Preparation of Dissolving Pulp by Totally Chlorine-free Bleaching

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Abbreviation

Abbreviation	Description
AA	Active Alkali
AQ	Anthraquinone
C_rI	Crystallinity Index
DoP	Degree of Polymerization
DP	Dissolving Pulp
E_p	Extraction with Hydrogen Peroxide
GC	Gas Chromatography
GHG	Greenhouse Gas
GPC	Gel Permeation Chromatography
HexA	Hexenuronic Acid
HPLC	High Performance Liquid Chromatography
IC	Ion Chromatography
M_w	Weight Average Molecular Weight
NBO	Nitrobenzene Oxidation
O	Oxygen
PC	Pulp Consistency
PHL	Prehydrolysate
P_{sa}	Peroxymonosulfuric Acid / H_2SO_5
S_a	Syringaldehyde
S/V	Syringaldehyde (S_a) to Vanillin (V_a) molar ratio
TCF	Totally Chlorine-Free
UV	Ultraviolet
V_a	Vanillin
XRD	X-ray Diffraction

Chapter 1. Introduction

1.1 Biorefinery concept

Fossil fuels have become the predominant energy and chemical source today. However, fossil deposits are limited and not renewable on a human civilization time scale. Therefore, alternatives, which are more environmental friendly, must be replaced. Practically available alternatives include renewable resources such as wind, solar energy, and biomass. Woody biomass is a reliable source of chemicals and energy that could be replenished at a rate of consistent with our needs. The biorefinery is a concept for the establishment of processes used to convert biomass to chemicals and energy.

Wood is the largest source of biomass in the world. Woody biomass presents more challenges than cereal grains for conversion to platform chemicals due to its stereochemical structures. In addition, its abundant availability, when its conversion to value added products could be carried out in an economic and sustainable manner, made this biomass even more valued (Gosselink, 2011). The abundant availability of woody biomass is supported by the large worldwide annual woody biomass production of about 200 billion (200×10^9) tons per year (Zhang, 2008).

Woody biomass can be thought of as comprised of at least four components: extractives, hemicellulose, lignin and cellulose. Each of these four components has a

different degree of resistance to chemical, thermal and biological degradation (Goldstein, 1975). The Biorefinery is a "catch and release" way of using carbon that is beneficial to the environment and economy. The key to the most efficient use of biomass is to design a suitable and sustainable integral biorefinery to separate biomass into its major compounds and generate the highest value-added products, chemical, and biopolymers from all fractions.

1.2 Chemical composition of wood

Wood is an organic material with numerous carbons. With a very limited variation between different species, all woods are composed of the three main elements carbon, oxygen, and hydrogen. Nitrogen as well as some inorganic elements, such as sodium, potassium, calcium, magnesium, and silicon, is also essential material that is mostly involved in the metabolism of the living cells during wood formation and growth (Fig. 1.1).

At a higher level, these elements form macromolecules and polymers, which represent the main cell wall (Fig. 1.2) compounds of cellulose, hemicelluloses, and lignin. These are the main constituents of all wood species while cellulose is desirable for pulp and paper making but lignin and hemicelluloses are not (Sixta, 2006).

Fig. 1.1 Structures of two different kinds of wood that difference in structure has given them different properties (Sixta, 2006)

Fig. 1.2 Cell structure of wood and its composition (Sixta, 2006)

As shown in Fig. 1.2, a cell wall of wood has several distinct layers, which are different in characteristic and structure. In addition, the substance between cells, which is called middle lamella, has its own characteristics. In other words, each layer of cell wall has specific amounts of lignin, hemicellulose and cellulose with different orientations of fibrils (Sixta, 2006).

In the following, the chemistry of cellulose, hemicelluloses and lignin are introduced.

To research about any topics, deep understanding of the fundamentally related concepts is essential, thus in this part some related basic definitions are explained. Various wood species requires different process conditions in order to separate the wood constituents from each other efficiently by the specific structure and characteristics of wood components and their proportions in wood.

A carbohydrate is an organic compound containing only carbon, hydrogen, and oxygen. Monosaccharide (Fig. 1.3) is the most basic unit of a carbohydrate. In other words, it is the simplest form of sugar and usually is colorless, water-soluble, crystalline solids. However, in aqueous solution monosaccharide rapidly interconverts between straight chain and cyclic forms, the cyclic forms are *inter*molecular hemiacetals (Fig. 1.4).

Fig. 1.3 Structure of monosaccharide: only D series are shown (Matsumoto, 2012)

Fig. 1.4 Ring formation (intermolecular hemiacetal) (Matsumoto, 2012)

Xylan is one of the main types of hemicelluloses (Fig. 1.5). In hardwood, xylan chains have groups of 4-O-methylglucuronic acids with an α-(1, 2)-glycosidic linkage at xylose units. Plenty of OH groups at C_2 and C_3 position of xylose units are replaced with O-acetyl groups producing O-acetyl-4-O-methylglucuronoxylan. Hemicelluloses in softwoods include arabinoglucuronoxylan, arabinogalactan, and galactoglucomannan, whereas the predominant hemicelluloses in hardwoods are glucuronoxylan and glucomannan (Sixta, 2006).

4-O-methylglucuronoxylan (Hardwood xylan)

Arabino 4-O-methylglucuronoxylan (Softwood xylan)

Fig. 1.5 Chemical structure of hardwood xylan and softwood xylan (Matsumoto, 2012)

Cellulose is an important structural component of the primary cell wall of green plants. One cellulose molecule is a linear polymer (Fig. 1.6) and due to the orientation of its hydroxyl groups, formation of intra-molecules (Fig. 1.7) and inter-molecular hydrogen bonding is possible. As a result of inter-molecular hydrogen bonding, cellulose molecules get together to form a crystalline structure.

Fig. 1.6 Linear structure of cellulose molecule (Matsumoto, 2012)

Fig. 1.7 Cellulose molecules get together to form crystalline structure
(Matsumoto, 2012)

1.3 Lignin

Lignin is one of the most abundant natural organic polymers on the Earth and found

in all woods. It has a complex structure containing both aromatic and aliphatic units. A

French scientist, first described the isolation of lignin from wood in a report in 1838,

and it was given its current name in 1857 by Schulze. Lignin is found mostly in the

middle lamella and secondary cell walls of higher plants and plays a key role in

structural tissues as a firming material, where it confers strength, rigidity, and resistance

to environmental stresses (Ralph *et al*., 2007).

Lignin is a hydrophobic material, which makes plant cell walls impermeable to

water, and thus ensures the efficient transport of water and nutrients between the cells

(Henriksson 2009; Norberg 2012). Lignin is also an amorphous polymer with a

distinctly different chemical structure from that of the other macromolecular

constituents of wood. The three-dimensional polymers of lignin contain phenylpropane

units, which consist of syringyl (S), guaiacyl (G), and *para*-hydroxyphenyl groups (Fig.

1.8). These components are biosynthesized by the polymerization of the three

monolignols *p*-coumaryl, coniferyl and synapyl alcohols (Freudenberg and Neish, 1968;

Sarkanen and Hergert, 1971, Lewis, 1999; Ralph *et al*., 2007). Lignin is generated by

the enzymatic dehydrogenative polymerization of these three alcohols. Lignin

composition of plants differs not only between species, but also between tissues of an individual plant variety. In softwood lignin, coniferyl alcohol is the predominant building unit (over 95% guaiacyl structural elements), while in hardwoods the ratio between coniferyl and synapyl alcohols shows considerable variation. Lignin contains a range of chemical functional groups, which is partly the result of the extraction method. The main groups in protolignin (native lignin) are hydroxyl (aromatic and aliphatic), methoxy, carbonyl, and carboxy groups (Alen, 2000).

Fig. 1.8 Three different structural units of lignin (Matsumoto, 2012)

1.4 Kraft and soda cooking methods and dissolving pulp

The essential effective chemical agents in the kraft cooking process are hydroxide and hydrosulfide which are found in the kraft cooking liquor, an aqueous solution of caustic sodium hydroxide and sodium sulfide, defined as white liquor. The hydrosulfide radical carries out an important function in kraft cooking by speeding up the delignification and turning non-selective soda cooking into a selective delignifying method. Delignification process includes three main phases, namely the initial, bulk, and residual or final phases. In the initial phase, delignification is caused by the cleavage of α-aryl and β-aryl ether bonds in the phenolic units of lignin, which accounts for approximately 15-25% of native lignin (Sixta, 2006). In this stage, the overcoming part of the total carbohydrate losses can occur. In the bulk delignification step the main part of the lignin is taken away while at the same time only small carbohydrate losses occur. The cleavage of β-aryl bonds in non-phenolic units of lignin is considered to be the main delignification factor. In the residual delignification phase, only approximately 10-15% of the native lignin is taken out. However, with continuous delignification, the dissolution of carbohydrates extremely increases. In order to maintain high yields and to preserve a sufficiently high quality of the pulp, delignification is limited to a certain degree of delignifying, targeting kappa numbers of about 25-30 for softwood and 15-20

for hardwood kraft.

The rates of the cooking reaction and of the consumption of effective alkali during soda cooking method are much slower than those during kraft cooking (Sixta, 2006). However, prehydrolysis soda-anthraquinone (AQ) cooking with a mild prehydrolysis step can be considered as an environmentally friendly sulfur-free alternative for prehydrolysis kraft cooking for dissolving pulp (DP) production. DP, which consists primarily of pure cellulose, is used as a material for manufacturing rayon and cellulose derivatives. It needs to be produced in a high-quality range, with a high degree of purity, an acceptable level of viscosity, and an extremely low lignin content.

1.5 Problem statements

The excessive utilization of fossil energy sources to produce chemicals and fuels is accompanied by increased air pollution and greenhouse gas (GHG) emission, necessitating the search for novel and renewable raw materials. Biomass is one of the potential sources that can reduce the dependency on fossil fuel. However, due to the shortage of wood supply and deforestation concerns, optimizing the use of this valuable source is intensely considered.

In the biorefinery concept, it is important that cellulose, hemicellulose, and lignin

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are effectively separated from lignocellulosic raw material. These three main biopolymers are then converted to basic sources for other value-added materials, chemicals, and fuels.

DP needs to be produced in a high-quality range, with a high degree of purity, an acceptable level of viscosity, and an extremely low lignin content. Therefore, for DP production, a high rate of cellulose purity in addition to acceptable levels of both cellulose yield and viscosity are important factors to be optimized.

1.6 Objectives

Various wood species require different cooking and bleaching conditions in order to achieve similar levels of delignification and brightness, respectively. The comparative ease of cooking and bleaching has been proven to be related to the structural characteristics of the lignin rather than its relative content in the wood and pulp. Therefore, in Chapter 2, objectives of the study were to determine the chemical compositions and lignin structures of plantation three hardwoods, to evaluate the delignification performance of the prehydrolysis-kraft cooking and the TCF bleaching capability for DP production from these species, and finally, to clarify the relationship between the chemical composition/lignin structure of the species and their

delignification and bleaching behavior.

Investigating the potential of furfural and DP production using a combination of prehydrolysis, soda-AQ cooking and TCF bleaching with P_{sa} employing the selected wood species as well as evaluating the effect of prehydrolysis and soda-AQ cooking conditions on structural changes of waste liquor lignin, are objectives of the study in Chapter 3.

