environmental regulations have been regularly evaluated and updated ever since.

The Ministry of Environment and Forestry of Indonesia has issued some regulations regarding the pulp and paper industry to restrict pollution including wastewater from rayon industry, which were last updated in 2014 (**Tables A2** of the **Appendix**).

Despite the environmental regulations, weak monitoring and law enforcement are the reasons behind some environmental problems in the pulp and paper industry. Inti Indorayon Utama Company (IIU) was accused of being responsible for water contamination in Asahan River in the 1990s, which caused bad smell, skin irritation, unsafe drinking water, and polluted agricultural and fishery products, while the local communities suffered severe illnesses and diseases. The local communities of Porsea, supported by an Indonesian non-government organization (NGO) called Indonesian Forum for the Environment (Walhi), protested to the government requesting the company to be shut down. The Indonesian government temporarily closed the IIU factory on March 19, 1999 to perform an international public audit. The audit turned out to be favorable for Indorayon, and the IIU factory opened again in 2003 with tight requirements for clean water treatment. Another incident was related to the water contamination in Siak River by Sinar Mas Indah Kiat in 1992, which resulted in an appearance of dead fish and affected agricultural and fishery products. The protests of local communities supported by Walhi were successful, and compensation in the form of community development was mandated. Currently, Siak River is clean after the installation of water treatment facilities by Sinar Mas Indah Kiat to prevent water pollution.

Meanwhile, global competition in the pulp and paper business is very tight, and the related environmental requirements are becoming increasingly strict. Energy efficiency and environmental friendliness became business requirements for export destination countries,

while customers increasingly demand pulp and paper produced from legitimate sources with official certification confirming the product legality. These conditions stimulate producers to increase their environmental management and performance in order to improve their competitiveness. The pulp and paper industry is an example of an industry with chemical facilities that can readily apply safer alternatives to eliminate or reduce unnecessary risks for their workers and local communities in the event of an accidental or deliberate chemical release.

Under these circumstances, the majority of pulp and paper mills in Indonesia utilize the elementary chlorine-free (ECF) bleaching process as a main process. Although the ECF is still considered one of the best bleaching alternatives today, the pulp and paper industry should start to consider its effect on the environment in the near future in order to remain competitive. The chlorine dioxide (D) stage of the ECF bleaching process is responsible for the release of organochlorine substances from processes and effluent. More than 97% of the produced chloroform does not decompose and is emitted into the atmosphere by volatilization⁴⁻⁷⁾. Possible ways of reducing organochlorine substances in wastewater effluent include minimizing the usage of D bleaching chemicals, introducing a sequence called, for example, an ECF-light bleaching sequence, and a complete substitution of the D bleaching stage by implementing a totally chlorine-free (TCF) bleaching sequence.

An ECF-light bleaching sequence has been recently introduced with the implementation of an ozone stage to decrease chemical consumption during the D stage⁸⁻¹⁰⁾. From an environmental point of view, this method is also compliant with the so-called 3R (reduce, reuse, recycle) policy and prevention against pollution measures achieved by reducing hazardous wastes at their source, modifying production process or promoting the use of less toxic substances¹¹⁾.

3.1.3 Using peroxymonosulfuric acid for delignification and pulp bleaching

Ozone, as the strongest oxidant of the TCF bleaching chemicals, has some disadvantages such as a hazardous gas and high energy consumption. On the other hand, peroxymonosulfuric acid (P_{sa}) or Caro's acid has been known for a long time as a strong oxidant. A method of P_{sa} synthesis has been patented since 1957¹²⁾. In the field of delignification of fibrous materials, peroxymonosulfate exhibited an ability to produce pulps with good properties for linerboard, corrugating medium and other applications. At low pH (below 2), P_{sa} with a dosage of 0.35-5% was more effective in delignification of aspen wood than hydrogen peroxide at 22°C¹³⁾. It can also be used for non-wood materials, such as maize stem, under mild conditions at 20°C for 144 h¹⁴⁾. In the pulp bleaching field, P_{sa} capabilities have been extensively studied and patented since 1983¹⁵⁾. In particular, P_{sa} shows a good compatibility with oxygen bleaching process¹⁶⁻¹⁹⁾. It has been recently shown that P_{sa} possesses the ability to decompose hexenuronic acid (HexA)²⁰⁾. Compared with ozone, P_{sa} also has a higher selectivity and effectiveness as indicated by kappa number decrements and viscosity losses²¹⁾.

The Application of P_{sa} to ECF bleaching was successfully installed as a conversion of acid bleaching stage by some Japanese bleached pulp mills²²⁾. A previous study has also confirmed that it can reduce ozone and chlorine dioxide charges²²⁾.

The objective of this study is to investigate the potential of P_{sa} application in the TCF bleaching without ozone treatment and in the ECF bleaching using small dosages of chlorine dioxide for hardwoods prehydrolysis-kraft (Ph-kraft) pulp.

3.2 Experimental

3.2.1 Materials

Wood chips of a hybrid of *Eucalyptus grandis* and *Eucalyptus pellita* (*E. hybrid*) pruced

in Indonesia was used. *Eucalyptus globulus* produced in Australia was used. The *E. hybrid* was utilized to study its potential to be used as a raw material for existing Indonesian dissolving pulp mills. P_{sa} was synthesized using a procedure reported in the second chapter.

3.2.2 Prehydrolysis and kraft cooking

Wood chips (*E. hybrid*) were prehydrolyzed at 147°C for 90 min, and kraft-cooked with 18% active alkali dosage and 30% sulfidity at 150°C for 180 min. The liquor-to-wood ratio was 4 mL/g. During the prehydrolysis stage, prehydrolysis liquor (PHL) was removed to separate some hemicelluloses in solution and increase cooking performance²³⁾. *Acacia mearnsii* pulps from a previous study²¹⁾ were used as a comparison. For *E. globulus*, wood chips were used to study the effects of prehydrolysis time and active alkali dosages. The length of prehydrolysis time was 90 and 150 min, while the active alkali dosages were 17-19% for 90 min of prehydrolysis, and 14-18% for 150 min.

