Hemicellulose and hexenuronic acid removal selectivity to give boosting effect to ECF bleaching

Trismawati\textsuperscript{1*}, Hendry Y. Nanlohy\textsuperscript{2}, Zainal A\textsuperscript{3}, D. Wikanaji\textsuperscript{4}, Muji Setiyo\textsuperscript{5}

1 Panca Marga University
Yos Sudarso, Pabean, Dringgu, Probolinggo, 67217, Indonesia
*Email: trismawati@upm.ac.id

2 Jayapura University of Science and Technology
Sosial Padang Bulan, Jayapura, 99351, Indonesia

3 Sebelas Maret University Surakarta
Sutami 36, Surakarta, 57126, Indonesia

4 Independent Researcher
Yos Sudsarso 1/15 Probolinggo, 67217, Indonesia

5 University of Muhammadiyah Magelang
Tidar 21, Magelang 59214, Indonesia

Abstract. Varies wood structure need difference way of treatment to get the appropriate quality of wood pulp. In pulp industry, wood chips should be cooked and bleached in order to have a good quality of pulp suitable for paper industry. A modified pulp cooking such as Continuous Isothermal Cooking and Super Batch Cooking followed by ECF bleaching is a good alternative for the achievement the necessary standard quality. Effort to achieve better quality in higher yield has so many times been done. Enzyme treatment using xylanase using Ecopulp TX-200 is a good alternative that could be done in the ECF bleaching stage. Two kinds of unbleached wood pulp from Eucalyptus camaldulensis from AA Thailand, Acacia mangium from RAPP Indonesia is used in this experiment. The bleaching results are analysed for yield, viscosity, hexenuronic acid content, and brightness. The results give an indication that wood structure has a close correlation with the accessibility of enzyme and chemistries in giving peeling effect of lignin from lignin carbohydrate complex (LCC) to get high brightness of pulp with minimum fibre losses. The presence of Na\textsubscript{2}CO\textsubscript{3} in the cooking liquor to gather with the xylanase has positive effect in the cleavage of hemicellulose and lignin through hydrogen bond at –OCH\textsubscript{3}.

Keywords: wood structure, enzyme, ECF bleaching, hexenuronic acid, LCC, yield, viscosity
1. Introduction

Tropical hardwood is the main raw material in pulp industry beside soft wood and non wood. Physically their structure is very complex. Wood density, coarseness, its fiber length, fiber width, and fiber-cell wall thickness is varies and this properties determine the easyness of chemical penetration into wood structure. How chemical able to react with wood fiber is very depend on the LCC in the fiber. LCC structure itself can be synthesis for carbohydrate-rich LCC and lignin-rich LCC. These LCC theoretically has a prospec for further used in pulping [1], but naturally the structure of LCC is very depend on the wood species eventhough the possibility of LC bond in LCC in the form of ester, ether, and phenyl glycoside types the acetylation on hemicelluloses played a key role in regulating LC bonds on the benzyl ether type [2]. Chemically, wood fiber consist of cellulose, hemicellulose and lignin as its major constituent. Other constutent are glucomannan, hexenuronic and pentoas as the minor constituent. Hemicellulose in various hard wood species is differ from each other both quantitatively and qualitatively, but the major component is an O – acetyl – 4 – O – methylglucurono - β – O – Xylan. The glucuronoxylan (xylan) content is 15 – 30 % [3]. Lignin itself might be isolated and degraded through the breaking of C-C and C-O inter-unit linkage through oxidative cleavage, hydrogenolysis, two steps redox neutral process, etc. [4]. Other research mention that the hydrogen bond at –OCH3 in lignin could be disrupted by Na2CO3 to facilitate the dissolution and degradation of lingin [5].

The use of molecular chlorine as a bleaching agent results in the formation and release of chlorinated organic compounds, sometimes at concentrations that present an unacceptable risk to the receiving environment and the food chain [6]. This chemical has been totally substituted by chlorine dioxide in elementary chlorine free (ECF) bleaching for ecological and environmental reason. Alternatives to the use of chlorine dioxide, result in reductions the degree of chlorine substitution in the organochlorines formed. This leads to the reduction of the potential of bioaccumulation and food chain transfer, and sequencely reduces toxicity and ecological effects [6]. Research to substitute molecular chlorine as a bleaching agent has been done. Research concering bleaching sequences such as TCF [7] and ECF [8] have also been done.

