IIETA International Information and Engineering Technology Association
Advancing the World of Information and Engineering

Annales de Chimie - Science des Matériaux
Vol. 48, No. 5, October, 2024, pp. 709-719
Journal homepage: http://iieta.org/journals/acsm

Observing Fiber Morphology Pores Size to Achieve Successful Lignin Removal

Trismawati[1], Darono Wikanaji[2], Ena Marlina[3], Hendry Y. Nanlohy[4], Singgih D. Prasetyo[5,6], Zainal Arifin[6*]

[1] Department of Industrial Engineering, Panca Marga University, Probolinggo 67271, Indonesia
[2] Independent Researcher, Yos Sudsarso 1/15 Probolinggo, Probolinggo 67217, Indonesia
[3] Department of Mechanical Engineering, Universitas Islam Malang, Malang 65144 Indonesia
[4] Department of Mechanical Engineering, Jayapura University of Science and Technology, Papua 99351, Indonesia
[5] Power Plant Engineering Technology, Faculty of Vocational Studies, State University of Malang, Malang 65145, Indonesia
[6] Department of Mechanical Engineering, Universitas Sebelas Maret, Surakarta 57126, Indonesia

Corresponding Author Email: zainal_arifin@staff.uns.ac.id

Copyright: ©2024 The authors. This article is published by IIETA and is licensed under the CC BY 4.0 license (http://creativecommons.org/licenses/by/4.0/).

https://doi.org/10.18280/acsm.480512

Received: 3 July 2024
Revised: 5 September 2024
Accepted: 11 September 2024
Available online: 29 October 2024

Keywords:
fiber, improving success, wood pulp, lignin removal, xylanase enzyme

ABSTRACT

Pulp with high brightness can only be obtained if the lignin content in the unbleached pulp can be optimally removed. For this reason, enzyme and bleaching chemicals must be able to reach the cellulose-hemicellulose-lignin (CHL) structure in the Lignin Carbohydrate Complex (LCC) to peel the lignin molecule. Most research uses enzymes and bleaching chemicals without considering how they reach the CHL structure. This research deeply considered the penetration of enzymes and bleaching chemicals into the CHL structure through the pores in each fiber wall. The molecular sizes of enzymes and bleaching chemicals that must diffuse into the fiber structure and the molecular sizes of fiber pores that allow them to penetrate to reach the CHL structure are also considered. All these results are used to evaluate the normative results of the ECF bleaching of Eucalyptus Camaldulensis and Acacia Mangium Pulp. The results indicated that pore size significantly affected the achievement of a higher brightness of Eucalyptus Camaldulensis Pulp than Acacia Mangium Pulp.

1. INTRODUCTION

Pulp with high brightness can only be obtained if the lignin content in unbleached pulp is optimally removed. Wood has a diverse morphological structure as a raw material for pulp and paper products. Differences in fiber morphology between wood genera are typical because the morphology differs within one wood genus, such as Eucalyptus, which has various species. Hence, the bleaching ability is also different. Thus, variations in raw materials greatly influence the efficiency of the bleaching process [1-3]. Apart from morphological differences, extractive content also impacts bleaching efficiency and causes a decreased brightness [4].

Lignin removal from lignocellulose biomass can be achieved if enzymes and bleaching chemicals reach the lignin bound in the cellulose-hemicellulose-lignin (CHL) structure. Bleaching chemicals such as chlorine dioxide, when they reach the structure of CHL from LCC, selectively oxidize lignin without reacting with carbohydrates but react with hemicellulose even though the hemicellulose structure does not change significantly. This chemical severely attacks lignin structure, especially the bonds of guaiacol (G) lignin, syringyl (S) lignin, and phenyl glycoside-type LC linkages [5]. In terms of enzymes, the mechanism of adsorption of enzymes on fiber wall substrates is affected by many parameters, such as the characteristics of the wood fiber (biomass) and enzymes, as well as the process environment [6]. Enzymes are specific catalysts used to replace less environmentally friendly chemical processes. Enzymes are applied in lignocellulose processing to obtain diverse products and maximize the use of raw materials. In the pulp and paper industry, the hemicellulose fraction of lignocellulose is relatively underutilized due to the heterogeneous chemical structure of hemicellulose polysaccharides dissolved in black liquor. Their composition varies significantly according to the raw materials “that have different CHL structures in their LCCs,” the cooking methods and the chemicals used [7].

To be able to reach the CHL structure, enzymes and chemicals must be able to penetrate the fiber wall layer, which has pores. In reactions involving solid substrates such as fiber, the reactivity is proportional to substrate accessibility, which is a function of the substrate's porosity and effective surface area. In wood fibers, the closure of pores with micro-meso-and macropores sizes (<2 nm, 2-50 nm, and >50 nm) is detrimental to chemical and enzymatic treatments [8-11].

To penetrate the tiny fiber pores, enzymes and chemicals that are also molecular in size must be able to compete with the pores of the fiber wall, which are also in molecular size. In a lignocellulose hydrolysis study using a minimum cellulase dose, it was found that hydrolysis was influenced by

the accessibility of cellulose in the lignocellulose mass. The research results showed that the rate-limiting step of hydrolysis is not the catalytic cleavage of the cellulose chain but rather the limited accessibility of the enzyme to the cellulose chain due to the physical structure of the cellulose substrate [12, 13]. The pore volume and size significantly affect the enzymatic hydrolysis of lignocellulose biomass [14]. The smaller pore size with diameters less than the cellulases (average diameter of 5.9 nm) has limited enzyme access to the substrates [15].

The structure of CHL in LCC in each layer of the fiber wall is different, and the content is different. Even if enzymes and bleaching chemicals can reach it, these materials still have to struggle to break the bonds in the CHL structure, starting from releasing lignin at the weakest bond. In the enzymatic hydrolysis of biomass, factors that have detrimental effects are the inherent reluctance of lignocellulose biomass and enzyme inhibition caused by various inhibitors [16, 17]. Lignin and polysaccharides (cellulose and hemicellulose) in native biomass are intricately bonded through strong covalent bonds and weak hydrogen bonds, such as benzyl ester, benzyl ether, and phenyl glycoside functional groups [18].

The structure of CHL in LCC of unbleached wood fiber and from Eucalyptus Camaldulensis, Acacia Mangium, and mixed tropical forest woods is unknown. In previous research, the prominent linkages in eucalyptus LCC were PhGlc and γ-Est. The LCC extracted from the pre-hydrolyzate only contains S-type lignin structural units and is linked by β-O-4', while the lignin of the other five fractions is GS-type lignin and the main linked is β-O-4', β-β' and β-5' [19]. Other research states the main lignin-carbohydrate links currently proposed were Phenyl glycosidic linked (PhGlc), Benzyl ether-linked (BE), γ-Ester linked (γ-Est), Ferulate/Coumarate esters linked, and Hemiacetal/Acetal linked [20].

The chemical composition of cellulose, hemicellulose, and lignin in LCC in each fiber cell wall has yet to be discovered. Middle lamella consists mainly of lignin, but the chemical composition of LCC in the primary and secondary walls is unknown. Even though the lignin in the LCC fraction is primarily composed of syringyl units connected by β-O-4′ linkage, the chemical composition of the primary and secondary walls is not yet known accurately except that they are known as hemicellulose and cellulose. The primary cell wall in research has proteins, cellulose, hemicellulose, and pectin constituents. In secondary cell walls, phenolic components such as lignin are located between polysaccharide molecules. The position previously occupied by pectin (as in the primary wall) is replaced by lignin, which has three monolignol subunits such as G (guaiacyl)-, S (syringyl)- and H (p-hydroxyphenyl)-lignin. The microfibril arrangement in the primary cell wall is loose, and the microfibril arrangement in the secondary cell wall is dense and tight [21]. Each structure's amount and composition in the cell wall may vary depending on the plant species.