3.2.3 P_{sa} treatment

A treatment with H_2SO_5 was conducted at 10% pulp consistency (PC) for 70 min at 70°C. A target dosage of H_2SO_5 was varied between 0.2 and 0.6% with small amounts of aqueous sodium hydroxide added to the pulp suspension to adjust its pH to 3. In addition, some experiments were conducted using higher dosages of H_2SO_5 in the range of 1.0-6.0%.

3.2.4 Bleaching

The conditions for each bleaching stage were set as follows:

Oxygen bleaching (O). Pulp consistency (PC): 10% and 30%; oxygen pressure: 0.75 MPa and 0.5 MPa, respectively; NaOH dosage: 1% and 0.6-1.0%, respectively; reaction temperature and time: 115°C for 60 min.

P_{sa} treatment (P_{sa}). Conditions are as described above.

Alkali extraction with hydrogen peroxide bleaching (E_p). PC: 10%; H₂O₂ dosage: 1.0-2.0%; NaOH weight ratio to H₂O₂: 0.7 g/g; reaction temperature and time: 70°C for 60 min.

Chlorine dioxide treatment (D). PC: 10%; reaction temperature and time: 70°C for 60 min; ClO₂ dosage: 0.5%, pH: 3.4; kappa factor: 0.20; maximum ClO₂ dosage: 1.5%.

Ozone treatment (Z). PC: 30% (high consistency); ozone dosage: 0.5%, pH: 3; reaction temperature and time: 25°C for 15 min.

Alkali extraction (E). PC: 10%; NaOH dosage: 1.0%; reaction temperature and time: 60°C for 60 min.

3.2.5 Pulp testing

Kappa number, viscosity, and pulp brightness were determined according to the Tappi Test Methods²⁴⁾ T236 om-13, T254 cm-10, and T452 om-08, respectively. Brightness was measured using a Tokyo-Denshoku digital colorimeter TC-1500 SX and a Technidyne Color Touch 2 Model ISO spectrophotometer. The contents of HexA, acid-insoluble (Klason) lignin, and acid-soluble lignin were determined according to the methods described in a previous paper²⁵⁾. A Dionex ICS 3000 ion-chromatograph was used to determine the carbohydrate composition after 72% sulfuric acid treatment followed by 4% sulfuric acid hydrolysis at 121°C for 1 h²⁶⁾.

3.3 Results and discussion

3.3.1 Characterization of raw materials

According to the results of previous studies, a prehydrolysis procedure can remove hemicelluloses and a very small part of lignin by a separation of PHL^{21, 23)}. A greater delignification degree was achieved during the subsequent kraft cooking process due to a favorable penetration of chemicals²⁷⁾.

Table 3.1 shows the chemical composition of the wood chips obtained from eucalyptus and acacia wood. It was found that eucalyptus woods have similar lignin contents (around 32%), while acacia wood possesses a lower lignin content (23.2%). The xylan content for acacia (17.1%) was higher than that for eucalyptus. **Table 3.2** shows that the *E. globulus* pulp has a higher yield with a lower kappa number and higher brightness, but lower viscosity than the *E. hybrid* and acacia pulps. The same table also indicates that the *E. hybrid* pulp has the highest HexA content, although the wood has a xylan content similar to that for *E. globulus*, which was found to be more easily penetrated by cooking chemicals to obtain a lower kappa number, while xylan was more easily removed to produce pulps with a lower HexA content.

Table 3.1 Chemical composition of materials from hardwoods

	Acid- insoluble lignin (%)	Acid- soluble lignin (%)	Glucan (%)	Xylan (%)	Other sugars (%)	Ash (%)	Unknown (%)
<i>Eucalyptus</i> hybrid	27.8	3.3	43.5	9.1	2.5	0.3	13.5
<i>Eucalyptus globulus</i>	28.6	4.0	40.2	11.6	4.0	0.4	11.2
<i>Acacia mearnsii</i> ^a	20.3	2.9	41.6	17.1	2.2	0.5	15.4

^a Chapter 2

Table 3.2 Properties of pulps prepared by prehydrolysis-kraft cooking

Materials	Prehydrolysis time (min)	Active alkali dosage (%)	Pulp yield (%)	Kappa number	Brightness (% ISO) ^a	Viscosity (cP)	HexA content (mmol/kg)
<i>E. hybrid</i>	90	18	45.6	13.0	40.3	47.8	41.2
<i>A. mearnsii</i>	90	18	45.2	13.2	41.9	46.1	18.0
<i>E. globulus</i>	90	18	48.9	6.2	51.9	32.3	13.2
<i>E. globulus</i>	150	14	44.9	7.6	44.7	39.6	3.4
<i>E. globulus</i>	150	17	44.6	5.4	53.1	21.3	6.1

^a Measured with a Tokyo-Denshoku digital colorimeter TC-1500 SX

3.3.2 Application of P_{sa} to the TCF bleaching sequence

E. hybrid oxygen-bleached pulp prepared with 10% pulp consistency was used for the experiments. Application of P_{sa} to the TCF bleaching with the P_{sa} -E- E_p sequence was investigated for H_2SO_5 dosages ranging from 1.0 to 6.0%. As shown in **Table 3.3**, the P_{sa} treatment decreased both kappa number and viscosity and increased brightness. A large decrease in kappa number from 8.9 to 6.0 at the 1.0% P_{sa} dosage should be caused by a decrement in the HexA content as shown in a similar way previously^{20, 21)}. At the end of the P_{sa} -E- E_p bleaching sequence with the 4.0% P_{sa} dosage, pulps with 79.5% ISO brightness and 4.1 mPa.s viscosity were produced, which are still far from the Indonesian standards²⁸⁾ (88% ISO and 6.2 mPa.s). To increase brightness after the final bleaching stage, higher dosages of H_2SO_5 or H_2O_2 were required. However, larger amounts of bleaching chemicals may also decrease the viscosity (which is undesirable). Some experiments conducted to increase the viscosity of the final bleached pulp are described in the upcoming sections.