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Chapter 2. Preparation of Dissolving Pulp by Totally Chlorine-free Bleaching: Roles of Hardwood Syringyl and Guaiacyl Lignins

2.1 Introduction

The differences in lignin structures and, consequently, those in the chemical compositions of wood species vary naturally and influence their delignification performance. Lignin is generally considered to be an undesirable wood constituent that is difficult to remove in cooking and bleaching. The lignin in softwood (gymnosperm) contains only guaiacyl aromatic nuclei, while the lignin in hardwood (angiosperm) is composed of both guaiacyl and syringyl aromatic nuclei in various proportions that depend on the wood species. The chemical reactivity of syringyl lignin is known to differ from that of guaiacyl lignin, and the importance of the syringyl units, in the alkaline cooking process, has been shown to be associated with its higher reactivity (Santos *et al*., 2013; Shimizu *et al*., 2012).

It is well known that hardwoods containing syringyl aromatic nuclei are more readily delignified than softwoods during alkaline delignification. The delignification efficiency depends on the specific syringaldehyde (S_a) to vanillin (V_a) molar ratio (S/V

ratio) of the hardwood species (Gonzalez-Vila, 1999). In addition, the wood species affects pulp properties more significantly than variations in the cooking process, and therefore the selection of the wood species is important from the perspective of cooking and bleaching responses (Clark and Hicks, 2003; Uchida, 2006; Patt *et al*., 2006). It has been reported that wood lignin from *Eucalyptus smithii* showed the highest S/V ratio (4.18) as determined by nitrobenzene oxidation of four species (*E. nitens, E. smithii, E. grandis, and E. macarthurii*), and exhibited the best performance during the kraft cooking and totally chlorine-free (TCF) bleaching processes using ozone (Homma, *et al*., 2009). *E. smithii* pulp exhibited the highest level of brightness (86.7% ISO) among the species tested (Homma *et al*., 2009).

Prehydrolysis-kraft cooking is one of commonly used processes in the industrial production of dissolving pulp (DP), which is a sought-after commodity for the production of textiles, cellulose derivatives, and films. Performing prehydrolysis prior to kraft cooking softens the cell walls of the lignocellulosic materials, decreases the number of linkages between the lignin and carbohydrates, and removes some of the hemicelluloses. The prehydrolysis intensity influences DP purity, cellulose yield and degree of polymerization (*DoP*) (Li *et al*., 2010; Testova *et al*., 2014). In addition, the conditions used in the subsequent cooking process affect the chemical composition and

physical properties of the unbleached pulp, and its bleaching efficiency, which is defined as the amount of consumed bleaching chemicals required to achieve the desired brightness and viscosity. During such prehydrolyzed alkaline cooking, lignin is more dissolved, compared to non-hydrolyzed alkaline cooking.

In this study, kraft cooking at low temperatures and prolonged reaction times was conducted in order to increase pulp viscosity, which is a key requirement for producing high-quality pulp for the bleaching process. Under a given condition, hardwood kraft pulps from some species show considerable variations in pulp yield, quality, and bleachability. Some of these variations arise from the various conditions for each wood, but many of them depend on variabilities in the wood itself. The cooking conditions affect the residual lignin content and other oxidizable structures in the pulp, which consequently influences the bleaching response. Bleachability is related to the severity of the cooking conditions; milder cooking conditions afford pulp that is easier to bleach (Neto *et al.*, 2002).

In addition, to further decrease the environmental load generated during the bleaching stages, the TCF bleaching of prehydrolysis-kraft pulp, without the use of ozone, was proposed in a previous study by Rizaluddin and others (Rizaluddin *et al.*, 2015); the use of peroxymonosulfuric acid (P_{sa}) was shown to potentially decrease

ozone usage, since it is more selective and effective, based on kappa number and viscosity measurements, compared to treatment with 0.5% ozone (Rizaluddin *et al.*, 2015). During TCF bleaching, the levels of discharged organochlorine substances, as adsorbable organic halogen, are reduced. Furthermore, in a previous paper, the prehydrolysis-kraft pulp of a *Eucalyptus* hybrid (*grandis* and *pellita*) wood has been bleached using an oxygen (O)-P_{sa}-alkali extraction with hydrogen peroxide (E_p)-P_{sa}-E_p sequence (Rizaluddin *et al.*, 2016). This sequence resulted in a final pulp viscosity of 6.0 mPa·s, which is below the minimum requirement of the Indonesian National Standard (SNI), which specifies a minimum of 6.2 mPa·s [National Standard Agency of Indonesia (BSN), 2015].

Various wood species require different cooking and bleaching conditions in order to achieve similar levels of delignification and brightness, respectively. The comparative ease of cooking and bleaching has been shown to be related to the structural characteristics of the lignin rather than its relative content in the wood and pulp. However, the reasons behind this observation are not completely understood. Furthermore, the delignification behavior and performance of some wood species, such as between *Eucalyptus* and *Acacia* species are still not well understood, despite their growing importance as raw materials for the pulp and paper industry (Pinto *et al.*,

2005).

This study compares the cooking and bleaching performance of four hardwoods (*Eucalyptus globulus*, *Acacia mearnsii*, an *Acacia* hybrid, and Japanese mixed hardwoods) with various lignin structures and S/V ratios using the nitrobenzene oxidation method. The objectives of this study were to determine the chemical compositions and lignin structures of plantation three hardwoods, to evaluate the delignification performance of the prehydrolysis-kraft cooking and the TCF bleaching ability for DP production from these species, and finally, to clarify the relationship between the chemical composition/lignin structure of the species and their delignification and bleaching behavior.

2.2   Experimental

2.2.1 Materials

E. globulus wood chips from Chile*, A. mearnsii* from South Africa, an *A.* hybrid (*mangium* and *auriculiformis*) from Vietnam, and Japanese mixed hardwoods (*Quercus* spp.) were provided by the Hokuetsu Co., Ltd, Japan. H_2SO_5 was prepared in a laboratory by dropping 95% sulfuric acid (Wako Pure Chemical Industries, Ltd.) into 45% aqueous hydrogen peroxide solution (Mitsubishi Gas Chemical Company, Inc.) at

70 °C in accordance with a previously reported procedure (Rizaluddin *et al*., 2015). The

final solution contained 0.19 mmol/L H_2SO_5, 0.81 mmol/L H_2SO_4, and 0.14 mmol/L

H_2O_2.

2.2.2 Chemical analysis of the materials

Wood chips of each species were milled, and particles of 40–60 mesh size were

separated and used in subsequent analyses. The extractive content was determined

according to TAPPI Test Method, T204 om-88 (1996) using Soxhlet extraction with

acetone. After extraction, the amount of acid-insoluble lignin (Klason lignin) was

determined according to a modification of TAPPI Test Method, T222 om-01 as follows

(Ohi *et al*., 1997): 0.5 g of oven-dried milled material was hydrolyzed with 7.5 mL of

72% sulfuric acid at 20 ± 2 °C for 2.5 h and then further hydrolyzed with 4% sulfuric

acid at 121°C for 1 h. The mixture was then filtered using a glass filter (1GP16) to

obtain a residue and filtrate. The oven-dried weight of the residue was measured as the

amount of acid-insoluble lignin. The amount of acid-soluble lignin was determined

from the absorbance of the filtrate at 205 nm using a UV spectrophotometer. The

monosaccharides in the filtrate were analyzed after 1000-times dilution using a Dionex

ICS 3000 ion chromatograph (Dionex, Sunnyvale, CA, USA) to know carbohydrate

composition of pulp.

A suppressor of 0.3 M NaOH is used to reduce the conductance of the eluent and at the same time enhance the conductance of the sample ions. The ion chromatograph included a pulsed amperometric detector (PAD), a single pump model (SP-1), a CarboPac PA 1 column (Φ4 mm $\times$ 250 mm), a CarboPac PA 1 guard column (Φ4 mm $\times$ 50 mm), and an auto sampler (AS). The eluent used in this system is a mixture of 0.15 M NaOH, 0.1 M KOH, 0.125 M Na_2CO_3 and filtrated distilled water.

The ash content was determined according to TAPPI Test Method, T211 om-93 (1996) by incinerating the material at 575 °C for 4 h.

2.2.3 Nitrobenzene oxidation of the lignin in the materials

Following a modification of a previously reported method (Chen, 1992), approximately 200 mg (oven-dried weight) of the prepared sample, 7.0 mL of 2 mol/L NaOH (Wako Pure Chemical Industries, Ltd.), and 0.4 mL of nitrobenzene (analytical grade, Wako Pure Chemical Industries, Ltd.) were placed in a 10-mL stainless steel reactor and reacted at 170 °C for 2 h. Following oxidation, S_a and V_a were separated from the mixture and then subjected to gas chromatography (GC).

The GC conditions equipped with flame ionization detector (FID) were as follows:

GC system, GC-17A (Shimadzu, Japan); column, DB-1 (30 m × 0.25 mm; film thickness: 0.25 μm) with helium gas as a carrier. Temperature profile for analysis: 15 min at 110 °C, 110-160 °C (at a rate of 5 °C/min), 160-280 °C (at a rate of 20 °C/min), and 7 min at 280 °C. The FID response factors for estimating the amounts of S_a and V_a were obtained by making calibration lines between the weight ratios and area ratios of S_a and V_a to the internal standard. Calibration lines were created by injection with various concentrations of the compound (approximately 2, 4, and 2 mg/mL) with the internal standard (2, 1, and 0.2 mg/mL). The amounts of S_a and V_a and the S_a/V_a molar ratio were determined using the FID response factors of S_a and V_a.

2.2.4 Prehydrolysis, kraft cooking, and TCF bleaching

Wood chips (50 g, oven-dried weight) were prehydrolyzed with 195 mL of distilled water at 150 °C for 2.5 h. After removing 130 mL of the prehydrolyzate, the prehydrolyzed wood chips were kraft-cooked with 30% sulfidity and an active alkali dosage of 15% (*E. globulus*) or 17% (*A. mearnsii*, *A.* hybrid, and Japanese mixed hardwoods) at 150 °C for 3 h. The liquor-to-wood ratio was 4 mL/g. The following TCF bleaching sequence was used: O-P_{sa}-E_p-P_{sa}-E_p. The conditions for each stage were:

1. Oxygen (O) bleaching: Pulp consistency (PC), 30%; oxygen pressure, 0.5

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MPa; NaOH dosage, 0.6%; reaction temperature, 115 °C; and time, 60 min.

2. Peroxymonosulfuric acid (P_{sa}) treatment: PC, 10%; P_{sa} (H_2SO_5) dosage, first stage 0.2%, second stage 0.1%; pH = 3.0 by adjustment with a small amount of NaOH to the pulp suspension; reaction temperature, 70 °C; and time, 70 min.

3. Alkaline extraction with hydrogen peroxide (E_p) bleaching: PC: 10%; H_2O_2 dosage, first stage, 2.0%, second stage 1.0%; ratio of NaOH to H_2O_2, 0.7 (w/w); reaction temperature 70 °C; and time, 60 min; 0.1% $MgSO_4$ (as weight of Mg) was added at the E_p stage to maintain pulp viscosity.

2.2.5 Analysis of pulp quality

Kappa number, viscosity, α-cellulose content and pulp brightness were determined according to TAPPI Test Methods T236 om-13 (2013), T230 om-94 (1996), T203 cm-09 (2009) and T452 om-92 (1996), respectively. Brightness was measured using a Tokyo-Denshoku TC-1500 SX digital colorimeter. To determine the hexenuronic acid (HexA) content, pulp samples were acid hydrolyzed with formic acid (pH 2.5) at 120°C for 3 h. After acid hydrolysis, the two furancarboxylic acids formed from HexA in the hydrolyzate were analyzed using a Shimadzu LC-6A HPLC apparatus fitted with a Zorbax ODS column (Φ4.6 × 250 mm) at a column temperature of 40 °C, with 20:80

acetonitrile/water at pH 2.5 as the eluent, and UV detection at 265 nm7). The amounts

of acid-insoluble lignin and acid-soluble lignin, and the carbohydrate composition of the

pulp were determined by following the methods mentioned earlier (**2.2.2**).