Acacia Mangium has no specific pattern of vessel arrangement, mainly in the form of 2-3 vessels in radial rows. The average tangential vessel diameter is 120-160 μm, with a 4-9 boats/mm² frequency. They are alternating intervessel pits with an average diameter of 6-9 μm equipped with vestures [22]. In the case of Eucalyptus Camaldulensis, the porous wood vessels are distributed in diagonal and radial patterns; the vessels are exclusively solitary (90% or more), with simple perforation plates. The average tangential vessel diameter is 100-200 μm, with 5-20 vessels/mm² frequency. Alternating intervessel pits are medium size with a diameter of (7-10 μm) and the large size has a diameter of (≥ 10 μm), vestured [23]. On the fiber itself, the size and variation of fiber pore size in unbleached pulp from Eucalyptus Camaldulensis, Acacia Mangium, and mixed tropical forest woods are unknown. Similarly, the distribution of pores in each fiber wall (primary cell wall, outer secondary cell wall, middle secondary cell wall, and inner secondary cell wall) and their interconnections are also unknown. The only thing known is that fibers have lumens and pores in their wall. The sizes of the fiber lumen of Acacia Mangium, Eucalyptus Camaldulensis, and Mixed Hardwoods are 13.35, 7.1, and 16.0 μm respectively [22, 24]. They have several pits in their fiber wall, and the pores are of unknown size.

The molecular sizes of enzymes (in this case, the xylanase enzyme) and bleaching chemicals have never been known or considered, so the ease of these materials penetrating the fiber structure and interacting with the CHL structure in LCC has never been considered in previous studies. To penetrate the fiber structure, the size of enzymes and chemical molecules must be much smaller than the size of the pores distributed in each layer of the fiber wall. The size of pores in each wall layer is also considerably varied, so they can be classified according to micro-meso- and macropores (<2 nm, 2-50 nm, and >50 nm). The pore size distribution in Eucalyptus was between 1.9-500 nm, and most mesopores and a small number of micro and macropores [25]. The composition and distribution of pore sizes also vary between wood fibers [8-11]. Eucalyptus Camaldulensis wood is diffuse-porous. The vessels are exclusively solitary (more than 90%), tiny to large (diameter 46.71-190.46 μm), and the frequency is 5-10/mm^2. There is considerable morphological variation within Eucalyptus Camaldulensis due to its geographic distribution. For Acacia Mangium from different seed provenance grown in Indonesia, the anatomical characteristics of the wood (fiber wall area, fiber wall thickness, fiber diameter, vessel lumen area, diffuse-porous solitary and radial with vessel diameter 132-142 μm, vessel frequency 7-9/mm^2 and wood density) are not significantly different [26, 27]. In the case of mixed tropical hardwoods, the wood has a more complex structure and morphological characteristics. The distribution of the vessels differs; trees have solitary and radially spreading pores, and others have ring pores [27, 28]. Another constraint is the presence of pitch in the wood fibers of Acacia Mangium, Eucalyptus, and hardwood. This pitch is a fatty acid molecule that has lipophilic properties. The pitch content in the unbleached pulp of Acacia Mangium and Betula verrucosa (silver Birch) is 20 and 4 times higher than that of Eucalyptus [29].

The differences in CHL structure and CHL content in each fiber wall layer are unknown. The type of bond that determines the breaking of the CHL structure chain and the number of bonds in the CHL structure is not yet known, so the success of lignin removal in the bleaching process of Eucalyptus Camaldulensis, Acacia Mangium, and mixed tropical forest woods pulp is not yet known.

There are several LCC Linkages and substructures of lignin: (PhGlc) phenyl glycoside; (γ Est) γ-ester; (BE) benzyl ether; β-O-4′ linkages; β-O-4′ linkages with acetylated γ-carbon; β-O-4′ linkages with p-coumaroylated γ-carbon; resinol structures formed by β-β′, α-O-γ′ and γ-O-α′ linkages; phenylcoumarance structures formed by β-5′ and α-O-4′ linkages; spirodienone structures formed by β-1′ and α-O-α′ linkages; α,β-diaryl ether substructures; p-hydroxyphenyl unit; (G) guaiacyl unit; (S) syringyl unit; (FA) ferulic acid; (PCA) p-coumaric acid. In Eucalyptus Camaldulensis, the

most common LCC linkage is β-O-4′ aryl linkages; γ-acetylated β-O-4′ substructures; γ-p-coumaroylated β-O-4′ linkages; retinol substructures; caffeoyl alcohol units; (γ-Est) γ-ester; (S) syringyl units; (S') Cα-oxidized syringyl units; (G) guaiacol units; (PhGly) phenyl glycosides [19]. Even though the structure and linkage of LCC in wood are known, the composition of the components that have this linkage in each species of wood, such as Acacia Mangium, Eucalyptus Camaldulensis, and Mixed Tropical Hardwoods, still needs

Recent research has shown that the distribution of fiber pore size plays a crucial role in lignin removal efficiency during the bleaching process. Larger pores tend to increase the accessibility of enzymes and chemicals to lignin, accelerating the degradation process and reducing the need for harmful chemicals. Conversely, smaller pores may limit penetration and lead to uneven treatment, thus affecting the final quality of the fibers. This study highlights the importance of profoundly understanding micropore structures within fibers to optimize a more environmentally friendly bleaching process.

A comprehensive investigation into the interactions between enzymes, bleaching chemicals, and lignin within the carbohydrate-lignin complex (CHL) of lignin-carbohydrate complexes (LCC) in individual wood pulp fiber walls is imperative to optimize lignin removal while preserving the structural integrity of the pulp fibers. This research must meticulously consider the molecular dimensions of enzymes and bleaching agents, such as the pore diameter and the morphology of hollow tube-like structures within the fiber walls, which are critical for determining the feasibility of molecular passage.

A detailed understanding of the pore size distribution, dimensional variability, and connectivity within the fiber walls is essential for the rational selection of enzymatic and chemical treatments for lignin removal. The interconnected channels within the fiber matrix are pivotal in facilitating the diffusion of water-soluble enzymes and bleaching agents from the external fiber surface to the innermost layers of the fiber wall. These hollow channels must remain unobstructed at each process stage by potential blockages, such as large enzyme molecules or exudates from tyloses. This ensures efficient penetration and interaction with lignin, enabling effective and selective lignin removal while maintaining the mechanical properties and integrity of the pulp fibers.

This research aims to comprehensively evaluate the impact of pulp fiber pore size on the efficiency and effectiveness of lignin removal during the wood pulp bleaching process. The study will involve experimental and theoretical approaches to provide a holistic understanding of how pore size distribution within the fiber walls influences the interaction between lignin and bleaching agents. By integrating laboratory experiments with in-depth literature analysis, this research seeks to establish a clear correlation between pulp fiber pore size and lignin removal efficiency. The outcomes of this study are expected to contribute to optimizing bleaching processes in the pulp and paper industry, promoting more efficient lignin removal while minimizing damage to the structural integrity of the fibers. This research also aims to provide valuable insights into selecting appropriate bleaching agents and process parameters based on the specific pore characteristics of different wood pulp types.

2. METHOD

2.1 Experiment process

This research was conducted in two interrelated stages. The first stage was a laboratory experiment to release lignin molecules from the CHL (Carbohydrate-Hemicellulose-Lignin) structure within the LCC (Lignin-Carbohydrate Complex) to remove lignin effectively. This experiment involved chemical treatments of the pulp to understand how lignin can be separated from other components in the wood, with a particular focus on the mechanisms of lignin binding within the LCC structure.

In the second stage, an in-depth scientific review was conducted to identify and analyze the factors influencing the ease and difficulty of removing lignin from the CHL structure. This review encompassed the evaluation of various variables such as the type of chemicals used, temperature, pressure, reaction time, and the wood fibers' morphological properties. This review aimed to understand better the dynamics involved in the lignin removal process, thereby identifying the optimal conditions for efficient pulp treatment.

In the laboratory experiment, three types of unbleached pulp were used as test materials. These pulps were directly obtained from the brown-stock tank at the pulp mill, resulting from the initial processing of wood into pulp. Using unbleached pulp allowed researchers to observe the direct effects of chemical treatments on the intact lignin structure. It provided insights into how effective different lignin removal methods are under conditions practically relevant to the industry.