3.3.3 Improvements of the TCF bleaching

3.3.3.1 Effects of multi-stage treatments with P_{sa} and E_p

A previous study¹⁹⁾ showed that multistage bleaching sequences with mild chemical dosages improved the viscosity of final bleached pulp. A new O- P_{sa} - E_p - P_{sa} - E_p sequence is proposed in this study to improve the previously reported bleaching sequence. **Table 3.4** shows that the proposed sequence produces pulps with higher brightness than the sequence O- P_{sa} -E- E_p described in **Table 3.3**. Introduction of multistage P_{sa} and E_p treatments resulted in the increased pulp brightness. A mild exposure of bleaching chemicals during the bleaching process should induce little impact on pulp viscosity while improving high pulp brightness.

Table 3.3 Effect of H₂SO₅ application on properties of *E.* hybrid oxygen-bleached pulp^a

H ₂ SO ₅ dosage (%)	Properties after P _{sa} -E-E _p ^b		
	Kappa number	Brightness (% ISO) ^c	Viscosity (mPa.s)
1.0	6.0	73.5	6.9
2.0	3.2	75.5	5.2
4.0	2.5	78.0	4.7
6.0	1.8	79.5	4.1

^a Pulp consistency during oxygen bleaching: 10%; NaOH dosage: 1%; kappa number, brightness and viscosity of pulp: 8.9, 50.9% ISO and 23.0 mPa.s, respectively

^b NaOH and H₂O₂ dosages: 1.4% and 2.0%, respectively

^c Measured with a Technidyne Color Touch 2 Model ISO spectrophotometer

Table 3.4 Effects of multistage sequences with P_{sa}-E_p-P_{sa}-E_p stages on properties of *E.* hybrid oxygen-bleached pulp^a

Chemical dosage (%)					Properties after P _{sa} -E _p -P _{sa} -E _p			
P _{sa}		E _p		P _{sa}		E _p		Viscosity (mPa.s)
H ₂ SO ₅	H ₂ O ₂	MgSO ₄	H ₂ SO ₅	H ₂ O ₂	Total		Brightness (% ISO) ^b	
					H ₂ SO ₅	H ₂ O ₂		
0.2	1.4	0	0.2	1.4	0.4	2.8	84.5	4.7
0.2	1.4	0	0.2	2.0	0.4	3.4	85.4	4.4
0.4	1.4	0	0.4	1.4	0.8	2.8	84.6	4.3
0.4	1.4	0	0.4	2.0	0.8	3.4	85.6	4.0
0.2	1.4	0.2	0.2	1.4	0.4	2.8	85.1	5.1
0.4	1.4	0.2	0.8	2.0	0.8	3.4	86.4	4.1

^a Pulp consistency during oxygen bleaching: 10%; NaOH dosage: 1%; kappa number, brightness and viscosity of pulp: 8.9, 50.9% ISO and 23.0 mPa.s, respectively

^b Measured with a Tokyo-Denshoku digital colorimeter TC-1500 SX

3.3.3.2 Effect of MgSO₄ addition during the E_p and P_{sa} stages

It is well known that MgSO₄ addition during the E_p stage has a beneficial effect on pulp brightness and viscosity by stabilizing the peroxide and oxygen species²⁹⁻³¹). In this study, MgSO₄ application to the first E_p stage slightly increased the pulp viscosity and its brightness (**Table 3.4**), while 2.8% H₂O₂ with 0.2% MgSO₄ enhanced its brightness with a slight increment in viscosity. High brightness of 85.1% ISO with viscosity 5.1 mPa.s was reached with the 0.4% H₂SO₅ dosage.

To obtain information about the effect of MgSO₄ on H₂SO₅ stabilization, MgSO₄ was added during the P_{sa} stage. However, the results showed that the pulp brightness and viscosity for pulps after P_{sa} stage, with and without the addition of MgSO₄, were similar either at 0.2 or 0.4% H₂SO₅ dosages. The pulp brightness and viscosity of the pulps, with and without the addition of MgSO₄, were also similar even after the E_p stages.

3.3.3.3 Effect of pulp consistency during oxygen bleaching

Pulp brightness at the final bleaching stage did not reach 88% ISO. To increase it, an effect of pulp consistency during the O stage was investigated. High pulp consistency is characterized by the absence of most of the free liquid phase, resulting in a higher gas-liquid interface area and reducing the thickness of the liquid layer, which forces oxygen gas to diffuse through the liquid layer to reach the fiber³²). As shown previously in **Table 3.5** and **Table 3.6**, the increment of pulp consistency during the O stage from 10% to 30% improved both kappa number and brightness parameters from 8.9 to 5.7 and from 50.9 to 62.6% ISO, respectively. Unfortunately, it also caused a slight decrement in viscosity from 23.0 to 21.6 mPa.s. If the oxygen bleaching stage were followed by P_{sa} treatment, the differences in brightness (11.7 points) become smaller, while the differences in viscosity (1.4 points) remained the same (**Table 3.6**).

When oxygen-bleached pulps obtained by treatment with high pulp consistency were used, high brightness values 87.3-88.3% ISO were reached during the final stage of the bleaching sequence O-P_{sa}-E_p-P_{sa}-E_p as shown in **Table 3.6**. The final pulp brightness was high enough reaching the required minimum value of 88% ISO, while the viscosity parameters were 5.1-6.0 mPa.s and still low. The measured pulp qualities were better than those obtained for the sequence involving the ozone (Z) stage both in this experiment and a previous study with acacia wood²¹). **Table 3.7** shows that the ozone treatment stage can be completely replaced by a combination of P_{sa} and E_p stages.