2.2.6 Molecular weight distributions of bleached pulp

The bleached pulp was dissolved in *N*, *N*-dimethylacetamide (DMAc) according to

the procedure previously reported by Dupont (Dupont, 2003). The pulp (0.05 g) was

dispersed twice in 10 mL of water at 40 °C for 1 h, then dispersed twice in 8 mL of

methanol at 23 °C for 45 min, with the water removed without drying prior to the

addition of methanol. After removing most of the methanol with an aspirator, the pulp

was immersed in 8 mL of DMAc at 23 °C for 45 min and then filtered. The pulp was

re-immersed in 8 mL of DMAc with stirring (magnetic stirrer) at 23 °C for 24 h,

followed by filtering. Finally, 5 mL of DMAc containing 8 wt% of LiCl (8%

LiCl/DMAc) was added to the pulp containing a small amount of DMAc (0.2 g). The

pulp was then stirred (magnetic stirrer) at 23 °C for 24 h, at which time it had

completely dissolved. Samples were subjected to gel permeation chromatography

(GPC) to know molecular weight (*M*) distributions. The system consisted of a refractive

index detector (RI) and a Shodex KD-806M column (Showa Denko, Japan; ϕ8 mm ×

length 300 mm, 2 series). A 0.5% LiCl/DMAc solution was used as the eluent at a flow

rate of 0.6 mL/min, and some pullulan compounds (the molecular weight and

distribution are known) were used as the internal standards providing a following

equation: $\log_{10} M = -0.00442t + 12.30$ (t: s).

2.2.7 X-ray diffraction of the bleached pulp

The cellulose crystallinities of the bleached-pulp samples, with cellulose powder

(Toyo Roshi Kaisha, Ltd., Tokyo) as the standard, were determined by X-ray diffraction

using a Bruker D8 ADVANCE diffractometer (Bruker AXS GmbH, Karlsruhe,

Germany), fitted with a Cu-tube radiation source (0.154 nm) and operating at a voltage

of 40 kV and a current of 40 mA. Scans were of the θ–2θ type, with sample angles in

the 10–30° (2θ) range over scan times of 348 s (6000 steps at 0.05 s/step). According to

a previous paper by Hamidah and others (Hamidah, 2018), crystallinity indices (C_rI)

were calculated using following equation: $[(I_{max} - I_{min})/I_{max}] \times 100$.

2.3   Results and discussion

2.3.1 Chemical characteristics of the raw materials

Figure. 2.1 displays the chemical compositions of wood chips from each species. *E.*

globulus and *A. mearnsii* woods exhibited lower lignin contents (27.6% and 24.5%, respectively) and higher densities (525 and 611 kg/m^3, respectively) than the remaining woods. No correlations between density and lignin content were observed previously for *E. nitens*, *E. smithii*, *E. grandis*, and *E. macarthurii* (Homma *et al*., 2009) in addition to these. Wood chips with low lignin content and high density are usually desired as feedstock for pulp mills. It should be noted that *A*. hybrid wood exhibited the highest lignin content (30.3%) and the lowest density (433 kg/m3) among the woods tested. Little difference in glucan content was observed among these species. The xylan content of *E. globulus* was low compared to those of the other two species (*A. mearnsii* and Japanese mixed hardwoods), which suggests that it is likely to be suitable for producing DP.

Fig. 2.1 Chemical compositions of various hardwoods

Figure. 2.2 reveals that the wood of *E. globulus* gave the highest combined S_a and V_a yield (3.04 mmol/g-lignin) and S/V ratio (5.81) by nitrobenzene oxidation, while the *A*. hybrid wood gave lowest yield and S/V ratio (2.17 mmol/g-lignin and 1.38, respectively). During nitrobenzene oxidation, some aromatic aldehydes such as syringaldehyde (S_a) and vanillin (V_a) were generated as the main products. The composition and quantity of these aromatic carbonyl compounds represents the structure of non-condensed lignin because condensed lignin typically does not produce aromatic aldehydes other than dehydrodivanillin. The high combined S_a and V_a yield indicates high levels of non-condensed lignin, suggestive of a less-condensed type of lignin structure compared to the other species. The β-O-4 structure is dominant in lignin, and exists in two stereoisomeric forms: *erythro* (*E*) and *threo* (*T*). The *E* form is preferentially cleaved over the *T* form during delignification under alkaline conditions, and a positive correlation exists between the *E*/(*E*+*T*) and S/(S+V) ratios (Akitama *et al.*, 2005). Therefore, higher amounts of S-type structures in wood result in better delignification under alkaline conditions. We expected the wood of *E. globulus* to be the most desirable material for alkaline cooking because of its high S/V ratio and levels of non-condensed lignin structures.

Fig. 2.2 S/V ratios and combined yields of S_a and V_a by the nitrobenzene oxidation of various hardwoods

(white unfilled bars: S/V ratios; gray filled bars: combined S_a and V_a yields)

2.3.2 Prehydrolysis-kraft cooking and pulp characteristics

To generate DPs, prehydrolyses were performed on wood chips to remove hemicelluloses and small amounts of lignin from the wood by separation of the prehydrolyzate. The rate of delignification was also enhanced during the subsequent kraft cooking process mainly due to improved penetration of the reagents into the raw materials. The wood samples were treated for long prehydrolysis times and with low active alkali dosages compared to the previous conditions (Rizaluddin *et al*., 2016) to produce final bleached pulp with viscosities above the SNI minimum requirement of 6.2 mPa·s. As shown in Table 2.1, the wood from *E. globulus* and *A. mearnsii* exhibited higher pulp yields (43.2% and 41.1%, respectively) with lower kappa numbers (8.4 and 8.2, respectively) than those of the Japanese mixed hardwoods. It should be noted that the amount of active alkali required for *E. globulus* (15%) to reach low kappa numbers (8.4) was lower than that required for *A. mearnsii* (17%), which means *E. globulus* wood is easier to delignify than that of *A. mearnsii* . This is attributable to higher amounts of non-condensed lignins in *E. globulus* than in *A. mearnsii* . Non-condensed lignin structures bearing β-aryl ethers are known to decompose faster under alkaline cooking conditions than condensed lignin structures bearing β-5 and 5-5 carbon-carbon bonds (Chen, 1992). Moreover, the higher lignin content of the *A*. hybrid wood (30.3%),

with correspondingly higher amounts of condensed lignin structures, resulted in the

lowest levels of delignification during cooking among the species studied.

Table 2.1 Properties of various prehydrolysis-kraft pulps

		E. globulus	*A. mearnsii*	*A.* hybrid	Japanese mixed
Active alkali[a]	(%)	15	17	17	17
Pulp yield	(%)	43.2	41.1	48.8	38.5
Kappa number	-	8.4	8.2	28.6	11.5
Viscosity	(mPa·s)	72.7	51.1	35.0	68.3
Brightness	(% ISO)	48.1	49.2	43.7	38.0
HexA content	(mmol/ kg)	7.1	9.0	24.7	11.1
Glucan	(%)[b]	84.1	82.9	79.2	83.1
Xylan	(%)[b]	3.9	4.2	7.4	4.5
Unknown	(%)[b]	10.7	11.7	9.1	10.7

[a] Cooking conditions: 150 °C for 3 h; [b] Based on pulp

Pulp of the highest viscosity (72.7 mPa·s) and highest brightness (48.1%) was obtained from *E. globulus*, whereas pulp from *A.* hybrid exhibited the lowest viscosity (35.0 mPa·s), low brightness (43.7%), and the highest kappa number (28.6). Among the species studied, the highest glucan content (84.1%), the lowest xylan content (3.9%), and a HexA content of 7.1 mmol/kg were measured for *E. globulus*, which is desirable in terms of producing DP. On the other hand, *A.* hybrid has the lowest glucan content (79.2%), the highest xylan content (7.4%), and a HexA content of 24.7 mmol/kg.

2.3.3 Effect of oxygen bleaching on pulp properties

During oxygen bleaching, the delignification reaction is basically due to the oxidative degradation of the phenolic lignin. Thus, the pulp with high initial kappa number results pulp with high kappa number; kappa number decrease is proportional to NaOH addition. The viscosity reduction after oxygen bleaching is attributed to alkaline hydrolysis of the glycosidic linkages, a reaction which decreases the degree of polymerization of cellulose. As shown in Fig. 2.3, O bleaching decreased the kappa number of *E. globulus* pulp from 8.4 to 4.2, which is the best reduction in kappa number (50%) observed among the different wood samples; viscosity was also maintained at a higher level (42.9 mPa·s) than those of the other species, although the viscosity

reduction in a unit of kappa number decrement (7.1 mPa·s) was largest for this wood species. These results were probably caused by specific lignin structure (high S/V ratio) of this pulp and by further degradation of cellulose due to a low initial lignin content of the pulp. Higher brightness levels were also observed for the oxygen-bleached pulp of *E. globulus* and *A. mearnsii* (67.1% and 68.8% ISO, respectively). The pulp from *A. hybrid* with a high initial kappa number (28.6) exhibited the lowest viscosity (32.2 mPa·s), viscosity reduction in a unit of kappa number decrement (0.4 mPa·s) and brightness (51.3% ISO), and the highest kappa number (22.3) after oxygen bleaching; moderate results were obtained for the Japanese mixed hardwoods-pulp.

Fig. 2.3 Properties of prehydrolysis-kraft pulp after oxygen bleaching

Legend: ■, □: *E. globulus*; ●,○: *A. mearnsii* ; ◆, ◇: *A.* hybrid; ▲, △; Japanese mixed

(black filled symbols: unbleached pulp; white unfilled symbols: oxygen-bleached pulp)

2.3.4 TCF bleaching and characterization of the pulp produced

After TCF bleaching, the *E. globulus* wood, with the highest S/V ratio and combined yield of S_a and V_a, exhibited excellent DP properties, showing the highest levels of brightness and α-cellulose and glucan contents (89.4% ISO, 92.7%, and 94.9%, respectively), while its xylan content was the lowest (3.9%) among pulps from the species tested (Table 2.2). In contrast, the wood from *A*. hybrid, with the lowest S/V ratio and combined yield of S_a and V_a, provided the poorest results for the above-mentioned parameters. Hence, we concluded that the wood from *E. globulus* is the best for the production of TCF-bleached DP.

Table 2.2 Properties of TCF-bleached pulp for DP

		E. globulus	A. mearnsii	A. hybrid	Japanese mixed
Viscosity	(mPa·s)	7.1	7.4	12.1	7.2
(*DoP*[a])	-	(679)	(705)	(1026)	(688)
Brightness	(% ISO)	89.4	88.6	71.9	83.9
α-cellulose	(%)	92.7	92.0	86.7	91.3
Ash content	(%)	0.1	0.1	0.3	0.2
Glucan	(%)[a]	94.9	94.1	87.1	93.6
Xylan	(%)[a]	3.9	4.3	8.0	4.9
Unknown	(%)[a]	0.8	1.5	4.6	1.3

[a] Degree of polymerization, $DoP^{0.905} = 0.75[954 \log(x) -325]$; [b] Based on pulp

In addition to lower lignin content, a lower rate of HexA content observed for the

E. globulus kraft pulp is also a factor that influences the final brightness of the pulp

after the bleaching stages, as H_2SO_5 is consumed by reaction with HexA; lower H_2SO_5

consumption results in the more effective degradation of residual lignin and colored

substances. *A. mearnsii* and Japanese mixed hardwoods, with moderate S/V ratios and

combined yields of S_a and V_a, exhibited similar qualities (brightnesses of 88.6 and

83.9%, and viscosities of 7.4 and 7.2 mPa·s, respectively).