The results from these two stages of research are expected to provide a deeper understanding of the lignin removal process and offer practical guidelines for the pulp and paper industry to improve the efficiency of their processes, both on laboratory and industrial scales. Additionally, the scientific review conducted in the second stage will provide a solid theoretical foundation for developing more advanced lignin processing technologies.

The Bleach-Chase Method for Measuring Protein Half-Lives is a protocol for systematically measuring the half-life dynamics of multiple proteins in living cells. It involves time-lapse fluorescence microscopy, automated image analysis, and quantitative analysis. The method offers advantages such as simultaneous measurement, high temporal resolution, minimal cell disturbance, and no radioactive labeling. For chemical research, internal checking of critical results, co-workers without expertise, adequate experimental detail, and reviewers play a crucial role in ensuring reproducibility.

2.2 Materials

The pulps used in this research comprised three main types: *Eucalyptus camaldulensis*, *Acacia Mangium*, and *Tropical mixed hardwoods*. These three types of pulp were selected due to their differing morphological characteristics and chemical compositions, which can influence the effectiveness of the lignin removal process. The variation in fiber morphology among these three pulps—specifically in terms of fiber dimensions, cell wall thickness, and pore distribution—plays a critical role in determining the efficiency and effectiveness of the lignin removal process. These morphological characteristics directly influence the accessibility of lignin to chemical agents, thereby affecting

the overall efficacy of the delignification process. Understanding these differences is essential for optimizing chemical treatment protocols and ensuring efficient lignin extraction across different wood types.

(a) Eucalyptus camaldulensis

Eucalyptus camaldulensis is known for having fibers of medium length with relatively thick cell walls. This cell wall thickness provides excellent resistance to chemical penetration, meaning that lignin removal in this wood requires more intensive chemical treatment. Additionally, the pores in *Eucalyptus camaldulensis* tend to be small and uniformly distributed, allowing for more efficient chemical distribution during lignin removal. However, the cell wall thickness remains a limiting factor that must be considered.

(b) Acacia Mangium

Acacia Mangium fibers are generally shorter than those of *Eucalyptus camaldulensis* but have relatively thinner cell walls. This thinner cell wall allows for easier chemical penetration, making lignin removal in *Acacia Mangium* more efficient than in *Eucalyptus camaldulensis*. The pores in *Acacia Mangium* are also uniformly distributed, although they may be slightly larger, which further supports effective lignin removal.

(c) Tropical mixed hardwoods

Tropical mixed hardwoods represent a group with varied fiber morphology. These hardwoods generally have shorter fibers with thicker cell walls than *Acacia Mangium* but thinner than *Eucalyptus camaldulensis*. The pores in tropical mixed hardwoods are often more extensive and less uniformly distributed, hindering chemical penetration and making lignin removal less efficient. The high variation in fiber morphology among species within this group requires a more tailored approach to the lignin removal process.

3. RESULTS AND DISCUSSION

3.1 Result analysis

Table 1 shows that the lignin content in the unbleached pulp from the brown stock of Eucalyptus Camaldulensis is significantly higher than in Acacia Mangium pulp. This high lignin content dramatically contributes to the lower brightness of the pulp, as lignin is a dark component that absorbs light and reduces the pulp's reflectivity. As a result, Eucalyptus Camaldulensis pulp exhibits a lower brightness than Acacia Mangium, which has a lower lignin content.

This difference indicates that the chemical composition of the two pulp types directly impacts their visual characteristics. The lower lignin content in Acacia Mangium means that the bleaching process will be more effective in enhancing its brightness compared to Eucalyptus Camaldulensis, where the higher lignin content requires a more intensive bleaching effort to achieve the same brightness level. In other words, the initial properties of the pulp significantly affect the outcome after the bleaching process.

A comprehensive and in-depth investigation of the bleaching process is essential to remove lignin from the unbleached wood pulp fibers effectively. This study standardized the enzyme dosage, chemical agents, experimental operating conditions, and treatment protocols, ensuring that enzymatic and chemical methods were directly comparable in their efficacy for lignin removal. Enzymes and chemicals were assessed for their ability to disrupt lignin within the Carbohydrate-Hemicellulose-Lignin (CHL) structure of Lignin-Carbohydrate Complex (LCC) molecules under identical conditions.

The operating parameters for the pre-bleaching and bleaching stages were carefully aligned with those typically employed in industrial pulp mills to ensure the results' applicability to large-scale operations. The lignin removal sequence utilized in this study was the X-O-D-E_{op}-D process, involving enzymatic pre-treatment (X), oxidative delignification (O), chlorine dioxide (D), alkaline extraction (E_{op}), and final chlorine dioxide (D) stages. This standardized approach evaluates the relative efficiency of enzymatic versus chemical methods in breaking down lignin and enhancing pulp brightness, mirroring industry-relevant conditions.

The structure of CHL in wood fibers is still being determined, as is the structure of CHL in LCC of unbleached pulp from Eucalyptus Camalduensis, Acacia Mangium, and mixed tropical forest wood. So far, research on removing lignin from the CHL structure in LCC has never considered this and only shows that bleaching with specific enzymes and chemicals under certain operating conditions gives better results than the previous process.

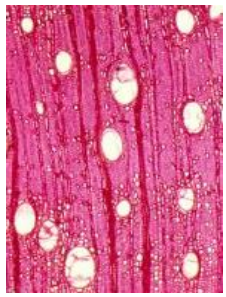
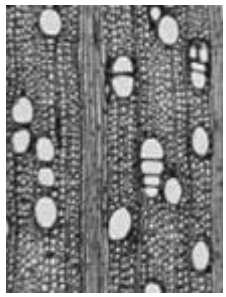
The results are presented in Table 1. Logically, Acacia Mangium pulp should produce bright pulp with the lowest lignin content or the highest brightness. Eucalyptus Camaldulensis pulp provides the pulp with the lowest lignin content or highest brightness. What is the secret behind this? What is the probability of bleaching chemicals and enzymes penetrating the fiber's physical structure or tracing the fiber morphology to reach the CHL structure in LCC? According to the literature, the morphology of Acacia Mangium and Eucalyptus Camaldulensis fibers is as follows (Table 2).

The pore size of Acacia Mangium and Eucalyptus Camaldulensis wood can vary depending on the specific species and growing conditions. Generally, eucalyptus wood tends to have larger pores than Acacia Mangium wood. Because the Eucalyptus Camaldulencis was planted in Prachinburi province, Thailand, the Acacia Mangium was planted in Riau Province, Sumatra, Indonesia, and the mixed hardwoods from Sumatra forest, the growing conditions are relatively the same.

Table 1. The properties of brown stock unbleached pulp used in this research

Properties	Acacia Mangium	Eucalyptus Camaldulensis	Mixed Tropical Forest Woods
Kappa number	13.19	18.57	12.24
Lignin content, %	1.71	2.41	1.59
Brightness, oISO	43.1	33.4	32.6
Viscosity, cm^3/g	792	918	654