3.3.3.4 Further approach by introducing different raw materials

As already stated earlier, *E. globulus* wood was easier to be penetrated by cooking chemicals to produce pulps with lower kappa numbers, and hemicelluloses of the wood were easier to remove to produce pulps with lower HexA contents. We assumed that the pulp will be easier to be penetrated by bleaching chemicals. In this section, *E. globulus* was used to investigate the possibility of TCF bleaching using the O-P_{sa}-E_p-P_{sa}-E_p sequence.

Wood was treated for longer time of prehydrolysis and lower active alkali dosages to produce pulps with higher viscosities. As shown in **Table 3.2**, a pulp with a viscosity of 39.6 mPa.s and HexA content of 3.4 mmol/kg was obtained at a prehydrolysis time of 150 min and active alkali dosage of 14%. A pulp with a similar kappa number (6.2 and 7.6) could also be produced by the prolonged prehydrolysis time and lowering the active alkali dosage, which resulted in a higher viscosity, lower HexA content, but also lowering brightness from 51.9 to 44.7% ISO. Unfortunately, after the bleaching using the O-P_{sa}-E_p-P_{sa}-E_p sequence the viscosity was already low, while the brightness above 88% ISO also could not be achieved. Further studies with better qualities of raw materials are required to investigate this possibility.

Table 3.5 Effects of prehydrolysis time, active alkali dosage of kraft cooking and oxygen bleaching on properties of pulps

Materials	Prehydrolysis time (min)	Active alkali dosage of kraft cooking (%)	Conditions and pulp Properties of oxygen bleaching ^a				
			NaOH dosage (%)	Kappa number	Brightness (% ISO) ^b	Viscosity (cP)	HexA content (mmol/kg)
<i>E. hybrid</i>	90	18	1.0	5.7	62.6	21.6	41.5
<i>A. mearnsii</i>	90	18	1.0	5.3	67.5	27.4	19.1
<i>E. globulus</i>	90	18	1.0	3.5	74.5	16.4	12.6
<i>E. globulus</i>	150	14	0.6	3.3	69.7	25.1	3.3
<i>E. globulus</i>	150	17	0.6	2.6	73.3	13.8	5.8
<i>E. globulus</i>	150	17	1.0	2.2	76.2	11.4	6.0

^a Pulp consistency: 30%

^b Measured with a Tokyo-Denshoku digital colorimeter TC-1500 SX

Table 3.6 Effect of pulp consistency during oxygen bleaching of *E.* hybrid prehydrolysis-kraft pulp on brightness and viscosity after P_{sa} treatment

Pulp consistency (%) during oxygen bleaching	H ₂ SO ₅ dosage (%)	Kappa number	Brightness (% ISO) ^a	Viscosity (cP)
10	Untreated	8.9	50.9	23.0
	0.2	-	61.5	14.2
	0.4	-	62.6	12.4
30	Untreated	5.7	62.6	21.6
	0.2	-	65.3	13.4
	0.4	-	66.3	11.1

^a Measured with a Tokyo-Denshoku digital colorimeter TC-1500 SX

Table 3.7 Comparison between brightness and viscosity at the end of the O^a-P_{sa}-E_p-P_{sa}-E_p sequence and the sequence using ozone (Z)

Materials	Sequence	Total chemical dosage (%)				Brightness (% ISO) ^b	Viscosity (mPa.s)
		O ₃	H ₂ SO ₅	H ₂ O ₂	MgSO ₄		
<i>E. hybrid</i>	O ^a -P _{sa} -E _p -P _{sa} -E _p	0	0.4	4.0	0.2	87.3	6.0
	O ^a -P _{sa} -E _p -P _{sa} -E _p	0	0.8	4.0	0.2	88.3	5.1
	O ^a -P _{sa} -Z-E _p	0.5	0.4	2.0	0	83.1	5.4
	O ^a -Z-E _p	0.5	-	2.0	0	81.7	8.3
<i>A. mearnsii</i> ^{ref.21)}	O ^a -P _{sa} -Z-E _p	0.5	0.4	1.4	0	85.8	5.2
	O ^a -Z-E _p	0.5	-	1.4	0	83.7	6.8
Indonesian standards ^{ref.28)}						88.0	6.2

^a Pulp consistency during oxygen bleaching: 30%; NaOH dosage: 1.0%

^b Measured with a Tokyo-Denshoku digital colorimeter TC-1500 SX

Table 3.8 Effect of P_{sa} application on properties of *E.* hybrid prehydrolysis-kraft pulp bleached using O^a-P_{sa}-D-E_p sequence

H ₂ SO ₅ dosage (%)	ClO ₂ dosage (%)	ClO ₂ reduction (%)	Brightness (% ISO) ^b			Viscosity (cP)		
			O-P _{sa}	O-P _{sa} -D	O-P _{sa} -D-E _p ^c	O-P _{sa}	O-P _{sa} -D	O-P _{sa} -D-E _p ^c
0.0	1.54	-	-	-	87.6	-	-	15.0
0.2	1.51	2	61.5	73.7	87.9	14.2	14.2	10.1
0.4	1.32	14	62.1	74.2	88.0	12.4	11.5	8.9
0.6	1.24	20	62.6	75.3	88.2	10.9	10.8	8.1
1.0	1.18	23	63.5	75.2	88.3	9.6	9.5	7.5