Research of ECF bleaching has so many time been done and the result have been applied in pulp and paper industries, but effort to get an improvement in bleaching is very interesting. The use of xylanase treatment in pulp before bleaching promote increase efficiency of the subsequent delignification. The kinetics of enzyme of bleached hardwood has been investigayed [9]. Effort to boost the bleaching effect of ECF bleaching of several hardwoods (acasia mangium, eucalyptus camaldulensis, and mixed tropical hardwood) using xylanase enzyme with a marginal brightness improvement has been done. In this study, the responses of these hardwoods to ECF bleaching are completely difference [10]. For SW kraft pulps, it is determined that ~60% to 65% of the overall ClO2 charge should be applied in the D0-stage. Peroxide addition to an (EOP) can replace 0.6 to 2.5 kg. ClO2 per kg H2O2. Boosting the (EO) temperature to 80°C is equivalent to a 70°C (EOP) with 0.25% to 0.30% H2O2,whereas a 90°C (EO) is equivalent to 0.50% – 0.75% H2O2 in a 70°C (EOP) [11]. It is also mention that the alkaline extraction variables, such as temperature and/or peroxide inclusion, affect overall chlorine dioxide consumption and distribution for various bleach sequences [11]. Residual of peroxide from EP or EOP stage can carry over into D1 stage that may consume additional ClO2. The amount of ClO2 displaced by an (EOP) stage can vary from 0.6 – 2.5 kg per kg H2O2 that depend on the process condition and wood species [12].

In other case the response of Eucalyptus camaldulensis and Acacia mangium kraft pulp to other type of ECF bleaching is also studied. A conventional Do stage followed by DZ or (ClO2 and O2), hot acid treatment before Do, and hot acid treatment before DZ, hot ClO2 treatment and hot acid followed by hot ClO2, after these previous stage then the pulp were bleached using D2. In this research, the first steps of bleaching that give the best result is Do – DZ [13]. Prehydrolysis of kraft
pulp using H$_2$SO$_4$ in ECF bleaching O$_3$-P$_{sa}$-D-EP sequences for Eucalyptus globulus and Eucalyptus hybrid able to reduces the consumption of ClO$_2$ to only 0.5 % to achieve target brighness 88 % ISO [14].

Cooking condition has an effect on the degradation of hexenuronic acid, xylan, glucomanan and cellulose of softwood pulp [15]. It is reported that in hardwood kraft pulp about 20 – 55 % of kappa number is attributed to hexenuronic acid, whereas for softwood kraft pulp the contribution of hexenuronic acids to the pulp kappa number was not as substantial. It is also reported that the formation of this unsaturated hemicellulose could be influenced by the extent of delignification [16]. Other researcher mention that hemicellulose is easier to be pre extracted prior to pulping to preserve it for further use, instead of losing it in the black liquor. This leading to the LCC structural change that in turn more accessible for pulping and enzymatic hydrolysis and have positive impact in bleaching [17].

Cooking of plantation hardwood by pre-hydrolysis polysulfide – anthraquinone with low liquor to wood ratio show that the kappa number is clearly decrease with slightly decease of pulp yield, but the hexenuronic acid content is not affected [18]. In Kraft cooking the chemicals used in NaOH and Na$_2$S and in the chemical recovery process produces green liquor that consist of Na$_2$S and Na$_2$CO$_3$ with the the purpose to produces NaHCO$_3$. These chemical NaHCO$_3$ and Na$_2$CO$_3$ are presence in the recovered liquor that mixed with NaOH and Na$_2$S for cooking purposes.

2. Experimental

2.1 Materials

Unbleached hard wood pulp request from pulp mill before ECF bleaching stage. The unbleached pulp are Eucalyptus Camalulensis pulp from AA Thailand, Acasia Mangium pulp from RAPP Indonesia. Xylanase enzyme used is Ecopulp TX-200 from AB Enzyme Oy Finland. The chlorine dioxide, H$_2$O$_2$ and MgSO$_4$ are supplied from the local supplier. Oxygen gas is supplied from Samator Gas Probolinggo, Indonesia.

2.2 Operating condition

The unbleached pulp was taken and performed for sequential steps of bleaching O-D-EOP-D with xylanase bleaching before and after O$_2$ delignification alternately. The design of experiments shown in Figure 1. All unbleached hardwoods pulp was washed thoroughly to remove the remaining black liquor to eliminate the effect of on the subsequent treatment and systematic error in the experiment results. O$_2$ delignification was prepared by 15 minutes heating up period to 90 °C at 350 kPa O$_2$ pressure and 1 hr at 700 kPa operating pressure and less than 5 minute to release pressure. For Eop the preparing step was 15 minute heating up period to 80 °C at 200 kPa and 1 hr at 400 kPa and less than 5 minute to release pressure. For xylanase treatment, conditioning pH to 5.5 – 6.5 before heating at water bath for 120 minute at 70 °C and kneading every 15 – 20 minute. For D$_0$ and D$_1$ bleaching, heating at 75 °C was performed for 60 and 120 minute for D$_0$ and D$_1$ respectively and kneading every 15 – 20 minute.
Figure 1. Experimental sequences of bleaching

Xylanase activity was analyzed in accordance with interlaboratory testing method using DNS solution [19]. Eucalyptus camaldulensis xylan (extracted from Eucalyptus camaldulensis saw dust) was used as a substrate for xylan activity determination. The operating condition used in this research were shown in Table 1. Some of the chemical composition of woods used in this experiment are shown in Table 2.