Table 2. Fiber Morphology data of Woods Fiber

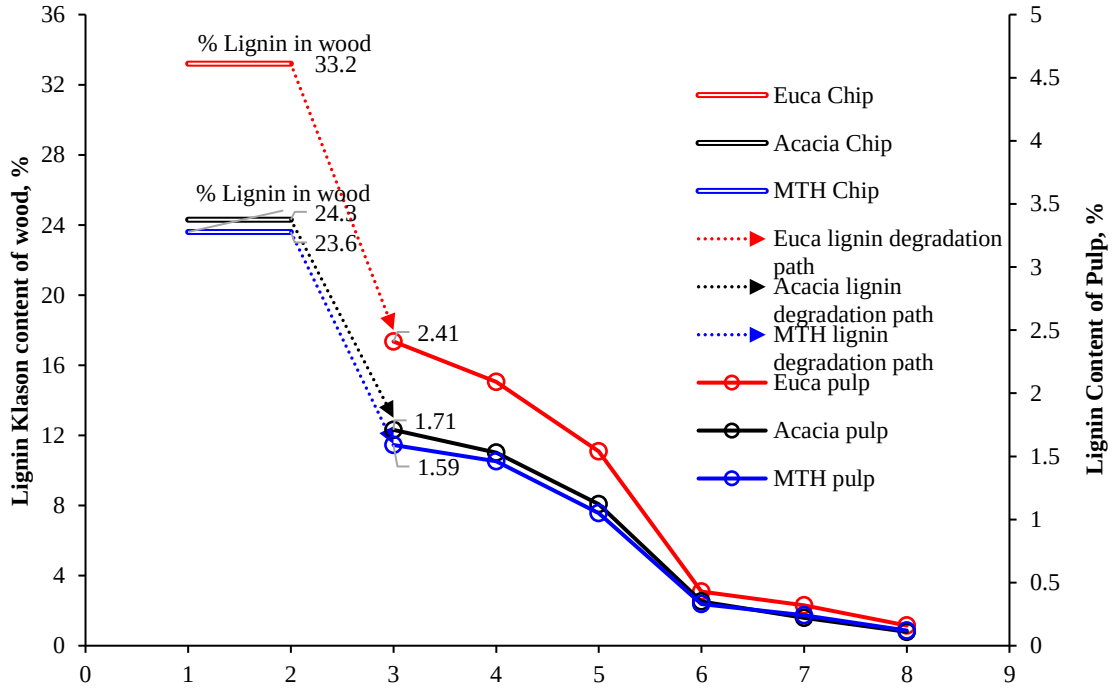
Description	Acacia Mangium	Eucalyptus C.	HW	Note: References
Fiber length, µm	930	940	1200	[22, 24, 30]
Fiber diameter, µm	17.43	11.1	15-35	[22, 24, 30]
Fiber wall thickness, µm	2.03	1.88	> 3.0	[22, 24, 30]
Lumen diameter, µm	13.35	7.1	14.69-24.37	[22, 24, 31]
Fiber coarseness, mg/100 m.	7.5	7.7	12.9	Data research
Pore size (nm)	Pits restricted to radial walls, 94 % mesopores 5 % micropores	Numerous and distinctly bordered pits. 1.9-500 nm (very small to large), mainly (2-50 nm)	Vary (meso-macro)	[25, 27, 32]
Pore distribution	Diffuse porous, mostly solitary	Exclusively diffuse porous (> 90%), mainly mesopores	Some are porous and solitary and radially, and others are ring porous.	[25, 27, 28]
Light micrographs of transverse sections show vessels and pores.	 Bar 100 um			[22, 23, 26]
Vessel frequency, no./mm^2	7-9	16	14.84	[22, 26, 33]
Percentage of fibers, vessels, Parenchyma rays	85.8-84.8, 9.1-9.8, 5.2-5.3	76.8 15.0 8.3	44.8 13.1 41.0	[33-35]
PS:	micro- meso- and macropores: (<2 nm, 2-50 nm and >50 nm)			

From Table 2, it can be seen that there are very significant differences in fiber morphology. This is undoubtedly one of the causes of differences in the lignin removal process's success in these pulp types, especially between Eucalyptus Camaldulensis and Acacia Mangium, how chemicals and enzymes can pass through fiber pores, lumen, or any cleavage in fiber body and have an intimate interaction with the structure of CHL in LCC.

From the data above, chemical and xylanase enzymes are microscopic. The size of chemicals is less than 1 nm, while the enzyme xylanase is 3.56 nm (much smaller than a micron). What about the pore size of the fiber? Eucalyptus Camaldulensis fibers (tracheids) have numerous and distinctly bordered pits. Morphologically, the average pore size of Eucalyptus fiber is 5 nm [25], and for unbleached pulp, "without any wood species specification," is 9-11 nm [34] and 1.2-6 nm [36]. For Acacia Mangium, no data is available, but the pore size in the fiber wall can be predicted from any fiber morphology data [24, 26]; for non-wood fiber such as Hemp fiber, pore sizes vary micropores (3-10 nm), mesopores> 50 nm, and macropores (0.1-1 µm and 20-80 µm). This data on non-wood pores strengthens the belief that the pore sizes in the fiber walls are micro and meso sizes [37].

Pits and border pits are numerous in each fiber (tracheid), but the size of these pores or pits is rarely measured or evaluated. In Acacia Mangium, fiber/tracheid pits are mainly restricted to radial walls and simple to minute borders. Acacia Mangium fiber has dimensions of fiber length, fiber diameter, lumen diameter, and fiber wall thickness of 860 µm, 15.8 µm, 8.0 µm, and 3.9 µm respectively [26] and 930 µm, 17.4 µm, 13.3 µm, and 2.8 µm respectively. It must have pits with a pore diameter much smaller than the lumen diameter and be mesoporous [24]. In the case of mixed tropical hardwood fibers, the dimensions of fiber length, fiber diameter, lumen diameter, and fiber wall thickness are respectively 1200 µm, 13-15 µm, 16-28 µm, and> 3.0 µm [30]. For Eucalyptus Camaldulensis, fibers/tracheids have numerous and distinctly bordered pits. Eucalyptus Camaldulensis has pits with a pore diameter of micropores (< 4.0 %), primarily mesopores (> 91.0 %), and few macropores (< 5.0 %) calculated from BJH adsorption pore volume [25]. In this case, Eucalyptus Camaldulensis has dimensions of fiber length, fiber diameter, lumen diameter, and fiber wall thickness of 940 µm, 11.1 µm, 7.1 µm, and 1.88 µm respectively [22]. From this fiber dimension, Eucalyptus fiber appears to have the smallest dimension among the others. However, the tree's age significantly influences this condition, but Eucalyptus Camaldulensis and Acacia Mangium come from plantation areas, except for mixed tropical hardwoods. So, the pore size of Eucalyptus fiber can be predicted to be the smallest. From this point of view, the pore size of the fiber should not hurt the penetration of any chemical into the fiber structure because the diameter (considered to have a spherical shape) of any chemicals involved in the bleaching process is well below 1 nm.

Figure 1 shows the initial lignin content in wood pulp. It was also seen that the lignin content in the wood pulp decreases as it goes through several stages of the bleaching process. Changes in the lignin content of the wood pulp are different than expected. Although the treatments were the same, the reduction in lignin content was not the same. The decrease in lignin content in Eucalyptus wood pulp was faster than in Acacia M and tropical forest wood pulp.



Note: 1-2: wood chip 3: unbleached, 4: Xylanase treated, 5: O2 delignified, 6: Do treated, 7: Eop treated, 8: D1 treated. At point 3 the brightness of Acacia M, Euca, and MTH are 43.1, 33.4, and 32.6 % ISO respectively

Figure 1. Lignin degradation processes during the wood processing steps and the brightness of un-bleached pulp