Furthermore, the viscosity-average molecular weight (M_v) can be calculated from

the degree of polymerization (*DoP*), itself determined from the viscosity (x) via TAPPI

Test Method T230 om-94 (1996). Based on the equation: $DoP^{0.905} = 0.75[954 \log (x) -$

325] (Sihtola *et al*., 1963), the *DoP* and M_v of *E. globulus* pulp were determined to be

679 and 1.10×10^5 g/mol, respectively.

Figure. 2.4 displays the molecular weight distributions of the TCF-bleached pulps

obtained from the wood species. The weight-average molecular weight (M_w) and the

number-average molecular weight (M_n) of the *E. globulus* bleached pulp were $3.04 \times$

10^5 g/mol and 5.56×10^4 g/mol, respectively (polydispersity: $M_w/M_n = 5.47$). These

GPC results and the above-mentioned viscosity values are acceptable, although it was

reported that the M_w of methyl cellulose obtained by GPC, using pullulan as the

standard, was overestimated compared to that determined by light scattering (Poche, *et al.*, 1998).

Fig. 2.4 Molecular-weight distributions of TCF-bleached pulps

Legend: 1: *E. globulus*; 2: *A. mearnsii* ; 3: *A.* hybrid; 4: Japanese mixed

Based on the SNI, which requires 94% α-cellulose to be present in the pulp, our results reveal that the α-cellulose content of the pulp from all species falls below the standard (Table 2.2). However, the α-cellulose content of the *E. globulus* pulp is only slightly less than the standard. We expected that with slightly modified prehydrolysis or O bleaching conditions, the α-cellulose content can be improved to meet the standard; this approach ultimately proved to be successful. As it is displayed in Table 2.3, with a slight increment of NaOH dosage in O stage, the obtained pulp showed a higher viscosity while the α-cellulose content also was above the standards.

Table 2.3 Properties of *E. globulus* TCF-bleached pulp prepared under different conditions

No.	Prehydrolysis time (min)	NaOH dosage in O stage (%)	α-Cellulose (%)	Viscosity (mPa·s)	Brightness (% ISO)	Ash content (%)
1[a]	150	0.6	92.7	7.1	89.4	0.1
2	150	0.8	94.2	7.0	90.1	0.1
3	210	0.6	94.8	6.8	90.5	0.1

[a] from **Table 2.2**

Figure. 2.5 displays brightness and viscosity profiles of the second pulp listed in Table 3 during the O-P_{sa}-E_p-P_{sa}-E_p bleaching sequence. The maximum brightness increment occurred after the first E_p stage. This bleaching sequence for *E. globulus* resulted in a final brightness of 90.1% ISO, a viscosity of 7.0 mPa·s, α-cellulose content of 94.2%, and ash content of 0.1%, which are desirable results.

Fig. 2.5 Brightness and viscosity profiles during the TCF bleaching of *E. globulus* pulp
(white unfilled bars: brightness; gray filled bars: viscosity)

The XRD spectrum in Fig. 2.6 reveals that bleached pulp from *E. globulus* exhibits a high C_rI (80.7); there are no significant differences in the crystallinities of the bleached pulp produced from the four wood types. The removal of hemicellulose and delignification are known to affect crystallinity by altering the ratio of the crystalline to amorphous regions, and oxygen bleaching increases C_rI by degrading the amorphous portion of cellulose in addition to removing lignin (Roncero *et al.*, 2005).

Fig. 2.6 XRD spectra of TCF bleached pulp

Legend: 1: *E. globulus*; 2: *A. mearnsii* ; 3: *A.* hybrid; 4: Japanese mixed; 5: cellulose powder
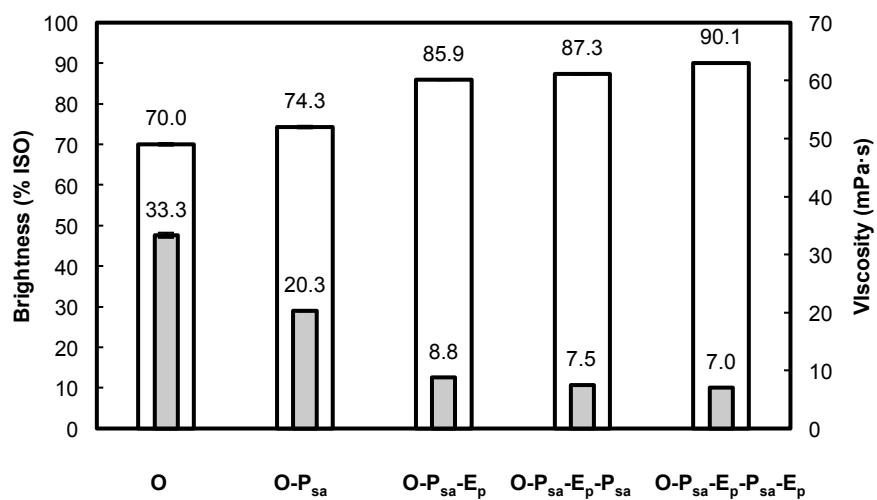
2.4   Conclusions

The lignin structure of the wood species significantly influences the quality of the corresponding prehydrolysis-kraft pulp. The highest viscosity of 72.7 mPa·s and glucan content of 84.1%, and a low kappa number of 8.4, which are the most important properties of unbleached pulp for the production of DP, were obtained from the wood of *E. globulus*, which exhibited the highest S/V ratio of 5.81 and a combined yield of syringaldehyde and vanillin of 3.04 mmol/g-lignin among the hardwoods tested. During the TCF bleaching of *E. globulus* pulp using the O-P_{sa}-E_p-P_{sa}-E_p sequence, high-quality DP: brightness of 90.1% ISO, viscosity of 7.0 mPa·s, α-cellulose content of 94.2%, and ash content of 0.1% was produced using peroxymonosulfuric acid.

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Chapter 3. Totally Chlorine-free Bleaching of Prehydrolysis-soda Pulp from Plantation Hardwoods Consisting of Various Lignin Structures

3.1 Introduction

In the biorefinery concept, it is important that cellulose, hemicellulose, and lignin are effectively separated from lignocellulosic raw materials; these three main biopolymers are then converted to basic sources for other value-added materials, chemicals, and fuels. Dissolving pulp (DP), which consists primarily of pure cellulose, is used as a material for manufacturing rayon and cellulose derivatives. DP needs to be produced in a high-quality range, with a high degree of purity (>94% α-cellulose), an acceptable level of viscosity (>6.2 mPa·s), and an extremely low lignin content (<0.05%) [Standard National Indonesia (NSI), 2015]. Meeting such requirements renders the yield of the overall DP production process relatively low (30–35%) when compared that of regular pulps for papermaking use (Christov *et al.*, 1998). Therefore, for DP production, a high rate of cellulose purity in addition to acceptable levels of both cellulose yield and viscosity are important factors to be optimized.

In turn, hemicelluloses, which are released by prehydrolysis of lignocellulosic

material in the DP production process, are very useful in the biorefinery process. Hemicelluloses in softwoods include arabinoglucuronoxylan, arabinogalactan, and galactoglucomannan, whereas the predominant hemicelluloses in hardwoods are glucuronoxylan and glucomannan (Aseed *et al.*, 2012). In the prehydrolysis step, the formation of acetic acid from acetyl groups bound to the hemicelluloses raises the hydrolytic cleavage of glycosidic bonds and the subsequent degradation of carbohydrates, particularly hemicelluloses (Alvaro *et al.*, 2009; Mosier *et al.*, 2005). Furthermore, the severity of the prehydrolysis conditions and an extent of hydrolytic cleavage of glycosidic bonds controls the remaining amount of partly hydrolyzed cellulose in the raw material residue and its final degree of polymerization (Testova *et al.*, 2014).

During the prehydrolysis, hemicelluloses and other organics are dissolved in the prehydrolysate (PHL). The major reactions include depolymerization and dissolution of hemicellulose (Alvaro *et al.*, 2009; Liu and Wyman, 2005), along with further degradation of pentose to products such as furfural and hydroxymethylfurfural (Garrote *et al.*, 2001). Furfural constitutes a natural dehydration product of xylose, which constitutes glucuronoxylan and glucuronoarabinoxylan. In particular, furfural has been identified as one of the top thirty platform chemicals able to be generated from biomass

(Cai *et al*., 2014). Accordingly, numerous studies on the prehydrolysis of lignocellulosic raw materials have been implemented. (Li *et al*., 2010) reported that the prehydrolysis conditions, such as time and temperature, should be controlled in order to produce the targeted final products (e.g., oligomeric sugars, monomeric sugars, or furfural). For the purpose of hemicellulose utilization from the prehydrolysis liquor, a prehydrolysis temperature of 170 °C is optimal. Putra *et al*., 2017 showed that upon 1 h dehydration of nitric acid PHL with sulfuric acid at 6% concentration as a catalyst, furfural yield from the PHL reached 6.2% of the raw material weight.

Prehydrolysis soda- anthraquinone (AQ) cooking with a mild prehydrolysis step can be considered as an environmentally friendly sulfur-free alternative for prehydrolysis kraft cooking, with AQ and its derivatives comprising nucleophiles and oxidation-reduction catalysts used to replace sulfide. (Francis *et al*., 2008; Alaejos *et al*., 2006) compared soda-AQ and kraft pulping of holm oak, reporting that a lower kappa number, higher brightness level, and slightly lower viscosity was obtained for soda-AQ pulp. Moreover, the use of soda-AQ cooking eliminates the risk of environmental damage caused by sulfur emissions. As a consequence of the cooking process, lignin is dissolved from the raw material, being separated in the form of a liquor rich in phenolic compounds, which represents the process effluent. The method normally used by the

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pulp and paper industries to deal with the waste liquor from the kraft cooking process is recovery, concentration, and combustion. However, the lignin can be isolated and used as the starting material for a series of useful products (Yoon *et al.*, 2015; Yoon *et al.*, 2016). As a potential biorefinery process, the latter method is attractive; moreover, the separation of lignin following non-sulfur soda-AQ cooking is simpler and more efficient than that following kraft cooking, as the kraft cooking liquor contains sulfide, sulfite, and sulfate, which can produce toxic gases such as hydrogen sulfide and sulfur dioxide.

Several applications for the lignin obtained from cooking processes have been considered. The use of lignin for the synthesis of new polymeric materials is the most promising alternative for its revalorization. Mixing lignin with thermoplastic polymers such as polypropylene has yielded good thermal and mechanical properties (Cazacu *et al.*, 2004). Therefore, it is important to estimate the structure and weight average molecular weight (M_w) of lignin dissolved by the cooking process for describing the behavior of lignin more clearly to facilitate investigations of its utilization, and to optimize the method adopted in the cooking process, which influences the characteristic of the dissolved lignin (Ohi and Ishizu, 1989).

Delignification capability constitutes an important technological characteristic of wood species in the cooking process, with the alkaline cooking response varying

according to the hardwood species used. In our previous study, we evaluated the delignification capability of several hardwood species with various syringaldehyde (S_a) to vanillin (V_a) ratios (S/V ratios) by nitrobenzene oxidation of lignin (Salaghi *et al.*, 2017). Notably, the lignin structure of wood species significantly influences the final quality of DPs obtained by prehydrolysis kraft cooking and totally chlorine-free (TCF) bleaching with the sequence of oxygen (O)-peroxymonosulfuric acid (P_{sa})-alkali extraction with hydrogen peroxide (E_p)-P_{sa}-E_p. The study showed that *Eucalyptus globulus* wood, with the highest S/V ratio of 5.81, has the potential of producing high quality DP using the P_{sa} bleaching stages. Moreover, during the P_{sa} bleaching, cellulose was partially depolymerized, resulting in a loss of pulp viscosity. The viscosity loss was presumed to result from the attack of hydroxyl radicals, which must be originated from residual hydrogen peroxide in the P_{sa} mixture. Thus, further research is required to investigate viscosities and pulp strength properties after the application of P_{sa} in TCF bleaching (Rizaluddin *et al.*, 2015).