^a Pulp consistency: 10%; NaOH dosage: 1.0%

^b Measured with a Tokyo-Denshoku digital colorimeter TC-1500 SX

^c NaOH and H₂O₂ dosages of the final E_p stage: 1.4% and 2.0%, respectively

3.3.4 Application of P_{sa} to the ECF bleaching sequence

An ECF bleaching sequence was performed to replace a part of D treatment with P_{sa} treatment. The ECF sequence with O-P_{sa}-D-E_p stages resulted in fully bleached pulps with 87.9-88.3% ISO brightness as shown in **Table 3.8**. Brightness of 87.6% ISO was reached after the E_p stage with 1.54% ClO₂ and 0.0% H₂SO₅ dosages. Higher brightness was achieved after increasing the H₂SO₅ dosage and decreasing the ClO₂ dosage. The 0.4% H₂SO₅ dosage with 1.32% ClO₂ was sufficient to achieve the brightness and viscosity values suggested by the Indonesian standards for dissolving pulp²⁸⁾. These experiments indicate that the specified P_{sa} treatment can improve pulp brightness and decrease the amount of ClO₂ consumption during the ECF bleaching. A reduction in the ClO₂ consumption by 14% was reached at a H₂SO₅ dosage of 0.4%. However, the replacement of chlorine dioxide with P_{sa} also caused a 40% viscosity loss from 15.0 to 8.9 mPa.s. Although the viscosity value decreased after an increase in the P_{sa} dosage, all viscosities of the fully bleached pulps remained above the minimum standard level of 6.2 mPa.s²⁸⁾. The obtained results indicate a benefit of the decreased chlorine dioxide amount during the D stage after its partial replacement with P_{sa}, and suggest a potential application of P_{sa} in the ECF bleaching.

As shown in **Table 3.9**, brightness above 88% ISO and viscosity above 7.3 mPa.s can be easily reached by the ECF bleaching with the O-P_{sa}-E_p-D sequence consuming only 0.2% H₂SO₅ and 0.5% ClO₂ for *E. globulus* Ph-kraft pulp. Compared with the EFB pulp from a previous study²³⁾, the O-P_{sa}(0.4)-D-E_p sequence for *E. hybrid* Ph-kraft pulp was characterized with a lower ClO₂ consumption.

Table 3.9 Application of P_{sa} to prehydrolysis-kraft pulps bleached using O^a-P_{sa}-E_p-D sequence

Wood	Kappa number of O-bleached pulp	H ₂ SO ₅ dosage (%)	H ₂ O ₂ dosage (%)	ClO ₂ dosage (%)	Brightness (% ISO) ^b	Viscosity (cP)
<i>E. globulus</i>	3.3	0.2	0.7	0.50	88.1	7.3
<i>A. mearnsii</i>	5.3	0.2	0.7	0.50	86.0	11.8

^a Pulp consistency: 30%^b Measured with a Tokyo-Denshoku digital colorimeter TC-1500 SX

Table 3.9 Application of P_{sa} to ECF bleaching of prehydrolysis-kraft pulps

Wood	Sequence	H ₂ SO ₅ dosage (%)	ClO ₂ dosage (%)	H ₂ O ₂ dosage (%)	Brightness (% ISO) ^c	Viscosity (mPa.s)
<i>E. hybrid</i>	O ^a -P _{sa} -D-E _p	0.4	1.32	2.0	88.0	8.9
<i>E. globulus</i>	O ^b -P _{sa} -E _p -D	0.2	0.50	0.7	88.1	7.3
<i>A. mearnsii</i>	O ^a -P _{sa} -E _p -D	0.2	0.50	0.7	86.0	11.8
EFB ^{ref.23)}	P _{sa} -D-E _p -D	0.2	3.40	1.4	90.7	8.5

^a Pulp consistency during oxygen bleaching: 30%; NaOH dosage: 1%

^b Pulp consistency during oxygen bleaching: 30%; NaOH dosage: 0.6%

^c Measured with a Tokyo-Denshoku digital colorimeter TC-1500 SX

3.4 Conclusions

1. Application of P_{sa} to the TCF bleaching of hardwood prehydrolysis-kraft pulp with the $O-P_{sa}-E_p-P_{sa}-E_p$ sequence can be considered a new modified TCF bleaching method. Brightness between 87.3-88.1% ISO can be obtained after the final bleaching of *E.hybrid* pulp, while the viscosity was in the region of 5.1-6.0 mPa.s, which is below the minimum Indonesian standard level. This result is higher than that obtained by the $O-P_{sa}-Z-E_p$ sequence with 83.1% ISO brightness and 5.4 mPa.s.
2. The Z stage can be completely replaced with a combination of the P_{sa} and E_p stages in the TCF bleaching resulting from the $O-P_{sa}-E_p-P_{sa}-E_p$ sequence.
3. As a result of the ECF bleaching of *E. globulus* prehydrolysis-kraft pulp using the $O-P_{sa}-E_p-D$ sequence, 88.1% ISO brightness with 7.3 mPa.s viscosity can be reached at a P_{sa} dosage of 0.2% and a ClO_2 dosage of only 0.5% during the D stage. The obtained brightness and viscosity levels can be above the Indonesian standard level.

Appendix

Indonesian quality standards for dissolving pulp²⁸⁾ and wastewater from the rayon industry³³⁾ are given in **Tables A1** and **A2**, respectively.

Table A1 Indonesian quality standards for dissolving pulp²⁸⁾

No	Parameter	Unit	Standard
1	α -Cellulose	%	Min 94
2	S ₁₈	%	Max 4.9
3	S ₁₀	%	Max 7.9
4	Extractive content (dichloromethane)	%	Max 0.2
5	Ash content	%	Max 0.15
6	Acid insoluble ash	mg/kg	Max 80
7	Calcium content (Ca)	mg/kg	Max 150
8	Fe content	mg/kg	Max 8
9	Viscosity (intrinsic)	mL/g	Min 400
10	Viscosity (cupric ethylenediamine)	mPa·s	Min 6.2
11	Brightness	% ISO	Min 88
12	Water content	%	Max 11

Table A2 Indonesian quality standards for wastewater from rayon industry^{ref. 33)}

Parameters	Unit	Maximum level
pH	-	6-9
BOD	mg/L	60
COD	mg/L	150
TSS	mg/L	100
Sulfide	mg/L	0.3
Zn	mg/L	5
Maximum quantity wastewater	m ³ /ton product of rayon fiber	130

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Chapter 4 General Conclusion

In the experiment reported in this dissertation, a modification of the TCF bleaching process by P_{sa} application to its sequence has been developed. The results showed the possibility of diminishing or eliminating the use of ozone bleaching by a combined O, P_{sa} and E_p stage. Unfortunately, the viscosity of the product was below the Indonesian standard. Further research is required to optimize the chemical dosages, modified sequence bleaching process, and process conditions.