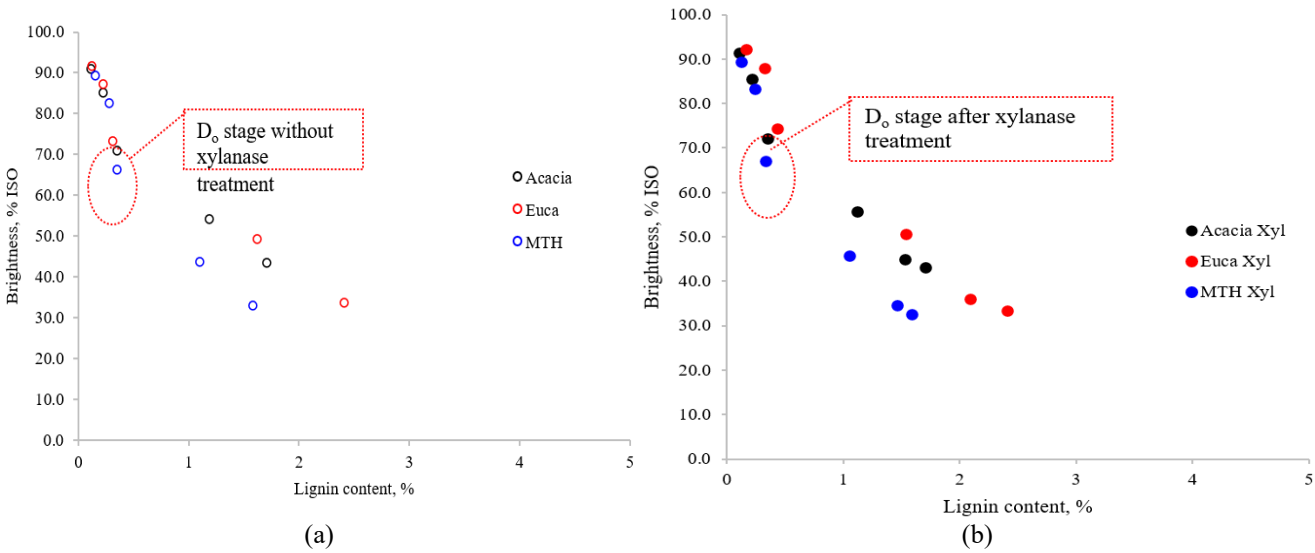


Figure 2. Brightness and lignin content of bleached wood pulp: (a) ordinary bleaching; (b) xylanase treated before bleaching

Theoretically, if the wood fiber morphology is the same and the structure of CHL in LCC is the same, then the lignin removal process and speed should be the same. The degradation of lignin in the cooking process of Eucalyptus Camaldulensis is the highest compared to Acacia Mangium and MTH (see the lignin degradation path). Some exceptional cases may occur due to the wood structure's physical properties and some chemical properties in the woods. The physical properties of the wood structure encourage chemicals and enzymes to penetrate the wood structure and reach the lignin molecules of CHL in LCC. Chemical properties are closely related to the structure of CHL in LCC and seem closely related to the bond dissociation energy. Before discussing further, look at the following wood pulp bleaching results.

Figure 2 shows the results of bleaching Acacia Mangium, Eucalyptus Camaldulensis, and tropical forest hardwood pulp. This indicates that achieving pulp brightness from bleaching Eucalyptus Camaldulensis wood pulp is much more significant than Acacia Mangium and tropical forest wood. The brightness of Eucalyptus has surpassed Acacia Mangium since in the D_o stage (as indicated by an oval dashed line) and continued in the E_{op} and D_1 stages. The brightness result was the highest compared to other wood pulps (Figure 2a). In the case of xylanase treatment carried out before oxygen delignification, the brightness achievement of Eucalyptus Camaldulensis was also the highest compared to the others. However, the remaining lignin left in the pulp was also the highest compared to the others (Figure 2b).

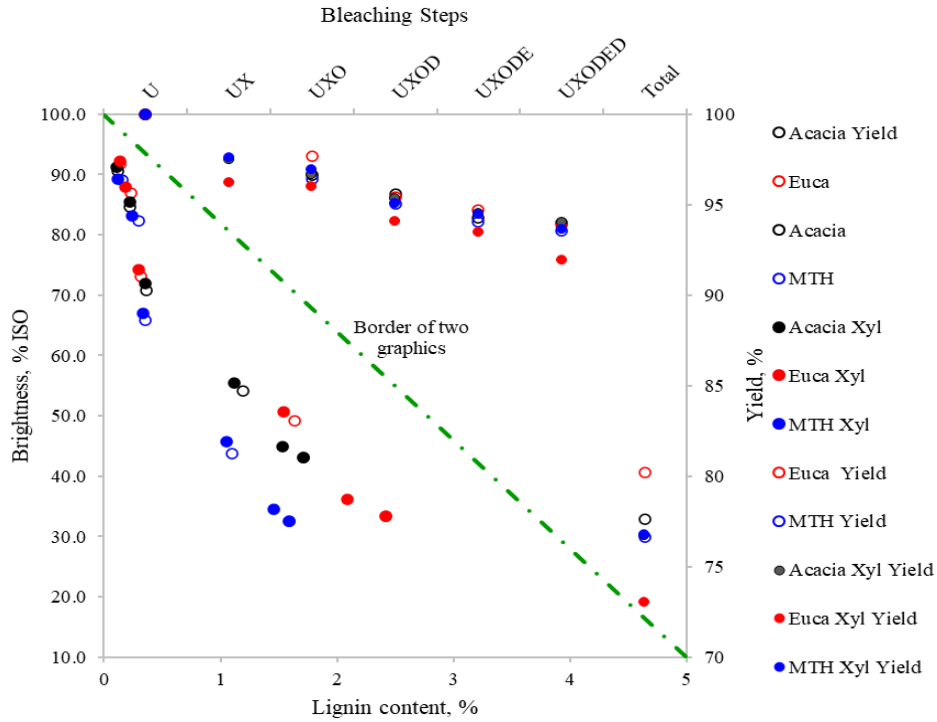


Figure 3. Brightness vs. lignin content and Yield vs. bleaching steps of wood pulp, with and without xylanase treatment

Observing the yield as shown in Figure 3, Eucalyptus achieved the highest yield at each stage of the bleaching process, so there was the most minor fiber loss during the bleaching process compared to the others. From these results, it can be predicted that bleaching chemicals can directly attack the structure of CHL in LCC at the structure that connects the lignin molecules so that the molecules disconnected from the LCC structure are mostly lignin. From these results, it is believed that the release of lignin from the structure of CHL in the LCC of Eucalyptus Camaldulensis occurs without attacking many hemicellulose and cellulose molecules. On the contrary, unexpected results occurred when the xylanase enzyme was used to increase the achievement of brightness. Eucalyptus Camaldulensis got the highest brightness, but the yield lost was also the highest among others. This means that too much cellulose and hemicellulose were degraded. Is there any influence on the fiber morphology?

In reactions involving solid substrates such as fiber, the reactivity is proportional to the substrate accessibility, which is a function of the porosity and the effective surface area of the substrate. In wood fibers, the closure of the micro- meso- and macropores (<2 nm, 2-50 nm, and >50 nm) is detrimental to enzymatic treatments [8-11]. Let us examine the basic concept behind all of these. Scientifically, the size of the molecules O_2, H_2O, the material substance +ClO2, and the enzyme xylanase Ecopulp TX-200 were studied. It is known that the O_2 molecule has a size of 0.299 nm [38], and the H_2O molecule has a size of 0.292 nm, assuming they are spherical [39].

The $^{+}ClO_2$ substance the size is 0.124 nm [40, 41]. Water molecules as a medium for any chemicals and enzyme transportation into the fiber also have molecule sizes below 1 nm. In Figure 3, it is seen that the brightness gain of Eucalyptus Camaldulensis reaches the highest point as compared to the other (the same as in the previous case of O-D-Eop-D stages). However, at this X-O-D-Eop-D stage, the bleached Eucalyptus Camaldulensis pulp yield is bellowed of Acacia Mangium dan mixed tropical hardwood. Higher fiber losses have occurred than previously. Micropores in the pulp fibers restrict the enzyme molecules from passing through. The TX-200 xylanase enzyme from Trichoderma reesei growth media with a 19-20 kDa mass has a minimum diameter of 2xRm of 3.56 nm [42]. The cell wall pores of low-yield pulp fibers are mainly in the range of 10-30 nm [36] and belong to the mesopore size. For Acacia Mangium and mixed hardwood pulp, the enzyme treatment seems to have no detrimental effect on yield reduction. This may be because the size of pits in the fiber tracheid is large enough for the xylanase enzyme to pass through but not for Eucalyptus Camaldulensis that has around 5 % of micropore and 10 % of the lowest region of mesopore 2 - 3 nm [25]. In plant cells, nanomaterials must pass through the cell wall barrier with a pore size of around 13 nm. Related to this condition, nanomaterials (chemicals and enzyme particles) with at least a dimension close to or less than 13 nm have a better opportunity to interact with the plasma membrane and pass through it [4].