Table 1. Operating condition of ECF bleaching

| Operating Condition | Xylanase treatment pre O₂ delig. | Oxygen delig. | Xylanase treatment post O₂ delig. | ClO₂ treatment | Extracton EOP | ClO₂ treatment |
|---------------------|---------------------------------|---------------|-----------------------------------|----------------|---------------|----------------|
| Temperature °C      | 70                              | 90            | 70                                | 75             | 80            | 75             |
| Ph                  | 5.5 – 6.5                       | 5.5 – 6.5     | 2.5                               | 4 – 5          |               |                |
| Pressure, kPa        | Atmosferic                      | 700           | Kneading atmosferic               | 400            |               |                |
| Time (minute)        | 120                             | 60            | 120                               | 60             | 60            | 120            |
| Od pulp g            | 250                             | 250           | 225                               | 200            | 175           | 150            |
| Consistency %        | 10                              | 10            | 10                                | 10             | 10            | 10             |
| Dosage               | 1 IU 10/ g od pulp              | 3 % NaOH      | 1 IU 10/ g od pulp                | 0.27–0.3 x kappa (act. Cl) | 2 % | 1.5 % |
| Mg SO₄               | 0.5 %                           |               |                                   |                |               |                |
| H₂O₂                |                                  |               |                                   |                |               |                |

Table 2. Woods chemical composition

| Wood composition | Acacia mangium [2] | Eucalyptus camaldulensis [1] | Birch [1] | Spruce [1] |
|------------------|--------------------|------------------------------|-----------|------------|
| Cellulose (%)    | 44                 | 45                           | 41        | 37         |
| Hemicellulose %  |                    |                              |           |            |
| - Glucomannan (%)| 1.3                | 3.1                          | 2.3       | 17.2       |
| - Glucoronoxylan (%)| 14               | 14.1                         | 27.5      | 10.4       |
| - Other polysacharides (%)| 0.8         | 2.0                          | 2.6       | 3          |
| Lignin           | 29.7               | 31.3                         | 22        | 27.5       |
| Total Extractive | 4.45               | 2.8                          | 3         | 2.1        |
3. Results and discussion

Conventional ECF bleaching has been applied in fiber line operation. Effort to improve the bleaching result without any pulp viscosity reduction has been done by using \( \text{O}_2 \) delignification process in the previous step of ECF bleaching. Research of xylanase treatment in ECF bleaching has been done several times and mostly focused on the final result achievement. In this research, xylanase in used as pretreatment before and after \( \text{O}_2 \) delignification in ECF bleaching of pulps of acacia mangium, eucalyptus camaldulensis, and mixed tropical hardwood harvested from Sumatra forest.

The ECF bleaching stage in this experiment is O-D-EOP-D for Acacia mangium and Eucalyptus camaldulensis and O-D-EOP-D-D for Mixed tropical hardwood pulp in order to achieve the target brightness \( \geq 90 \% \) ISO. This ECF bleaching stage is choosed in this experiment as a standard bleaching stage because it is a common ECF bleaching stage applied in fiber line operation.

Kappa number is evaluated to see the beneficial effect of xylanase treatment and the role of every step in the ECF bleaching stage to reduce the removeable lignin content. In Figure 2, it is shown that the decrease of kappa number of Eucalyptus camaldulensis pulp in ECF bleaching is faster than others. It is also shown that the decrease of kappa number is very fast up to the first step of chlorine dioxide stage that mostly known as D\(_o\) stage. After this step, the kappa reduction is slower eventhough the temperature used in this ClO\(_2\) stage (D\(_o\) and D\(_1\) and even D\(_2\)) is reasonable high = 75 \(^\circ\)C. Temperature of 75 \(^\circ\)C was choosed for D\(_o\), D\(_1\), and even D\(_2\) stages because this reasonable high temperature give the beneficial effect to ECF bleaching. This fact is supported by other research, mention that high temperature for D stages is better than hot acidic treatment prior to D stage or (A/D) stage especially in case of ClO\(_2\) consumption [13]. Also shown that hot ClO\(_2\) treatment offers many benefits compared to hot acid treatment followd by ClO\(_2\) bleaching, in term of bleaching chemical consumption, bleaching yield, and development of tensile strength [20].