As the next step to understanding and optimizing this process, in the present study I first focused on determining the characteristics of the prehydrolysis step and furfural production in the PHL using *E. globulus* as the selected wood species. I next compared the bleaching capability of pulps obtained by prehydrolysis soda-AQ cooking with that

obtained by prehydrolysis kraft cooking, followed by a modification of P_{sa} bleaching to decrease the viscosity loss. Thirdly, alkali lignin was separated from the black liquor of prehydrolysis soda-AQ cooking using different prehydrolysis and cooking conditions, and its chemical characteristics were analyzed.

3.2 Materials and methods

3.2.1 Materials

E. globulus and *Acacia mearnsii* wood chips from plantation areas in Chile and South Africa, respectively, were provided by Hokuetsu Corporation, Japan. P_{sa} was synthesized in the laboratory by dropping 95% sulfuric acid (Wako Pure Chemical Industries, Ltd., Osaka, Japan) into 45% aqueous hydrogen peroxide solution (Mitsubishi Gas Chemical Company, Inc., Tokyo, Japan) at 70 °C according to a previously reported procedure (Rizaluddin *et al*., 2015), The synthesized solution contained 0.19 mmol/L H_2SO_5, 0.81 mmol/L H_2SO_4, and 0.14 mmol/L H_2O_2.

3.2.2 Nitrobenzene oxidation (NBO) of the lignin in the materials

Following a modification of a previously reported method (Chen, 1992), approximately 200 mg (oven-dried weight) of the prepared sample, 7.0 mL of 2 mol/L

NaOH (Wako Pure Chemical Industries, Ltd.), and 0.4 mL of nitrobenzene (analytical grade, Wako Pure Chemical Industries, Ltd.) were placed in a 10 mL stainless steel reactor and reacted 170 °C for 2 h. Following oxidation, S_a and V_a were separated from the mixture by ether extraction and then subjected to gas chromatography (GC). The GC conditions and instrumentation were as previously described (Nakagawa-Izumi *et al*., 2017).

3.2.3 Chemical analysis

The amount of acid-insoluble lignin (Klason lignin) in the materials was determined according to a modification of the TAPPI test method, T222 om-01 (Ohi *et al*., 1997). Extractive and ash content were determined following TAPPI test methods T204 om-88 and T211 om-93, respectively. Carbohydrate compositions were determined by ion chromatography (IC) of the filtrates of the acid hydrolysis, which had been diluted 1,000 times using a Dionex ICS 3000 system (Dionex, Sunnyvale, CA, USA) equipped with a single pump (SP-1), an electrochemical detector, a CarboPac PA 1 column (ϕ4 mm × 250 mm), a CarboPac PA 1 guard column (ϕ4 mm × 50 mm), and an auto sampler (AS) (Tanifuji *et al*., 2011). The amount of acid-soluble lignin was determined according to TAPPI test method T222 om-88 from the UV absorbance of

the filtrate at 205 nm using a spectrophotometer. Kappa number, viscosity, and

α-cellulose content of the pulps were determined according to TAPPI test methods T236

om-13, T230 om-94, and T203 cm-09, respectively. The ISO brightness was measured

based on TAPPI test method T452 om-92 using a digital color meter (TC-1500 SX,

Tokyo-Denshoku, Japan). The hexenuronic acid (HexA) content of the pulps was

determined using a high-performance liquid chromatograph (Shimadzu LC-6A HPLC)

with a Zorbax ODS column: ϕ 4.6 × 250 mm (Shimadzu, Kyoto, Japan).

3.2.4 Prehydrolysis soda-AQ cooking

Wood chips (50 g, oven-dried weight) were prehydrolyzed with 195 mL of

distilled water at 150, 155, 160, 165, or 170 °C for 1.5, 2.0, 2.5, or 3.0 h. After the

prehydrolysis, 130 mL of the PHL was separated and freeze-dried. The chemical

composition of freeze-dried PHL was determined according to the same procedure as

previously described in Chemical analysis. For furfural content determination, the PHL

was distillated at 102 °C, and furfural was collected into the distillate. The furfural in

the distillate was analyzed using the same high-performance liquid chromatograph as

described in Chemical analysis according to a previously reported method (Li *et al.*,

2010). In addition, the prehydrolyzed wood chips were subjected to soda-AQ cooking

with 15–18% active alkali (AA) dosages at 150 °C for 3 h, applying 0.1% dosage of AQ. The liquor-to-wood ratio was 4 mL/g.

3.2.5 Acid catalytic dehydration and acid post-hydrolysis of PHL

Wood chips were prehydrolyzed under different prehydrolysis conditions (time: 1.5–3.0 h and temperature: 150–170 °C). Following prehydrolysis, PHL was subjected to acid catalytic dehydration by dropwise addition of concentrated sulfuric acid (95%) to reach a final sulfuric acid concentration of 6–12%. The acid catalytic dehydration reaction was implemented for 1 h at 98 °C under atmospheric pressure. To further hydrolyze the xylooligomers in the PHL into monomeric xylose, prior to acid catalytic dehydration of the PHL, an acid post-hydrolysis of the PHL was performed after dropwise addition of 95% sulfuric acid to reach a sulfuric acid concentration of 4%. This step was conducted for 3 h at 100 °C under atmospheric pressure.

3.2.6 Chlorine-free bleaching

The TCF bleaching sequence of O-P_{sa}-E_p-P_{sa}-E_p was used in this research, and the conditions for each stage were as follows:

(1)Oxygen bleaching (O)

Pulp consistency (PC): 30%; oxygen pressure: 0.5 MPa; NaOH dosage: 0.6% or

0.8%; reaction temperature and time: 115 °C for 60 min

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

PC: 10%; P_{sa} (H_2SO_5) dosage for 1st stage of P_{sa}: 0.2%; that for 2nd stage of P_{sa}: 0.1%; pH: 3.0 by adding a small amount of NaOH to the pulp suspension; reaction temperature and time: 70 °C and 70 min

(3) Alkali extraction with hydrogen peroxide bleaching (E_p)

PC: 10%; H_2O_2 dosage for 1st stage of E_p: 2.0%; that for 2nd stage of E_p: 1.0%; NaOH dosage ratio to H_2O_2: 0.7 g/g; reaction temperature and time: 70 °C and 60 min; $MgSO_4$ dosage: 0.1% (applied to maintain the pulp viscosity)

3.2.7 Modification of the P_{sa} bleaching process by mixing a small amount of chlorine dioxide (ClO_2)

A small amount of ClO_2 was mixed with P_{sa} during the 1st and 2nd stages of P_{sa} bleaching. The ClO_2 solution was provided from the R8 process at the pulp bleach mill, and its concentration was 7–10 g/L as active chlorine concentration. Conditions for O and E_p stages of the modified bleaching process were the same as described for chlorine-free bleaching. The bleaching sequence of this process was O-(P_{sa}+ClO_2)-E_p-(P_{sa}+ClO_2)-E_p. The conditions for the (P_{sa}+ClO_2) stage were as

follows:

PC: 10%; H_2SO_5 dosage for 1st stage of (P_{sa}+ClO_2): 0.2% (as weight); that for 2nd

stage of (P_{sa}+ClO_2): 0.1%; ClO_2 dosage for 1st stage of (P_{sa}+ClO_2): 0.083% (as active

chlorine); that for 2nd stage of (P_{sa}+ClO_2): 0.042%; pH: 3.0 by adding a small amount

of NaOH to the pulp suspension; reaction temperature and time: 70 °C and 70 min

3.2.8 Preparation of purified soda lignin

To purify the lignin, the pH of black liquor was adjusted to 2.0 with 20% (w/w)

sulfuric acid. The solution was then centrifuged to recover the precipitate, and the

precipitate was washed with distilled water. The centrifuging and washing procedures

were repeated eight times. The precipitate was then vacuumed-dried for 24 h and used

as purified lignin.

3.2.9 Structure and molecular weight distribution of purified soda lignin

For identifying the structure of purified lignin, NBO was carried out as described

above analyzed by GC. For molecular weight determination, the purified lignin powder

was dissolved in 0.5 M NaOH and subjected to gel permeation chromatography (GPC),

which was conducted using a Sephadex G-50 column (ϕ 1.8 cm × 500 mm) and

detected with the absorbance at 280 nm. Polystyrene sulfonic acid was used as the internal standard, and M_w was obtained as the equation: $\log_{10} M_w = 3.95 - 2.01 \times$ relative retention volume.

3.2.10 Experimental design of the whole process

Experimental procedure for the whole process, including all previous sections, is shown in a flowchart (Fig. 3.1).

Fig. 3.1 Scheme of the whole experimental processes

3.3 Results and discussion

3.3.1 Characterization of the lignin structure in each wood species

Figure. 3.2 displays the variation of syringyl and guaiacyl nuclei in lignin as determined based on NBO among 11 to 14-year-old *E. globulus* (Eg11, Eg12, Eg13, Eg14, and Eg1 (a mixed sample of Eg 11–14)) and 8 to 12-year-old *A. mearnsii* (Am8, Am9, Am10, Am11, and Am12) woods cut from several areas of plantation with specified ages. *E. globulus* wood samples showed higher combined S_a and V_a yields and S/V ratios than those of *A. mearnsii* samples. The β-O-4 structures, a dominant structure of lignin, has two stereoisomers: the *erythro* (E) form and *threo* (T) forms, with a strong correlation between E/(E+T) and S/(S+V) ratios. During the delignification reaction under alkaline condition, cleavage of the E form occurs dominantly compared to that of the T form (Matsumoto, 2007). Hardwoods with higher S/V ratios are richer in β-O-4 structures and have higher *erythro*/*threo* ratios. Thus, a higher S/V ratio of lignin in wood results in better alkaline delignification (Akiyama *et al*., 2005). It has been also reported that higher combined yields of S_a and V_a obtained by NBO suggest the higher contents of non-condensed lignin (Jin *et al*., 2012). Therefore, mixed wood chips of various ages of *E. globulus*, possessing a high S/V ratio of 5.81 with S_a and V_a yields of 3.04 mmol/g-lignin, were used as the raw material of this study.

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Fig. 3.2 Nitrobenzene oxidation of eucalyptus and acacia woods (white unfilled bars: S/V ratios; gray filled bars: combined S_a and V_a yields). S_a - syringaldehyde; V_a - vanillin; S/V - S_a to V_a ratio

3.3.2 Behaviors of wood components during prehydrolysis soda-AQ cooking

Table 3.1 shows the amounts of wood components such as hemicelluloses dissolved in PHL during the prehydrolysis at 150 ºC. The content of xylooligosaccharide indicated as xylan in the PHL showed a sudden increment from 2.9 to 7.2% (based on wood) after 2.5 h prehydrolysis. At this point, 47% of the xylan in the raw material (15.3%) was removed from the wood chips during the prehydrolysis. However, a further 0.5 h extension of the prehydrolysis time caused little increment of xylooligosaccharide dissolution in PHL (from 7.2 to 7.8%). It has also been reported (Li *et al*., 2010) that after a point, further extending the prehydrolysis time causes further hydrolysis of xylose oligomers in PHL into monomeric xylose, some of which was further dehydrated to produce furfural, rather than dissolution of hemicelluloses in the wood to PHL. Moreover, the dissolution of glucan into the PHL was low (0.12% at pretreatment for 3.0 h), and that of lignin, not shown in Table 3.1, was very low.