The molecular composition of cellulose, hemicellulose, and lignin in the CHL structure in LCC at each fiber wall layer is unknown. Besides the ease of chemicals and enzymes penetrating the fiber structure through molecular diffusion, when they successfully diffuse into each layer of the fiber wall and reach the CHL structure in LCC, chemicals, and enzymes will attack the weakest hydrocarbon bond to break the chain. The chain break will occur at the lowest dissociation energy of the bonding [43].

The condition of the brightness of Eucalyptus C is the highest compared to other wood pulps (Acacia M and MTH), while the yield of Eucalyptus C pulp obtained is the highest among others, which means that the hydrocarbon chains that are broken due to the bleaching process are the least among other pulps. In other words, lignin's breaking or cleavage occurred directly on the bonds that bind lignin molecules with the lowest dissociation energy. On the contrary, the yield of bleaching for Eucalyptus Camaldulensis in the X-O-D-Eop-D stage is the weakest among others, as shown in Figure 3. These might have any correlation not only with the size and

distribution of the pores but also due to the linkage structure of lignin in LCC and the size of enzyme xylanase that should have destructive action into the pits of fiber.

The linkage of lignin in LCC of hardwoods has several possibilities: β-O-4′ linkages; β-O-4′ linkages with acetylated γ-carbon and p-coumaroylated γ-carbon; retinol structures formed by β-β′, α-O-γ′ and γ-O-α′ linkages; and phenylcoumarance structures formed by β-5′ and α-O-4′ linkages [43, 44]. There has yet to be a detailed study of the composition of this linkage in the fiber wall of Eucalyptus Camaldulensis, Acacia Mangium, and mixed tropical hardwood pulp. Materials with the highest amount of the lowest dissociation energy should have the highest possibility of lignin removal if there are no other recalcitrant substrates to maintain good integrity between lignin and chemicals and enzymes. This is the most challenging part to answer and explain, as well as an in-depth study of lignin interactions with enzymes and chemicals.

From Table 3, it can be concluded that those with the highest amount of α-O-4, β -1 (C-C), and β-O-4 linkage have a higher possibility of the amount of lignin to be peeled off from the CHL structure of LCC. It is suggested that the α-O-4 and β -1 (C-C) linkage is in the outermost part of the fiber wall or the middle lamella, so there is no yield loss when the lignin is peeled off in this portion. When the peeling action of lignin occurs in the β-O-4 linkage, which is primarily located in the primary and secondary walls (suggested starting from the outer part of the secondary wall), which are found in or be part of the hemicellulose structure, some yield loss might happen. These cause fiber rupture, as shown in Figure 4.

Table 3. The bond dissociation energy of Hardwood [43]

Bond Type	Hardwood (%)	BDE (kJ/mol)
α-O-4	4 - 8	222
β-1 (C-C)	5 - 7	285
β-O-4	45 - 65	313
4-O-5	6 - 7	335
5-5	4 - 10	481
β-5	3 - 11	523
β-1 (C=C)	minor	690

BDE: Bond Dissociation Energy, kJ/mol [43]

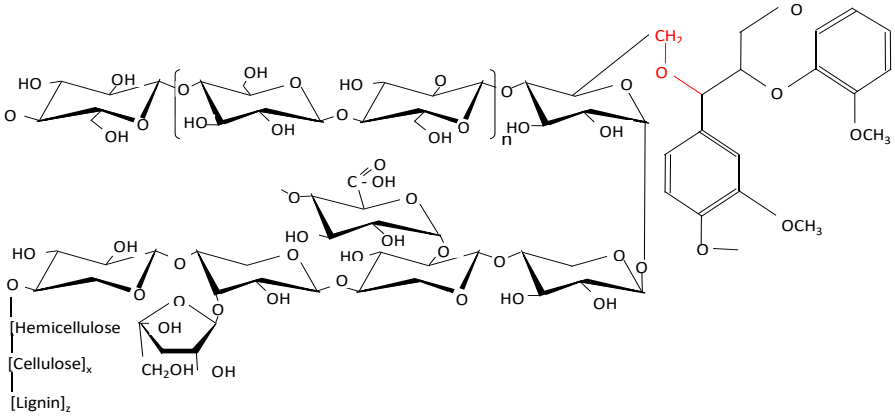


Figure 4. Interactive situation in the interaction between chemicals, enzymes, and lignin in CHL structure

Table 4. Research on the role of pore size in delignification

Insights	Methods Used	Limitations	Future Research	Ref.
Pore size significantly impacts lignin diffusion during delignification, with smaller pores hindering large lignin transport and larger pores facilitating it, thus affecting the process's efficiency.	Model cellulose membranes. UV-vis spectra and SEC analysis.	• Small pores hinder large lignin molecules/clusters. • Delignification efficiency requires increased average pore size.	Investigate the effects of pH and temperature on lignin diffusion. Further studies are recommended to use the present method for detailed analysis.	[45]
Tuning mesopore size in lignin-based porous carbon affects kraft lignin decomposition. Pore size plays a crucial role in delignification processes by influencing the efficiency of lignin breakdown.	Salt templating for mesopore size tuning. Kraft lignin decomposition analysis.	It is limited by the specific lignin source used. Challenges in controlling the mesopore size accurately.	Investigate the catalytic performance of lignin-based porous carbon. Explore the potential applications in energy storage systems.	[46]
The zeolite pore size influences delignification during catalytic pyrolysis of Kraft lignin, impacting the efficiency of the process by affecting the accessibility of the lignin molecules to the catalyst.	Catalytic pyrolysis of Kraft lignin. Study of zeolite pore size and acidity effects	A limited number of zeolites were studied. Lack of detailed kinetic analysis.	Investigate other types of catalysts for pyrolysis reactions. Explore the scalability of the process for industrial applications.	[47]
Delignification alters pore size distribution, increasing macropore importance. The drying method impacts final porosity, with freeze-drying showing 13% higher porosity in harsh delignified samples than oven-dried ones.	Acidic delignification of beech wood Mercury intrusion porosimetry (MIP) for structural characterization	The drying process affects the final porosity. Impact of delignification and drying on cellulose scaffold porosity.	Impact of Delignification and drying on cellulose scaffold functionalization Further modification treatments for enhanced material properties	[32]

Pore size plays a crucial role in delignification, affecting the transport of lignin fragments and catalytic efficiency. Smaller pore sizes restrict larger lignin molecules, while larger ones facilitate their transport. Optimized pore sizes improve catalytic performance, such as in molybdenum carbide supported on porous carbon. However, huge pores may reduce selectivity, indicating the need for balance in pore size optimization. Some studies on the role of pore size in delignification are shown in Table 4.

3.2 Environmental impact and sustainability

Enzymes, as a sustainable alternative to traditional chemical bleaching processes, offer significant environmental benefits that address the increasing demand for eco-friendly industrial practices. Enzymatic bleaching involves using enzymes such as laccases, xylanases, and cellulases, specifically targeting lignin and hemicellulose bonds under milder conditions than the harsh chemicals used in conventional methods. This sub-section explores the environmental impacts of enzymatic bleaching compared to chemical bleaching, highlighting the advantages of reduced chemical usage, lower energy consumption, and a minimized ecological footprint.

(a) Reduced chemical usage: Enzymatic bleaching dramatically reduces reliance on harmful chemicals like chlorine, sodium hydroxide, and hydrogen peroxide, which are prevalent in traditional bleaching processes. The enzymatic approach minimizes the release of toxic effluents into the environment, reducing water pollution and lessening the need for complex wastewater treatment systems. This aligns with global sustainability goals by promoting cleaner production methods that safeguard aquatic ecosystems.

(b) Lower energy consumption: Chemical bleaching often requires high temperatures and pressures, contributing to significant energy consumption. In contrast, enzymatic processes operate at lower temperatures and neutral pH levels, reducing energy requirements and associated greenhouse gas emissions. This decrease in energy usage lowers the carbon footprint of pulp production and translates into cost savings, enhancing the economic feasibility of enzymatic bleaching as a sustainable alternative.