![Figure 2](image_url)

**Figure 2.** Effect of xylanase treatment on the ECF bleaching stage O-D-EOP-D on: a) Kappa number achievement, b) Hexenuronic acid content of Acacia mangium, Eucalyptus camaldulensis, and Mixed tropical hardwood

Instead of hot acid treatment and hot ClO\(_2\) bleaching, xylanase treatment is used for pre treatment in ECF bleaching. The use of xylanase treatment before \( \text{O}_2 \) delignification gave better result in case of kappa number reduction than the one if the xylanase treatment was performed after \( \text{O}_2 \) delignification and also if using conventional treatment only with out xylanase treatment.
The purpose xylanase treatment is to cleavage the covalent bond between lignin and cellulose in lignin carbohydrate complex (LCC). Eventhough there is no evidence shown any cleavage of bond between lignin and carbohydrate as reported by [21,22], it is beliave that the xylanase treatment initiate the cleavage of them [10].

Figure 2b shows that there was a hexenuronic acid reduction in ECF bleaching stage when xylanase treatment is applied in this sequence prior and after O$_2$ delignification. In this case the prior one shown higher reduction than others. In this case Eucalyptus camaldulensis shows far better in hexenuronic acid reduction as it was compared to other pulps (acacia mangium and mixed tropical hardwood). This must be has any corelation with the physical wood structure and physical properties of cell wall that affected by lignin – carbohydrate bond [23]. The nature and amount of LCC linkages and lignin substructures affect the efficiency of pulping, hydrolysis, and digestibility of biomass [24]. In hardwood, esters and phenyl glycosidic bonds were found to be dominant in LCC, and these negatively affect kraft pulping and delignification performance because this lingkage has alkali resistance.

In Figure 2b it is shown also that the xylanase treatment prior to O$_2$ delignification has improved the hexenuronic acid reduction better than others. This mean xylanase treatment before O$_2$ delignification has initiate the cleavage of lignin and hexenuronic acid from LCC. This fact seem contradictive with the fact that the esters and phenyl glycosidic bonds that found to be dominant in LCC has negatively affect kraft pulping and delignification performance because this lingkage has alkali resistance [24]. By this fact that seem contradictive it can be inferred that the xylanase treatment able to reduce the resistance toward alkali treatment and has boosting the delignification process in the ClO$_2$ treatment. Instead of that, enzymatic hydrolysis may preserve xylan better from degradation as it has been mentioned by other research [25].

![Figure 3](image-url)

**Figure 3.** a) Effect of xylanase treatment on the ECF bleaching stage O-D-EOP-D on the brightness achievement of Acacia mangium, Eucalyptus camaldulensis, and Mixed treopical hardwood, b) Possibility reduction of ClO$_2$ consumption as a result of xylanase treatment and the highest possible achievement of ECF bleaching using xylanase pretreatment before O$_2$ delignification.

In Figure 3a it is shown that, the initial brightness of Eucalyptus camaldulensis after kraft cooking is lower that that of Acacia mangium but the final brightness is higher than that of Acacia mangium. The crossing point of this anomaly is at ECF bleaching step number 5 or D$_0$ step of O-D$_0$-EOP-D$_1$ stage. The use of xylanase treatment prior and after O$_2$ delignification stage is studied to get an improvement in having a higher brightness achievement or a reduction of ClO$_2$.
consumption while achieving a target brightness 90 % ISO. This target brightness of 90 % ISO is rarely needed for industrial purposes except for high brightness and high whiteness of paper, for ordinary paper the quality of pulp with brightness of 88 % ISO is commonly used. This fact has shown an indication that the xylanase treatment has initiate the cleavage of lignin and hexenuronic acid prior ClO₂ bleaching so that the achievement of brightness is higher or the ClO₂ consumption to achieve the same brightness is lower.