Table 3.1 Carbohydrate composition of PHLs with various prehydrolysis conditions

Prehydrolysis time (h)	Prehydrolysis temperature (°C)	pH	Freeze-dried solid (%)[a]	Glucan (%)[a]	Xylan (%)[a]	Others (%)[a]
1.5	150	3.3	6.0	0.03	2.0	4.0
2.0	150	3.1	7.3	0.05	2.9	3.0
2.5	150	3.0	8.4	0.07	7.2	1.2
3.0	150	2.8	10.4	0.12	7.8	2.5
2.5	155	2.9	9.7	0.28	7.9	1.5
2.5	160	2.8	11.0	0.36	8.2	2.2
2.5	165	2.8	11.5	0.43	7.8	2.8
2.5	170	2.7	12.1	0.61	7.6	3.1

[a] Based on raw material (acid-insoluble lignin content: 22.2%, acid-soluble lignin content: 5.4%, glucan content: 49.4%, xylan content: 15.3%)

As shown in Fig. 3.3, furfural content in the PHL increased gradually upon extending the prehydrolysis time at a stable rate to reach 0.13% (based on wood weight) after 3.0 h. By adding sulfuric acid and a dehydration reaction of PHLs at 100 ℃ for 1 h with 6% sulfuric acid concentration, the furfural yield increased from 0.13 to 0.60% for the PHL obtained by 3.0 h prehydrolysis. However, the yield was less than one tenth of the xylooligosaccharide yield (7.8%) in the PHL, and far lower than that obtained from nitric acid prehydrolysis of empty fruit bunch (6.2%) in a previous study (Putra *et al.*, 2017). The low amount of furfural in the PHL might be due to the high amount of xylose oligomers in the PHL and acetic acid generated during the prehydrolysis, as added sulfuric acid as catalyst causes more dissolution of xylose oligomers rather than conversion of xylose monomers to furfural (Li *et al.*, 2010).

Fig. 3.3 Effect of prehydrolysis time on furfural production (prehydrolysis conditions: 1.5–3.0 h and 150 °C; dehydration conditions: 6% sulfuric acid concentration, at 98 °C and for 1 h)

Next, the effect of maximum temperature of the prehydrolysis on hemicellulose removal from the raw material was investigated (Table 3.1). No significant difference was observed in the xylooligosaccharide yield in the PHL by increasing the temperature to 170 ºC. At 160 °C, the yield reached the maximum point of 8.2%; it can be calculated that about 54% of the xylan content of the wood (15.3%) was removed under this condition. The decrement of the yields at the higher temperatures might be explained by the further hydrolysis of xylose oligomers into monomeric xylose, which was partially dehydrated to produce furfural, resulting in the increment of furfural concentration in the PHL (Tunc and Van, 2008; Shin and Cho, 2008). Furthermore, the final pH of PHL tended to decrease with the increment of temperature; this might also affect the furfural generation in PHL.

Table 3.2 shows the amount of furfural produced in PHL under various prehydrolysis temperatures, without and with acid catalytic reaction. It can be seen that by increasing the maximum temperature from 155 to 170 °C, the amount of furfural in the PHL significantly increased (0.41 to 1.66%). Moreover, by adding sulfuric acid to the PHL with final concentration of 6%, the furfural concentration increased after 1 h dehydration reaction, although this increment of furfural production in the PHL was smaller at higher temperatures. The increment of furfural production in the PHL

obtained under 170 °C after 1 h acid catalytic dehydration reaction was from 1.66 to 1.80% of raw material weight. This result suggested that 6% sulfuric acid concentration could not significantly induce the acid dehydration reaction, likely because of the higher generation of acetic acid in the PHL during the prehydrolysis under higher maximum temperature, which catalyzes the degradation of xylooligomer to furfural during the prehydrolysis process. Thus, adding sulfuric acid with a moderate concentration of 6% was not sufficient to cause a significant increment in furfural production after 1 h dehydration reaction. A previous study (Esteghlalian *et al*., 1997) also reported that the prehydrolysis temperature, rather than the acid catalytic reaction, could significantly affect the hydrolytic pretreatment of poplar.

Table 3.2 Furfural production in the PHLs without and with acid catalytic dehydration

Prehydrolysis temperature (°C)[a]	Dehydration reaction (h)[b]	Sulfuric acid concentration (%)	Furfural production (Yield, %)[c]
155	-	-	0.41
160	-	-	0.73
165	-	-	1.17
170	-	-	1.66
155	1	6	1.03
160	1	6	1.17
165	1	6	1.47
170	1	6	1.8
170	1	9	2.38
170	1	12	2.62

[a] Prehydrolysis time: 2.5 h; [b] Dehydration temperature: 98 °C; [c] Based on raw material

The effect of sulfuric acid concentration during 1 h dehydration reaction of the PHL obtained under prehydrolysis temperature of 170 °C is also shown in Table 3.2. Under these conditions, the furfural production yield increased to 2.6% of the raw material weight. It was confirmed that by increasing the sulfuric acid concentration during the 1 h dehydration reaction, the increment of furfural concentration in the PHL obtained under 170 °C was not significant. Based on these results, we concluded that 1 h dehydration reaction, even with higher concentration of acid catalyst, could not be highly effective toward both the degradation of xylose oligomers into xylose monomers and conversion of xylose monomers into furfural. Therefore, for further hydrolysis of the xylose oligomers of PHL into monomeric xylose, some of which consequently are further dehydrated to produce furfural, an acid post-hydrolysis process with a milder sulfuric acid concentration of 4% for 3 h was conducted prior to acid catalytic dehydration. As shown in Fig. 3.4, acid post-hydrolysis of the PHL resulted in an increment of furfural production in the PHL obtained under 170 °C up to 4.0% based on wood weight. These results supported the conclusion that conducting an acid post-hydrolysis of the PHL enhances the degradation of xylose oligomers into xylose monomers, which results in further conversion of xylose monomers into furfural in the PHL.

Fig. 3.4 Effect of post acid-hydrolysis on furfural production (prehydrolysis conditions: 2.5 h and 155-170 °C; dehydration conditions: 6% sulfuric acid concentration, at 98 °C and for 1 h; post-acidhydrolysis conditions: 4% sulfuric acid concentration, at 100 °C and for 3 h)

Considering the rather low yield and viscosity of DP, milder prehydrolysis conditions with rather high levels of hemicellulose removal function may constitute the optimum prehydrolysis conditions in the DP production processes. (Testova *et al.*, 2014) reported that applying moderate prehydrolysis intensities resulted in a pulp with higher viscosity. Therefore, based on the results shown in Table 3.1 and Table 3.2, for the aim of hemicellulose removal to produce a high quality DP, prehydrolysis under 150 °C for 2.5 h was considered as the optimum prehydrolysis conditions in this study.

Table 3.3 shows the properties of the pulps provided by prehydrolysis with optimum conditions followed by two alkaline (kraft and soda-AQ) cooking processes. In particular, the kappa number, brightness and viscosity of the pulp obtained by prehydrolysis soda-AQ cooking with active alkali of 18% were almost similar to those of the pulp obtained by prehydrolysis kraft cooking with active alkali of 15% (8.2, 47.5% ISO, 68.0 mPa·s and 8.0, 47.2% ISO, 70.8 mPa·s, respectively). In a previous study (Salaghi *et al.*, 2017), TCF bleaching of prehydrolysis kraft pulp obtained under AA of 15% resulted in a pulp with final brightness and viscosity of 90.1% ISO and 7.0 mPa·s, respectively. In the present study we subjected the pulps obtained by the two alkaline methods (kraft and soda-AQ) to the same TCF bleaching sequence to evaluate the potential of DP production using soda-AQ cooking.

Table 3.3 Properties of prehydrolysis kraft and soda-AQ pulps obtained under the same conditions

Cooking method	AA dosage (%)[a]	Yield (%)	Kappa number	Brightness (% ISO)	Viscosity (mPa·s)	Glucan (%)[b]	Xylan (%)[b]	HexA content (mmol/kg)
Prehydrolysis[c] kraft	15	42.9	8.0	47.2	70.8	81.9	4.6	5.1
Prehydrolysis[c] kraft	18	41.7	6.5	49.5	66.8	85.8	4.1	5.1
Prehydrolysis[c] soda-AQ	15	42.2	9.0	45.3	75.1	79.0	4.5	4.4
Prehydrolysis[c] soda-AQ	18	41.1	8.2	47.5	68.0	83.3	3.9	4.1

[a] Cooking conditions : 150 °C and 3 h; [b] Based on pulp; [c] Prehydrolysis conditions: 150 °C and 2.5 h

3.3.3 TCF bleaching and characterization of obtained pulps

Prehydrolysis kraft pulp obtained with the AA of 15% as a control and prehydrolysis soda-AQ pulps obtained with the AA of 15 and 18% were subjected to the TCF bleaching with the same sequence and conditions. As shown in Table 3.4, after TCF bleaching, the bleached pulp from prehydrolysis soda-AQ pulp with 15% AA showed a lower α-cellulose content (92.9%) than the prehydrolysis kraft pulp with 15% AA. In addition, the brightness and viscosity of the bleached soda-AQ pulp were 88.1% ISO and 6.3 mPa·s, respectively, which were lower than those of the bleached kraft pulp. By increasing the AA dosage to 18%, we observed an improvement of α-cellulose content to 94.0% along with a small viscosity loss to 6.0 mPa·s (Table 3.4 and Fig. 3.5). These results demonstrated that the combined process of prehydrolysis soda-AQ and TCF bleaching with sequence of O-P_{sa}-E_p-P_{sa}-E_p requires some modification, especially an increment of viscosity to produce a high-quality DP. As shown in Fig. 3.5, after the first P_{sa} stage, the decrement in viscosity (31.5 to 19.8 mPa·s) per unit brightness improvement (71.2 to 74.1% ISO) is much higher when compared with that after the first E_p stage. It is presumed that hydroxyl radicals formed from the residual H_2O_2 would cause the viscosity loss during P_{sa} treatment. This residual oxidant remains from the synthesis of peroxymonosulfuric acid solution, which is a mixture of H_2SO_5, H_2SO_4,
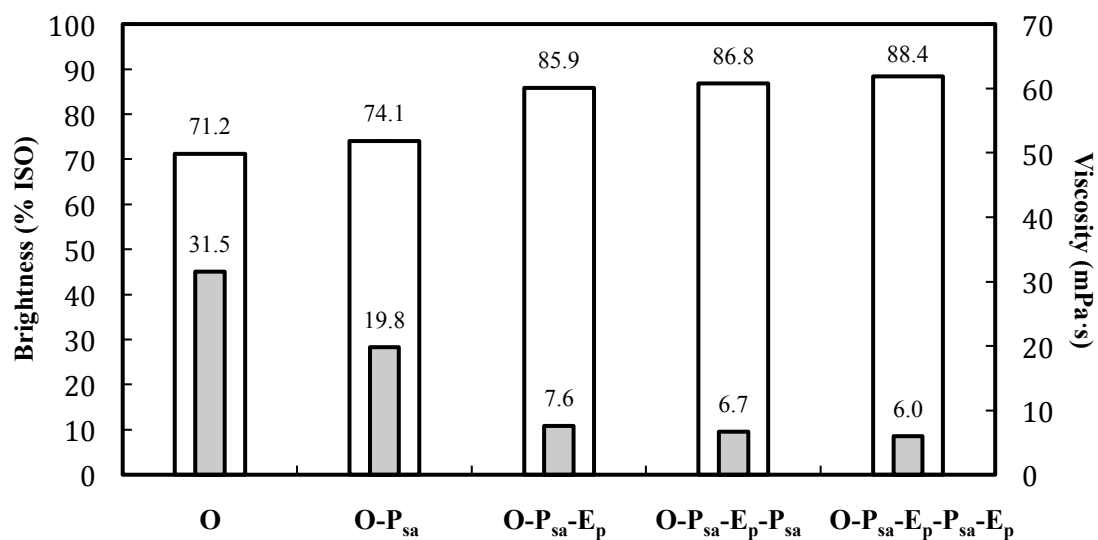
and H_2O_2 (0.19, 0.81, and 0.14 mmol/L, respectively). As an example of this assumption, the loss of viscosity during ozone treatment is reportedly due to the reaction between carbohydrates and hydroxyl, with perhydroxyl radicals generated as by-products (Van *et al*., 1996).