(c) Reducing environmental impact: One of the main drawbacks of chemical bleaching is the production of hazardous by-products such as dioxins and chlorinated organic compounds, which pose serious environmental and health risks. Enzymatic bleaching eliminates or significantly reduces the formation of these toxic pollutants, resulting in cleaner waste and a more minor ecological impact. Lower levels of total organic carbon (TOC) and biochemical oxygen demand (BOD) in wastewater also reduce the overall environmental waste.

While chemical bleaching remains effective for achieving high brightness levels, it often results in significant environmental trade-offs due to the extensive use of chemicals and energy. Enzymatic bleaching, on the other hand, provides a more sustainable solution by significantly lowering ecological costs. However, challenges such as optimizing enzyme performance and achieving high brightness levels without supplementary chemical treatments must be addressed. Continued advancements in enzyme technology promise to overcome these limitations, making enzymatic bleaching an increasingly viable option for the industry.

4. CONCLUSIONS

Based on the findings from the research conducted, the following conclusions have been derived:

(1) From this research, through laboratory experiments and literature studies, it is seen that fiber morphology and the fiber pits interconnection in fiber will have a significant effect on the achievement of lignin removal to give way for chemicals and enzymes to get intact with CHL structure of LCC.

(2) The size of chemicals and, especially, enzymes that have molecular size must be able to penetrate or pass through any pores (pits) in the fiber wall before they can interact chemically and biochemically with the lignin in the CHL structure of LCC.

(3) The success of peeling the lignin from the CHL structure in LCC depends on immersion into the fiber structure through various sizes of fiber pits and pores in the fiber wall.

(4) Therefore, conducting in-depth research on pulp fiber morphology and physical structure is compulsory to successfully obtain high brightness with shallow fiber loss and a few chemicals consumption for environmental protection purposes.

(5) Adopting enzymatic bleaching processes marks a significant step towards sustainable pulp production, balancing the need for effective lignin removal with environmental considerations. As research and technology in this field continue to advance, enzymatic bleaching has the potential to become a cornerstone of sustainable pulp and paper production, offering both environmental and economic benefits.

REFERENCES

[1] Liang, L., Wei, L., Fang, G., Xu, F., Deng, Y., Shen, K., Tian, Q. Wu, T., Zhu, B. (2020). Prediction of holocellulose and lignin content of pulp wood feedstock using near infrared spectroscopy and variable selection. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 225: 117515. https://doi.org/10.1016/j.saa.2019.117515

[2] Wu, T, Fang, G.G., Liang, L., Deng, Y.J., Lin, Y., Xiong, Z.X. (2018). Analysis of mixed pulping raw materials of Eucalyptus globulus and Acacia Mangium by near infrared spectroscopy technique combined with LASSO algorithm. BioResources, 13(1): 1348-1359. https://doi.org/10.15376/biores.13.1.

[3] Trismawati, Wikanaji, D., Marlina, E., Prasetyo, S.D., Bangun, W.B., Arifin, Z. (2024). Enhancement of pulp brightness and yield in ECF bleaching using xylanase treatment: A comparative study on different wood species. International Journal of Design & Nature and Ecodynamics, 19 (3): 899-906. https://doi.org/10.18280/ijdne.190319

[4] Liang, L., Wu, T., Fang, G., Xu, F., Jiao, J., Deng, Y., Xiong, Z. (2022). Predicting bleachability of Eucalyptus mechanical pulp by moisture content-dependent near-infrared spectroscopy. Industrial Crops and Products, 180: 114730. https://doi.org/10.1016/j.indcrop.2022.114730

[5] Han, J., You, X., Wang, S., Chen, C., Yao, S., Meng, C., Liang, C., Zhao, J. (2022). Chlorine dioxide oxidation of hemicellulose from alkaline hydrolysate bagasse to remove lignin unit in lignin-carbohydrate complex.

Carbohydrate Polymers, 277: 118817. https://doi.org/10.1016/j.carbpol.2021.118817
[6] Baig, K.S. (2020). Interaction of enzymes with lignocellulosic materials: Causes, mechanism and influencing factors. Bioresources and Bioprocessing, 7: 1-19. https://doi.org/10.1186/s40643-020-00310-0
[7] Østby, H., Várnai, A. (2023). Hemicellulolytic enzymes in lignocellulose processing. Essays in Biochemistry, 67(3): 533-550. https://doi.org/10.1042/EBC20220154
[8] Dahiya, D., Ceccherini, S., Maloney, T.C. (2023). Impact of high consistency enzymatic hydrolysis and defibration drying on cellulose fiber pore characteristics. Cellulose, 30(12): 7607-7618. https://doi.org/10.1007/s10570-023-05398-z
[9] Nopens, M., Sazama, U., König, S., Kaschuro, S., Krause, A., Fröba, M. (2020). Determination of mesopores in the wood cell wall at dry and wet state. Scientific Reports, 10(1): 9543. https://doi.org/10.1038/s41598-020-65066-1
[10] Lovikka, V.A., Khanjani, P., Väisänen, S., Vuorinen, T., Maloney, T.C. (2016). Porosity of wood pulp fibers in the wet and highly open dry state. Microporous and Mesoporous Materials, 234: 326-335. https://doi.org/10.1016/j.micromeso.2016.07.032
[11] Duan, C., Long, Y., Li, J., Ma, X., Ni, Y. (2015). Changes of cellulose accessibility to cellulase due to fiber hornification and its impact on enzymatic viscosity control of dissolving pulp. Cellulose, 22: 2729-2736. https://doi.org/10.1007/s10570-015-0636-9
[12] Arantes, V., Saddler, J.N. (2011). Cellulose accessibility limits the effectiveness of minimum cellulase loading on the efficient hydrolysis of pretreated lignocellulosic substrates. Biotechnology for Biofuels, 4: 1-17. https://doi.org/10.1186/1754-6834-4-3
[13] Wu, W., Li, P., Huang, L., Wei, Y., Li, J., Zhang, L., Jin, Y. (2023). The role of lignin structure on cellulase adsorption and enzymatic hydrolysis. Biomass, 3(1): 96-107. https://doi.org/10.3390/biomass3010007
[14] Zoghlami, A., Paës, G. (2019). Lignocellulosic biomass: Understanding recalcitrance and predicting hydrolysis. Frontiers in Chemistry, 7: 874. https://doi.org/10.3389/fchem.2019.00874
[15] Meng, X., Foston, M., Leisen, J., DeMartini, J., Wyman, C.E., Ragauskas, A.J. (2013). Determination of porosity of lignocellulosic biomass before and after pretreatment by using Simons' stain and NMR techniques. Bioresource Technology, 144: 467-476. https://doi.org/10.1016/j.biortech.2013.06.091
[16] Agrawal, R., Verma, A., Singhania, R.R., Varjani, S., Di Dong, C., Patel, A.K. (2021). Current understanding of the inhibition factors and their mechanism of action for the lignocellulosic biomass hydrolysis. Bioresource Technology, 332: 125042. https://doi.org/10.1016/j.biortech.2021.125042
[17] Arifin, Z., Prasetyo, S.D., Tribhuwana, B.A., Tjahjana, D.D.D.P., Rachmanto, R.A., Kristiawan, B. (2022). Photovoltaic performance improvement with phase change material cooling treatment. International Journal of Heat and Technology, 40(4): 953-960. https://doi.org/10.18280/ijht.400412
[18] Satlewal, A., Agrawal, R., Bhagia, S., Sangoro, J., Ragauskas, A.J. (2018). Natural deep eutectic solvents for lignocellulosic biomass pretreatment: Recent developments, challenges and novel opportunities. Biotechnology Advances, 36(8): 2032-2050. https://doi.org/10.1016/j.biotechadv.2018.08.009
[19] Chen, L., Liu, H., Jin, X., Wang, T., Guo, Z., Li, J., Wang, Y., Zhang, X., Liao, X. (2023). The extraction, structural characterization and bioactivity of LCC from eucalyptus chips and its Pre-hydrolysis solution. Industrial Crops and Products, 204: 117256. https://doi.org/10.1016/j.indcrop.2023.117256
[20] Giummarella, N., Pu, Y., Ragauskas, A.J., Lawoko, M. (2019). A critical review on the analysis of lignin carbohydrate bonds. Green Chemistry, 21(7): 1573-1595. https://doi.org/10.1039/C8GC03606C
[21] Loix, C., Huybrechts, M., Vangronsveld, J., Gielen, M., Keunen, E., Cuypers, A. (2017). Reciprocal interactions between cadmium-induced cell wall responses and oxidative stress in plants. Frontiers in Plant Science, 8: 1867. https://doi.org/10.3389/fpls.2017.01867
[22] Nezu, I., Ishiguri, F., Aiso, H., Diloksumpun, S., Ohshima, J., Iizuka, K., Yokota, S. (2020). Selection of Eucalyptus camaldulensis families for sustainable pulpwood production by means of anatomical characteristics. Forests, 12(1): 31. https://doi.org/10.3390/f12010031
[23] Richter, H.G., Dallwitz, M.J. (2000). Commercial timbers: Descriptions, illustrations, identification, and information retrieval. https://www.delta-intkey.com/wood/en/index.htm.
[24] Jusoh, I., Abu Zaharin, F., Adam, N.S. (2014). Wood quality of acacia hybrid and second-generation acacia Mangium. BioResources, 9(1): 150-160.
[25] Guo, W.J., Wang, Y., Huang, M.Z., Wan, J.Q., Ma, Y.W. (2011). An investigation of the variation of pore structure in eucalyptus fibre during recycling. BioResources, 6(2): 1029-1042.
[26] Nugroho, W.D., Marsoem, S.N., Yasue, K., Fujiwara, T., Nakajima, T., Hayakawa, M., Nakaba, S., Yamagishi, y., Jin, H.O., Kubo, T., Funada, R. (2012). Radial variations in the anatomical characteristics and density of the wood of Acacia Mangium of five different provenances in Indonesia. Journal of Wood Science, 58: 185-194. https://doi.org/10.1007/s10086-011-1236-4
[27] Savero, A.M., Kim, J.H., Purusatama, B.D., Prasetia, D., Park, S.H., Kim, N.H. (2022). A comparative study on the anatomical characteristics of Acacia Mangium and Acacia hybrid grown in Vietnam. Forests, 13(10): 1700. https://doi.org/10.3390/f13101700
[28] Rahman, M.H., Nugroho, W.D., Nakaba, S., Kitin, P., Kudo, K., Yamagishi, Y., Begum, S., Marsoem, S.N. Funada, R. (2019). Changes in cambial activity are related to precipitation patterns in four tropical hardwood species grown in Indonesia. American Journal of Botany, 106(6): 760-771. https://doi.org/10.1002/ajb2.1297
[29] Freire, C.S., Pinto, P.C., Santiago, A.S., Silvestre, A.J., Evtuguin, D.V., Neto, C.P. (2006). Comparative study of lipophilic extractives of hardwoods and corresponding ECF bleached kraft pulps. BioResources, 1(1): 3-17.
[30] Paavilainen, L. (1998). Quality-competitiveness of Asian short-fibre raw materials in different paper grades. Jaakko Poyry Magazine, 1: 4-8.
[31] Darwis, A., Purusatama, B.D., Iswanto, A.H., Kim, N.H., Hartono, R., Susilowati, A. (2024). Qualitative anatomical characteristics and fiber quality of tapped styrax sumatrana wood grown in North Sumatra, Indonesia. Forests, 15(3): 509.