Concerning industrial applications, P_{sa} shows some prospects in ECF bleaching, while further research is required for its application in TCF bleaching.

In the second chapter, we studied the effect of P_{sa} on lignin. We also proposed a new modified TCF bleaching process that includes P_{sa} bleaching for hardwood Ph-kraft pulp. The proposed sequence is O- P_{sa} -Z-E- E_p .

The results are as follows:

1. It was confirmed that the application of P_{sa} can oxidize lignin, increase the removal of hexenuronic acid from the pulp, and improve pulp brightness. Unfortunately, cellulose was also partially depolymerized during the process, decreasing the pulp viscosity. The viscosity loss was presumed to result from attack by hydroxyl radicals originating from the residual hydrogen peroxide.
2. High-brightness pulps between 85-86.0% ISO were produced using the proposed modified TCF bleaching process and P_{sa} dosages of 0.2-0.6%. *Acacia mearnsii* Ph-kraft pulps were used in the study.
3. The decrement of the kappa number plateaued when the P_{sa} dosage exceeded 0.2%. We concluded that at this dosage, the optimal amounts of lignin and HexA had

already reacted via acid oxidation, and a P_{sa} dosage of 0.2% was identified as the optimum dosage for the next set of experiments.

4. Compared with the 0.5% ozone treatment, the application of P_{sa} demonstrated a higher selectivity and effectiveness in terms of the kappa number and viscosity decrements. These preliminary results suggest that P_{sa} can be applied as an alternative to ozone.

In the third chapter, the objective is to investigate a new modification sequence of TCF bleaching that includes P_{sa} application but excludes ozone application. The proposed modification sequence is $O-P_{sa}-E_p-P_{sa}-E_p$. The study also investigated some quality improvements for the newly proposed TCF bleaching process.

The results are as follows:

1. We have developed a new bleaching sequence without a Z stage, as an alternative to TCF bleaching. The sequence is only uses a combination of O, P_{sa} and E_p stages ($O-P_{sa}-E_p-P_{sa}-E_p$). Using the proposed sequence and P_{sa} dosages of 0.8%, it is possible to achieve high-brightness pulps whose brightness (over 88.0% ISO) exceeds the minimum Indonesian standard level. This sequence is considered superior to the sequence $O-P_{sa}-Z-E_p$.
2. It was found that the effect of using a multistage process was more effective than adding magnesium salt or increasing the pulp consistency. In the multistage process, the pulp undergoes milder oxidation, and the cellulose is little affected.
3. Although *Eucalyptus* hybrid and *Eucalyptus globulus*, which are derived from the same genus and have relatively similar lignin, cellulose and hemicelluloses contents, the results showed that these woods exhibited different qualities after the $O-P_{sa}-E_p-P_{sa}-$

E_p sequence. We believe that the differences in the chemical structures of these hardwoods affect the effectiveness of this sequence.

4. Pulps with brightness above 88% ISO and viscosities above 6.2 mPa.s were difficult to obtain using the TCF bleaching sequence of $O-P_{sa}-E_p-P_{sa}-E_p$.
5. While the use of $MgSO_4$ in the E_p treatment increased the viscosity and brightness, the use of $MgSO_4$ in the P_{sa} treatment had no effect on the brightness or viscosity of the resulting pulp.

APPENDIXES

A1

High Consistency of Oxygen Bleaching

1. Measure the water content of the air-dried pulp sample.
2. Measure the pulp sample with 10.0 g of oven-dried weight, and then tear it, and put them in a polyethylene plastic bag
3. Prepare 20 mL (or A: 10 mL for $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}_2$ and B: 10 mL for NaOH) of distilled water for 30% of pulp consistency
4. Prepare the targeted NaOH and Mg dosage. Example 1.0% and 0.1% respectively.
5. If the pulp sample was 10.0 g, then add 2.5 mL of 1 N (1 mol/L) NaOH (0.1 g of NaOH) into the distilled water.
6. If the NaOH is 2N (2 mol/L), then add 1.25 mL.
7. Drop A: 10 mL of Mg solution containing 100 mg of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}_2$ to the pulp sample, and mix the pulp sample in a polyethylene bag with hands (**Figure A1.1**).

Drop B: 12.5 mL or 11.25 mL of the NaOH solution to the pulp sample, and mix the pulp sample in a polyethylene bag with hands (**Figure A1.1**).
8. Make pulp into small, bulky and fluffy particles (diameter 5-10 mm)
9. Put pulp in a polypropylene plastic bottle and put it in a reactor (**Figure A1.2**).
10. Charge oxygen gas into the reactor under 0.35-0.50 MPa (3.5-5.0 bars) at room temperature for several minutes. Release the oxygen gas from the reactor, and repeat the charging twice for purging air inside sufficiently.
11. Set the reactor in 123°C oil bath.
12. Count the reaction time from 91-115°C
13. Cool the reactor after 60 minutes in a water bath.

14. Transfer the pulp into a jar of a disintegrator and wash the pulp with 1.5 L of water. De-water the pulp suspension using a Büchner funnel.
15. Wash the pulp twice more, and make 2 pieces of hand-sheets and air-dry them.