Table 3.4 Properties of *E. globulus* TCF-bleached pulp prepared under different conditions

Cooking method	AA dosage (%)[a]	NaOH dosage in O stage (%)	α-Cellulose (%)	Viscosity (mPa·s)	Brightness (% ISO)	Ash content (%)
Prehydrolysis[b] kraft	15	0.8	94.2	7.0	90.1	0.1
Prehydrolysis[b] soda-AQ	15	0.6	92.9	6.3	88.1	0.1
Prehydrolysis[b] soda-AQ	18	0.6	94.0	6.0	88.4	0.1

[a] Cooking conditions: 150 °C and 3 h; [b] Prehydrolysis conditions: 150 °C and 2.5 h

Fig. 3.5 Brightness and viscosity profiles during the TCF bleaching of *E. globulus* pulp (white unfilled bars: brightness; gray filled bars: viscosity); P_{sa} - bleaching with peroxymonosulfuric acid; E_p – alkali extraction with hydrogen peroxide; O – delignification with oxygen; TCF – totally chlorine free

Therefore, by adding a small amount of ClO_2 to the P_{sa} stage to decompose the residual H_2O_2 of synthesized P_{sa} solution, following the sequences of O-(P_{sa}+ClO_2)-E_p-P_{sa}-E_p and O-(P_{sa}+ClO_2) -E_p-(P_{sa}+ClO_2)-E_p, the final viscosity of the obtained pulp improved significantly because the added ClO_2 reacts readily with the excess H_2O_2 and prevents it from reacting to any significant extent with carbohydrates. The final pulp viscosity improved from 6.0 to 6.6 mPa·s when a small amount of ClO_2 (0.083% as active chlorine) was applied only to the first stage of the P_{sa} (0.2% as H_2SO_5 weight), whereas by adding ClO_2 (0.083 and 0.042%, respectively) to both stages of P_{sa} (0.2 and 0.1%, respectively), the final pulp viscosity improved to 7.2 mPa·s (Fig. 3.6). However, under the modified bleaching process, the α-cellulose content of the pulp did not show a significant change. The brightness, α-cellulose content, and ash content of the bleached pulp were 90.5% ISO, 94.6%, and 0.1%, respectively. Table 3.5 shows the trends in viscosity and brightness improvement obtained by applying the modified bleaching sequence on prehydrolysis soda-AQ pulps.

Fig. 3.6 Brightness and viscosity profiles during the TCF bleaching of *E. globulus* pulp (white unfilled bars: brightness; gray filled bars: viscosity) [a]Modified sequence: (P_{sa}+ClO_2); P_{sa} - bleaching with peroxymonosulfuric acid; E_p – extraction with hydrogen peroxide; O – delignification with oxygen; TCF – totally chlorine free

Table 3.5 Properties of *E. globulus* soda-AQ TCF-bleached pulp by adding a small amount of ClO_2 to P_{sa} stage

	AA dosage (%)[a]	Viscosity (mPa·s)	Brightness (%ISO)	Glucan (%)	Xylan (%)	α-Cellulose (%)	Ash content (%)
P_{sa} bleaching[b]	15	6.3	88.1	94.0	4.9	92.9	0.1
P_{sa} bleaching[b]	18	6.0	88.4	95.4	2.5	94.0	0.1
P_{sa}+ClO_2 bleaching (1st stage)[c]	18	6.6	90.2	95.5	2.8	94.1	0.1
P_{sa}+ClO_2 bleaching (1st and 2nd stages)[d]	18	7.2	90.5	95.9	3.1	94.6	0.1

[a] Cooking conditions: 150 °C and 3 h; Prehydrolysis conditions: 150 °C and 2.5 h

Bleaching sequence: [b]O-P_{sa}-E_p-P_{sa}-E_p; [c]O-(P_{sa}+ClO_2)-E_p-P_{sa}-E_p; [d]O-(P_{sa}+ClO_2) -E_p-(P_{sa}+ClO_2)-E_p

3.3.4 Characterization of purified soda-AQ lignin obtained from various prehydrolysis and cooking conditions

The most abundant lignin substructure in wood is the β-*O*-4 type with two stereostructures of *erythro* and *threo*. It has been shown that β-*O*-4 type lignin substructures with the *erythro* side chain structure are removed more rapidly than those with *threo* side chains during alkaline delignification of wood. It is also empirically known that the β-*O*-4 bond of syringyl type lignin is chemically cleaved more easily than that of guaiacyl type lignin during the alkaline delignification process (Shimuzu *et al*., 2012). Furthermore, a positive correlation between *erythro*/*threo* and syringyl/guaiacyl ratios can be determined from the lignin structural analysis of various wood species (Akiyama *et al*., 2005). In the present study, the structure of the purified soda-AQ lignin was defined as S_a to V_a molar ratio (S/V ratio) and S_a and V_a combined yields, determined by the NBO method.

As shown in Table 3.6, the increment of AA dosage decreased both the S/V ratio and S_a and V_a yields of dissolved lignin. As explained above, the decrement of S/V ratio of soda-AQ lignin indicates that under milder alkaline cooking conditions, the syringyl type lignin is degraded more rapidly than the guaiacyl type whereas by increasing the severity of the alkaline condition, the amount of degraded guaiacyl type lignin could be increased. In addition, in alkaline media, phenolic units of degraded lignin may react

with formaldehydes, forming methylol derivatives that condense with themselves or with other phenols (Dence and Lin, 1992). Therefore, the decrement of S_a and V_a yields in more severe alkaline conditions can be explained by greater condensation of soda-AQ lignin during the cooking process. Table 3.6 also indicates that the prehydrolysis process condition is not as effective on the soda-AQ lignin quality as alkaline cooking severity. In particular, lignin obtained under a prehydrolysis temperature of 170 °C and 18% AA showed the lowest rate of S_a and V_a yields of 0.19 mmol/g-lignin with a rather low S/V ratio of 2.9.

Table 3.6 S/V ratio and combined yields of S_a and V_a of purified soda-AQ lignin obtained under various conditions

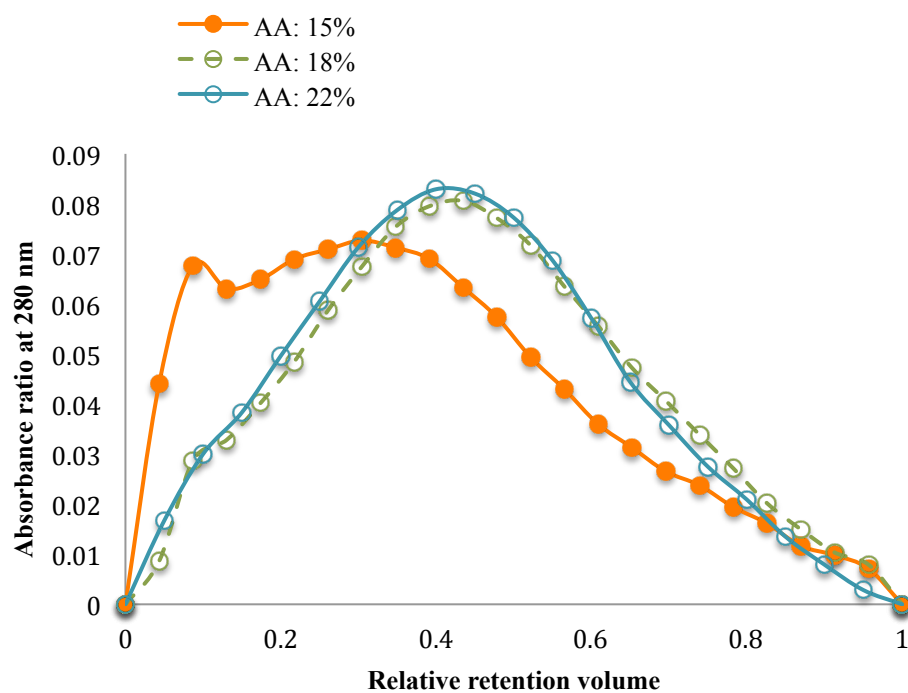| Prehydrloysis temperature $(°C)^a$	Active alkali dosage $(\%)^b$	Acid-insoluble lignin (%)	Acid-soluble lignin (%)	S_a and V_a yields (mmol/g-lignin)	S/V ratio
150	15	84.1	4.1	0.45	4.9
150	18	85.5	6.1	0.42	4.2
150	22	87.2	6.3	0.33	2.9
160	18	86.4	9.0	0.20	2.8
170	18	88.6	9.4	0.19	2.9

Molecular weight distribution of purified soda-AQ lignin obtained under various prehydrolysis and cooking conditions was determined using a GPC system. Soda-AQ lignin molecular weight is closely related to the number of bonds cleaved between the structural units of wood lignin during the cooking process. Guaiacyl-type lignin units are able to generate various types of C-C bonds, especially those involving the C5 position of the aromatic rings, which are not easily cleaved during the cooking process owing to their higher stability; however, this is not possible in the case of syringyl-type units as they have both C3 and C5 positions substituted by methoxy groups (Sjöström, 1981). Moreover, as previously noted, the β-O-4 bonds of syringyl type lignin are cleaved more easily and rapidly than those of guaiacyl type lignin under alkaline delignification processes (Shimuzu *et al.*, 2012). As shown in Table 3.7, based on GPC results, the M_w of purified lignin decreased upon increasing the AA dosage owing to the enhanced degradation initially of syringyl type lignin and subsequently guaiacyl type lignin of wood, and increased by increasing the prehydrolysis temperature owing to the release of high fractions of higher molecular weight lignin from the more softened wood during alkaline cooking. Moreover, it has been reported that holes that are created in the cell walls of the material after the dissolution of amorphous hemicellulose may allow the favorable penetration of chemicals during subsequent cooking (Ma *et al.*, 2011).