https://doi.org/10.3390/f15030509
[32] Vitas, S., Segmehl, J.S., Burgert, I., Cabane, E. (2019). Porosity and pore size distribution of native and delignified beech wood determined by mercury intrusion porosimetry. Materials, 12(3): 416. https://doi.org/10.3390/ma12030416
[33] Fichtler, E., Worbes, M. (2012). Wood anatomical variables in tropical trees and their relation to site conditions and individual tree morphology. Iawa Journal, 33(2): 119-140.
[34] Sahri, M.H., Ibrahim, F.H., Shukor, N.A.A. (1993). Anatomy of Acacia Mangium grown in Malaysia. IAWA Journal, 14(3): 245-251.
[35] Barotto, A.J., Fernandez, M.E., Gyenge, J., Meyra, A., Martinez-Meier, A., Monteoliva, S. (2016). First insights into the functional role of vasicentric tracheids and parenchyma in eucalyptus species with solitary vessels: Do they contribute to xylem efficiency or safety?. Tree Physiology, 36(12): 1485-1497. https://doi.org/10.1093/treephys/tpw072
[36] Stone, J.E., Scallan, A.M. (1965). Effect of component removal upon the porous structure of the cell wall of wood. Journal of Polymer Science Part C: Polymer Symposia, 11(1): 13-25. https://doi.org/10.1002/polc.5070110104
[37] Jiang, Y., Lawrence, M., Ansell, M.P., Hussain, A. (2018). Cell wall microstructure, pore size distribution and absolute density of hemp shiv. Royal Society Open Science, 5(4): 171945. https://doi.org/10.1098/rsos.171945
[38] Britannica, E. (2024). Oxygen. Encycl. Br. Inc. https://www.britannica.com/science/oxygen.
[39] Pu, P., Pu, J., Zhu, Z. (2020). Study on the structure model of water molecule and the reasons of formation of some characteristics of liquid & solid water. American Journal of Modern Physics, 9(2): 11-27. https://doi.org/10.11648/j.ajmp.20200902.11
[40] Chai, H.E., Hwang, C.A., Huang, L., Wu, V.C., Sheen, L.Y. (2020). Feasibility and efficacy of using gaseous chlorine dioxide generated by sodium chlorite-acid reaction for decontamination of foodborne pathogens on produce. Food Control, 108: 106839. https://doi.org/10.1016/j.foodcont.2019.106839
[41] Longstaff, J. (2020). Chlorin Dioxide Gas Decontamination vs. Liquid Disinfection. The Official Magazine of ISPE, 40(2): 70-74.
[42] Erickson, H.P. (2009). Size and shape of protein molecules at the nanometer level determined by sedimentation, gel filtration, and electron microscopy. Biological Procedures Online, 11: 32-51. https://doi.org/10.1007/s12575-009-9008-x
[43] Panke, D., Bechthold, G., Müller, T.E. (2022). Solvent effect in catalytic lignin hydrogenolysis. Catalysts, 12(6): 664. https://doi.org/10.3390/catal12060664
[44] Zhang, C., Lu, J., Zhang, X., MacArthur, K., Heggen, M., Li, H., Wang, F. (2016). Cleavage of the lignin β-O-4 ether bond via a dehydroxylation–hydrogenation strategy over a NiMo sulfide catalyst. Green Chemistry, 18(24): 6545-6555.
[45] Ghaffari, R., Almqvist, H., Nilsson, R., Lidén, G., Larsson, A. (2022). Mass transport of lignin in confined pores. Polymers, 14(10): 1993. https://doi.org/10.3390/polym14101993
[46] Wu, K., Liu, Y., Yang, C., Tang, S., Liu, C., Liu, Y., Lu, H., Liang, B. (2022). Tuning the mesopore size of lignin-based porous carbon via salt templating for kraft lignin decomposition. Industrial Crops and Products, 181: 114865. https://doi.org/10.1016/j.indcrop.2022.114865
[47] Zou, Q., Lin, W., Xu, D., Wu, S., Mondal, A.K., Huang, F. (2022). Study the effect of zeolite pore size and acidity on the catalytic pyrolysis of Kraft lignin. Fuel Processing Technology, 237: 107467. https://doi.org/10.1016/j.fuproc.2022.107467

NOMENCLATURE

U	Unbleached wood pulps of Acacia M, Eucalyptu C, and Mixed Tropical Hardwood
X	Xylanase Enzyme
O	Oxygen delignification
D	Chlorine Dioxide bleaching stage
E	Extraction with NaOH - oxygen and peroxide (Eop)
CHL	Cellulose Hemicellulose Lignin
LCC	Lignin Carbohydrate Complex
M	Mangium
C	Camaldulesnsis
MTH	Mixed Tropical Hardwoods