Figure A1.1 Put pulp in polyethylene plastic bag and make pulp into small particles (diameter 5-10 mm)



Figure A1.2 Put pulp in a polypropylene plastic bottle, and then put the plastic bottle into the reactor



Figure A1.3 Charge oxygen gas under 0.35-0.50 MPa at room temperature

A2

Peroxymonosulfuric Acid (P_{sa}) Synthesizing

1. P_{sa} is synthesized from concentrated sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) aqueous solution with high H_2O_2 concentrations.
2. Measure 3.8 g of 30% H_2O_2 (0.033 mol) or
Measure 2.5 g of 45% H_2O_2 or
Measure 2.3 g of 49% H_2O_2 and put them into a 100 mL volumetric flask
3. Measure 10.0 g of 98% H_2SO_4 (0.10 mol) or
Measure 10.3 g of 95% H_2SO_4 or
Measure 10.9 g of 90% H_2SO_4 and put them into 100 mL a glass beaker,
Prepare a small drop pipette.
4. Prepare tap water in a 1 L glass beaker and put the 100 mL flask containing H_2O_2 solution in the water bath, put a weight on the flask to sink it.
5. Put the 1 L glass beaker on a magnetic-stirrer-heater, and put a thermometer and a small stirrer bar into the 100 mL volumetric flask containing H_2O_2 solution.
6. Raise temperature of the heater until the temperature of H_2O_2 solution raises to $70^\circ C$ (control it with the thermometer), and then turn on the magnetic stirrer.
7. After the temperature of H_2O_2 solution reaching $70^\circ C$, drop the concentrated H_2SO_4 with a drop pipette little by little while stirred. The droplet of H_2SO_4 will increase the temperature.
8. Keep the temperature at $70^\circ C$ (keep the deviation as minimum as possible) while dropping the H_2SO_4 . Do the process (7 and 8) within/below 20 minutes.
9. After 20 minutes, keep it at $70^\circ C$ for 10 more minutes.
10. Turn off the heater, and cool the temperature solution to $50^\circ C$ (put a lot of ice into the 1 L glass beaker for a better result)

11. After reaching 50°C, add distilled water into the 100 mL volumetric flask containing mixed solution until 100 mL.
12. Measure the P_{sa} concentration

Titration of $Na_2S_2O_3$ 0.1 N

Prepare in a 100 mL elenmeyer flask

10 mL distilled water

10 mL H_2SO_4 20%

1 mL P_{sa} solution

10 mL KI

(Stirrer bar)

Titrate (while stir) with **$Na_2S_2O_3$ 0.1 N**

(confirm about the factor: f_1)

Drop a little starch solution when the color turns yellow

Watch the color change into white clear

Determine the amount: t (mL)

Calculate

$$t \text{ (mL)} \times 0.05 \times f_1$$

$$= T \text{ (mmol of both } H_2O_2 \text{ and } H_2SO_5)$$

Titration of $Ce(SO_4)_2$ 0.025 N

Prepare in a 100 mL elenmeyer flask

10 mL distilled water

10 mL H_2SO_4 20%

1 mL P_{sa} solution

3 drops of Ferroin indicator solution

(Stirrer bar)

Titrate (while stir) with **$Ce(SO_4)_2$ 0.025 N**

(confirm about the factor: f_2)

Watch the color change from

Red to blue

Determine the amount: a (mL)

Calculate

$$a \text{ (mL)} \times 0.0125 \times f_2$$

$$= A \text{ (mmol of } H_2O_2)$$

13. Measure the mmol/mL of H_2SO_5

$$P_{sa} \text{ (mmol/mL)} = (T - A) \div 1 \text{ (mL)}$$



Figure A2.1 The position of the thermometer and the small stirrer bar inside the 100 mL volumetric flask



Figure A2.2 The position of the 100 mL flask inside the beaker

A3

Ozone Bleaching

1. Measure the O₃ flow.
 - a. Prepare a mixture of 20 mL KI, 100 mL distilled water, and 50 mL H₂SO₄ 20%.
 - b. Open the valve of O₂ bomb to let O₂ flow, and put the mixture at the end of the plastic pipe.
 - c. Set the O₂ flow on 0.40 L/min (18 mmol/min).
 - d. Turn on the electric green switch of the ozone (O₃) generator (**Figure A3.1**) for 30 seconds (0.5 min), and then turn off the O₂ flow.
 - e. Titrate the mixture containing I₂, which is generated by the reaction of KI and O₃, with Na₂S₂O₃ 0.1 N (factor: f).
 - f. Repeat the titration and calculate the average data: a (mL). { a will be about 9 (mL)}
 - g. $a \times 0.1 \times f \div 0.5 = b$ (mEq/min)
 - h. b (mEq/min) = $b/2$ (mmol/min) {O₂ → O₃ = 2 equivalent}
 - i. $b/2$ (mmol/min) \times 48 (Molecular weight of O₃) = c (mg/min) = $c/1000$ (g/min)
2. Measure the water content of the air-dried pulp sample.

Prepare the sample (10.0 g of oven-dried weight), and then tear it, and put them in a polyethylene plastic bag
3. Prepare the targeted ozone dosage: x (%), for example in the range of 0.1-0.5%

x (%) = ozone weight / pulp oven-dried (OD) weight

Compare the ozone weight with c (mg/min), for example in the range of 10-50 mg for 10.0 g of pulp

Calculate how many minutes we need to charge O₃ gas: d (min), for example in the range of 0.2-1.0 min.

4. Prepare distilled water (20 mL) based on pulp weight to gain 30% pulp consistency, add a very small amount (for example in the range of 0.05-0.25 mL) of 20% H_2SO_4 to adjust the pH of the water to 3
5. Drop the water into the torn pulp, and mix it with hands and make the pulp into small, bulky and fluffy particles (diameter 5-10 mm)
6. Prepare again 2 sets of a mixture of 20 mL KI, 100 mL distilled water, and 50 mL H_2SO_4 20%, and put one at the end of the plastic pipe, while put the other after the first mixture and connect them with a plastic pipe (**Figure A3.3**).
7. Put all the samples into an 1-2 L of eggplant flask as a rotating reactor (**Figure A3.2**), and put all the equipment and utilities according to the photo (**Figure A3.4**).
8. Turn on the rotating reactor.
9. Open the valve to let the O_2 flow for 5 minutes.
10. Turn on the ozone generator for d minutes
11. Turn off the ozone generator, and after 1 minute close the O_2 flow.
12. Unplug the plastic pipe from the O_2 gas tube, and make sure it was already shut tight.
13. Plug in the plastic pipe to the O_2 gas tube again and open the O_2 flow for 5 minutes
14. Take the pulp from the eggplant flask.
15. Wash the pulp with water, and make handsheets.
16. Prepare another mixture of 20 mL KI, 100 mL distilled water, and 50 mL H_2SO_4 20% for another sample.