Therefore, higher prehydrolysis temperatures lead to more hemicelluloses being removed from the wood and consequent exposure of a larger area of lignin to the chemicals during the subsequent cooking process, which causes the removal of lignin from the wood with greater proportions of higher molecular weight molecules. In particular, by increasing the prehydrolysis temperature from 150 to 170 °C with the same AA dosage of 18%, M_w increased from 1653 to 2050 (M_w/M_n = 2.48–2.88, respectively). The molecular weight distributions of the purified soda-AQ lignin obtained under various conditions are displayed in Fig. 3.7 and Fig. 3.8.
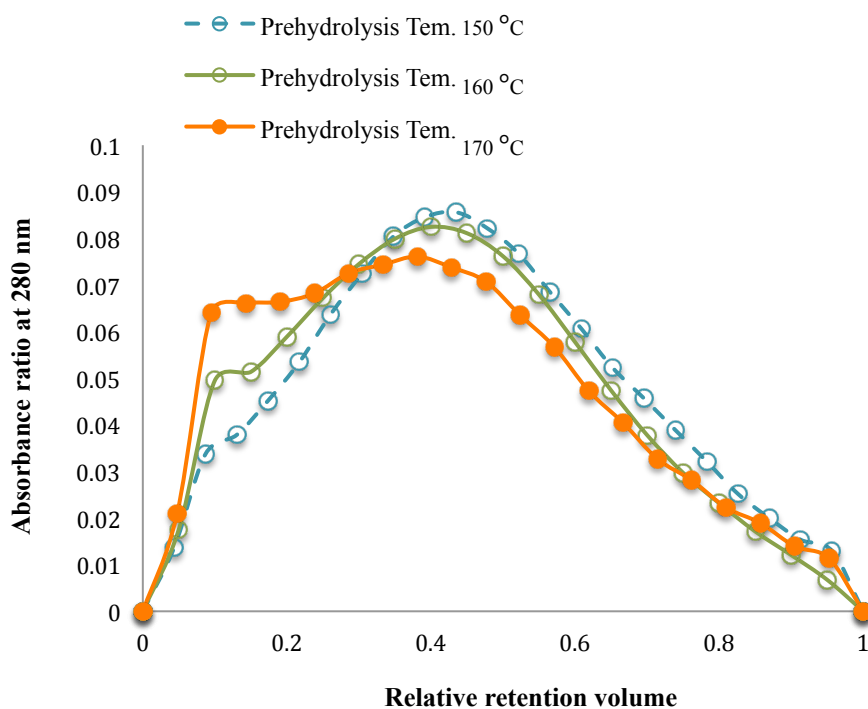
Table 3.7 M_w, M_n, and polydispersity (M_w/M_n) of purified soda-AQ lignin under various conditions

Prehydrloysis temperature (°C)[a]	Active alkali dosage (%)[b]	M_w	M_n	M_w/M_n
150	15	2029	826	2.46
150	18	1653	667	2.48
150	22	1559	678	2.30
160	18	1828	696	2.63
170	18	2050	712	2.88

[a] Prehydrolysis time: 2.5 h; [b] Cooking conditions: 150 °C and 3 h

Fig. 3.7 Molecular-weight distribution of purified soda-AQ lignin obtained under various AA dosages (prehydrolysis conditions: 2.5 h and 150 °C; Cooking conditions: 3 h, 150 °C and 15-22% AA). AQ-anthraquinone

Fig. 3.8 Molecular-weight distribution of purified soda-AQ lignin obtained under various prehydrolysis temperatures (prehydrolysis conditions: 2.5 h and 150 -170 °C; Cooking conditions: 3 h, 150 °C and 18% AA). AQ-anthraquinone

3.4 Conclusion

In this study, the yield of xylooligosaccharide in the PHL obtained by prehydrolysis at 150 °C for 2.5 h reached 7.2% based on wood weight, indicating that 47% of the xylan in the wood was extracted. However, no significant difference was obtained in the xylooligosaccharide yield in the PHL by increasing the prehydrolysis temperature to 170 ºC. The yields of furfural obtained from the PHLs increased with acid catalytic dehydration to the range of 1.0–1.8% of wood weight. Moreover, by conducting acid post-hydrolysis of the PHL prior to acid catalytic dehydration, furfural yield could be increased to 4% of raw material weight.

When prehydrolysis soda-AQ pulp was prepared with 18% AA and bleached using the O-P_{sa}-E_p-P_{sa}-E_p sequence, the final brightness and viscosity of the TCF-bleached soda-AQ pulp were 88.4% ISO and 6.0 mPa·s, respectively, which were lower than those of TCF-bleached kraft pulp prepared with 15% AA. However, using a modified bleaching process by mixing a small amount of ClO_2 with P_{sa}, the brightness and viscosity of soda-AQ pulp were increased to 90.5% ISO and 7.2 mPa·s, respectively.

Lignin obtained under prehydrolysis temperature of 170 °C and 18% AA showed the lowest rate of S_a and V_a yields of 0.19 mmol/g-lignin with a rather low S/V ratio of 2.9. Mw of purified lignin decreased by increasing the AA dosage and increased by

increasing the prehydrolysis temperature. By increasing the prehydrolysis temperature from 150 to 170 °C with the same AA dosage of 18%, M_w increased from 1653 to 2050 (M_w/M_n = 2.48–2.88, respectively).

Overall, the prehydrolysis soda-AQ process with a lower prehydrolysis temperature of 150 °C and a moderate AA dosage of 18% followed by a modified bleaching process with a small amount of ClO_2 resulted in: 1) High rate of hemicellulose removal (47% of the xylan in the wood). 2) High quality DP (α-cellulose content: 94.6%, brightness: 90.5% ISO and viscosity: 7.2 mPa·s). 3) Less lignin condensation reaction during the alkaline cooking (higher rate of S_a and V_a yields of 0.42 mmol/g-lignin for the lignin obtained under the conditions). 4) Lower molecular weight soda-AQ lignin, which is desirable for lignin utilization as this form is more reactive for polymerization reactions.

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Chapter 4. General Conclusions

The differences in lignin structures and, consequently, those in the chemical compositions of wood species vary naturally, and influence their delignification performance. Lignin is generally considered to be an undesirable wood constituent that is difficult to remove in cooking and bleaching processes. Lignin in softwood (gymnosperm) contains only guaiacyl aromatic nuclei, while lignin in hardwood (angiosperm) is composed of both guaiacyl and syringyl aromatic nuclei in various proportions that depend on the wood species. The chemical reactivity of syringyl lignin is known to differ from that of guaiacyl lignin, and the importance of the syringyl units, in the alkaline cooking process, has been shown to be associated with its higher reactivity. It is well known that the delignification efficiency depends on the specific syringaldehyde (S_a) to vanillin (V_a) molar ratio (S/V ratio) of the hardwood species. In addition, the wood species affects pulp properties more significantly than variations in the cooking process, and therefore the selection of the wood species is important from the perspective of cooking and bleaching responses. However, the conditions used in the cooking process affect the chemical composition and physical properties of the unbleached pulp, and its bleaching efficiency, which is defined as the amount of consumed bleaching chemicals required to achieve the desired brightness and viscosity.

To decrease the environmental load generated during the bleaching stages, the totally chlorine-free (TCF) bleaching of prehydrolysis-kraft pulp, without the use of ozone, was proposed in a previous study; the use of peroxymonosulfuric acid (P_{sa}) was shown to potentially decrease ozone usage, since it is more selective and effective, based on kappa number and viscosity measurements, compared to treatment with 0.5% ozone.

Dissolving pulp (DP), which has a cellulose purity of more than 94%, is a sought-after commodity for the production of textiles, cellulose derivatives, and films. Prehydrolysis-kraft cooking is one of commonly used processes in the industrial production of DP. Under a given condition, hardwood kraft pulps from some species show considerable variations in pulp yield, quality, and bleachability. Some of these variations arise from the various conditions adopted during kraft process, but many of them depend on variability in the wood itself. Various wood species require different cooking and bleaching conditions in order to achieve similar levels of delignification and brightness. The comparative ease of cooking and bleaching is related to the structural characteristics of the wood lignin rather than its relative content in the wood and pulp. However, the reasons behind this observation are not completely understood. In the first part of this study, dissolving pulp was produced from four different hardwoods by prehydrolysis-kraft cooking and TCF bleaching using oxygen (O), P_{sa},

and alkali extraction with hydrogen peroxide (E_p) in an O-P_{sa}-E_p-P_{sa}-E_p sequence. The hardwood lignin structures were characterized by the nitrobenzene oxidation method, which provided S_a to V_a molar ratio (S/V ratio) of the lignin. *Eucalyptus globulus* wood had the highest S/V ratio of 5.81 and a combined yield of S_a and V_a of 3.04 mmol/g-lignin, while the *Acacia* hybrid wood exhibited the lowest S/V ratio and the combined yield. The *E. globulus* wood provided a final pulp with an acceptable level of viscosity 7.0 mPa·s, a weight-average molecular weight (M_w) 3.04 × 105 g/mol, a number-average molecular weight (M_n) 5.56 × 104 g/mol, polydispersity (M_w/M_n) 5.47, a high brightness of 90.1% ISO, and a α-cellulose content of 94.2%. It is attributed to the high S/V ratio and the high combined S_a and V_a yield, which is suggestive of a less-condensed lignin structure compared to the other hardwoods tested. No significant differences in the cellulose crystallinities of the bleached pulp produced from the four hardwoods were observed.

In the second part of the study the process of prehydrolysis followed by soda-anthraquinone (AQ) cooking and TCF bleaching with Psa was investigated to develop a biorefinery process. Prehydrolysis soda AQ cooking with a mild prehydrolysis step can be considered as an environmentally friendly sulfur-free alternative for prehydrolysis kraft cooking, with AQ and its derivatives comprising

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nucleophiles and oxidation-reduction catalysts used to replace sulfide. *E. globulus*, which showed a high S_a to V_a molar ratio by nitrobenzene oxidation, was chosen as the raw material of this part. To enhance the quality of obtained pulp a small amount of chlorine dioxide was mixed with P_{sa}. The chemical composition of prehydrolysate (PHL) produced in the prehydrolysis step was analyzed. Furfural formation in the PHL with acid catalytic dehydration was quantified. The results showed that the yield of xylooligosaccharide in the PHL obtained by prehydrolysis at 150°C for 2.5 h reached 7.2% based on wood weight, and that is, 47% of xylan in wood was extracted. The yields of furfural obtained from the PHLs increased with acid catalytic dehydration to that in the range of 1.0%-2.6% on wood weight. For further hydrolysis of xylose oligomer into monomeric xylose, a post-acid hydrolysis process was conducted before acid catalytic dehydration, which resulted in the increment of furfural production in the PHL up to 4.0% based on wood weight. As a non-sulfur process, soda-AQ cooking was adopted in this study, because it is not complicated to isolate alkali lignin and sulfur compounds from black liquor of the cooking compared to kraft cooking. The purified lignin was obtained from prehydrolysis soda-AQ black liquor by acid precipitation with 20% (w/w) sulfuric acid followed by centrifuging and washing processes. Lignin structure was defined as S/V ratio and S_a and V_a yields determined by nitrobenzene

oxidation method. Lignin molecular weight distribution was determined by gel permeation chromatography system (GPC). The results showed that the increment of active alkali dosage decreased both S/V ratio and S_a and V_a yields of dissolved lignin. Increasing the prehydrolysis temperature showed no significant effect on S/V ratio while higher temperature resulted in lower S_a and V_a yields. Lignin obtained under prehydrolysis temperature of 170°C and 18% active alkali showed the lowest rate of S_a and V_a yields of 0.19 mmol/g-lignin with a rather low S/V ratio of 2.9. Based on GPC results, weight-average molecular weight (M_w) of purified lignin decreased by increasing of the active alkali dosage and increased by increasing the prehydrolysis temperature. Lignin obtained under prehydrolysis temperature of 150°C and 22% active alkali showed the lowest M_w of 1559 (M_w/M_n=2.3). By increasing the prehydrolysis temperature from 150°C to 170°C with the same active alkali dosage of 18%, M_w increased from 1653 to 2050 (M_w/M_n=2.48-2.88, respectively). TCF bleaching with the sequence of O-P_{sa}-E_p-P_{sa}-E_p resulted in a pulp with a rather low final viscosity of 6.0 mPa·s. Mixing a small amount of chlorine dioxide: 0.083% and 0.042% (as active chlorine) with P_{sa}: 0.2% and 0.1% (as H_2SO_5 weight) during the 1st and 2nd P_{sa} stages respectively, improved the pulp viscosity to 7.2 mPa·s while the brightness, α-cellulose content, and ash content 0.1% were 90.5% ISO, 94.1%, and 0.1%, respectively.

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