Figure A3.1 Ozone generator set with O₂ gas flow at 0.4 L/min



Figure A3.2 Pulp sample put in the eggplant flask and set in the rotating reactor

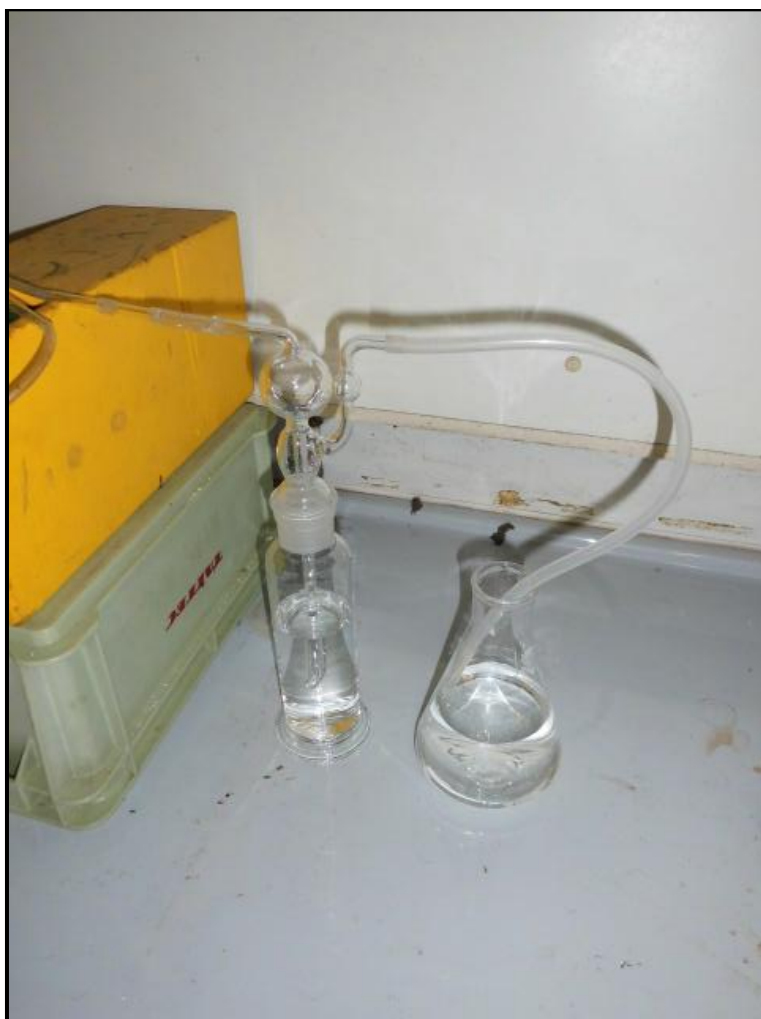


Figure A3.3 Two mixtures of 20 mL KI, 100 mL distilled water, and 50 mL H_2SO_4 20% at the end of the plastic pipe



Figure A3.4 Set of ozone bleaching equipment excluding O₂ gas tube

A4

Alkaline extraction with hydrogen peroxide and magnesium sulfate

1. Measure the water content of the pulp sample.
2. Prepare the sample with 10.0 g of oven-dried weight, and then put them in a polyethylene plastic bag
3. Prepare 90 mL of distilled water for 10% of pulp consistency in 100 or 200 mL beaker glass
4. Prepare the targeted $\text{Mg}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ dosage. Example: 0.01-0.1% (as Mg^{2+})
Weight 10-100 mg of $\text{Mg}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ (FW: 246): 1-10 mg as Mg^{2+} for 0.01-0.1% dosage as Mg^{2+} of 10.0 g of pulp.

Put it in the glass beaker with the distilled water, and mix it

Pour the mixture into the pulp in the polyethylene plastic bag, and mix it

5. Prepare the targeted H_2O_2 dosage. Example: 2.0%
Calculate H_2O_2 weight: e , 2% dosage for 10.0 g of pulp oven-dried weight is 0.2 g H_2O_2 .

If we use 45% H_2O_2 solution, the concentration is assumed to be 0.45 g/mL

$$\text{H}_2\text{O}_2 \text{ needed (mL)} = e / 0.45 \text{ (mL)}$$

Pour the H_2O_2 solution into the pulp suspension in the polyethylene plastic bag, and mix it.

Keep it for 10-15 minutes

6. Prepare the targeted NaOH dosage. Example: 1.4%
Calculate NaOH weight: g , 1.4% dosage for 10.0 g of pulp oven-dried weight is 0.14 g NaOH.
Calculate NaOH mmol: h , (1.4% dosage for 10.0 g pulp is 3.5 (mmol)
If the NaOH is 2N (2 mmol/mL), it is divided by 2

$\text{NaOH needed (mL)} = h / 2 \text{ (mL)}$

7. Pour the NaOH solution into the pulp in the polyethylene plastic bag, and mix it.
8. Remove the air from the plastic bag as much as possible.
9. Set the bag in a water-bath kept at 70°C
10. After the temperature reaching 70°C, put the sample for 60 minutes.
11. Cool the pulp suspension after the 60 minutes, wash the pulp with water and make hand-sheets



Figure A4.1 Put a mixture of sample and chemicals in a polyethylene bag, and remove the air in the bag, and then put a weight



Figure A4.2 Put the sample inside the water-bath, and make sure that the position of the sample is submerged under the water

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