Table 3. Chemical consumption and brightness

| STEP                      | Brightness of ACACIA | Brightness of EUCA | Brightness of MTH |
|---------------------------|----------------------|--------------------|-------------------|
|                           | O₂ X₁ before O₂     | X₁ after O₂       | O₂ X₁ before O₂  | X₁ after O₂ | O₂ X₁ before O₂ | X₁ after O₂ |
| EOP                       | 84,70                | 85,40              | 84,90             | 87,00       | 87,90           | 87,30       | 82,30 | 83,20 | 82,90 |
| ClO₂ consumption, %/g od  | 1,5                  | 1,5                | 1,5               | 1,5         | 1,5             | 1,5         | 1,5   | 1,5   | 1,5   |
| D₁ the best brightness achievement | 90,60  | 91,20              | 90,90             | 91,70       | 92,20          | 91,80       | 89,10 | 89,30 | 89,30 |
| Brightness Target         | 88,0                 | 88,0               | 88,0              | 88,0        | 88,0            | 88,0        | 88,0  | 88,0  | 88,0  |
| ClO₂ consumption to achieved target (calculated), %/g od | 0,84 | 0,67               | 0,77              | 0,32        | 0,03            | 0,23        | 1,26  | 1,18  | 1,20  |
| % ClO₂ reduction in D₁ (calculated) | 44,1% | 55,2%              | 48,3%             | 78,7%       | 97,7%           | 84,4%       | 16,2% | 21,3% | 20,3% |

In Figure 3b it is clearly shown that in the last steps of ECF bleaching, the xylanase treatment has promoted better result when it is performed before the O₂ delignification. In case to get a brightness target of 88 % ISO, the use of xylanase treatment before O₂ delignification gave the ClO₂ consumption around 97 % for the best result in case of Eucalyptus camaldulensis pulp, 55 % for Acacia mangium and 21 % for Mixed tropical hardwood. The ClO₂ consumption is listed in Table 3.
The result of bleaching of several hardwoods discussed above should have any correlation with the xylan–lignin and cellulose–lignin complexes in the LCC as it has been explain by other researcher [24]. The dissolution and degradation of lignin that promoted by the initial cleavage because of xylanase treatment, it may also affected by Na$_2$CO$_3$ presence in the cooking liquor as it has been reported by other research [5].

The xylanase enzyme may attack the ester and ether bond that might initiate the cleavage of lignin and HexA and also might cause hemicellulose degradation from cellulose in LCC. The HexA formation itself was happened in the cooking step. In Figure 4 shows that the possible attachment of either xylanase or ClO$_2$ are in ester and ether bonds. It is still not clear how the lignin and HexA removal from LCC, but this cleavage has been initiated in xylamase treatment followed by further step in ClO$_2$ bleaching stage. This fact can be seen from the analyses result of Kappa number, Hexa, and brightness that shows the figure of these are a little bit lower than the other one treated by only using O$_2$ delignification and ClO$_2$. In case of Eucalyptus camaldulensis, the progress is far better than other. It is suppose that it has a close correlation with the physical structure and chemical composition of this wood as compared with others. The covalent bond may also has effect to this situation [26]. This may has a correlation with the kinetic of enzyme treatment that the delignification is a function of the relative change of the reducing suger as the kinetic variable [9].

Table 4 shows that the viscosity of pulp treated by xylanase that performed before O$_2$ delignification give better reluts than that of others. It shows that the xylanase treatment before O$_2$ delignification has facilitated the cleavage of lignin from LCC so that further cellulose degradation can be eliminated. This fact is in accordance with other reasearch [25]. In case of the xylanase treatment was performed after O$_2$ delignification stage and then followed by D$_0$-EOP-D$_1$ stages the LCC cleavage in O$_2$ stage has severely occured and follows by others cleavages in the next step of stage in the bleaching sequence that mean further decrease of viscosity was occured.

| TREATMENT                  | Bleached Pulp viscosity, kg m$^{-3}$ after D$_1$ | Acacia mangium | Eucalyptus camaldulensis | MTH |
|---------------------------|--------------------------------------------------|----------------|-------------------------|-----|
| Cooked unbleached pulp    | 792                                              | 918            | 654                     |     |
| ECF - O2 delig only       | 590                                              | 542            | 501                     |     |
| ECF - X before O2 delig   | 604                                              | 625            | 624                     |     |
| ECF - X after O2 delig    | 537                                              | 589            | 573                     |     |

4. Conclusion

From fact obtained above, it can be infered that the cleavage of hydrogen bond in LCC plays an importance role di determining the hemicellulose and lignin left in the LCC after bleaching, and thus affected the brightnees achievement. In case of Eucalyptus camaldulensis that able to achieve the most highest brightness as it is compared to the achiement in Acacia mangium and mixed tropical hardwood, it suppose has a close correlation with the kinetic of enzyme treatment that facilitate further the kinetic of clorine dioxide bleaching in D$_0$ and D$_1$. The Na$_2$CO$_3$ presence in cooking liquor supposed affect the cleavage of hemicellulose. In case of the xylanase treatment, the steps is better performed before O$_2$ delignification to avoid to much decerase of viscosity.
5. References

[1] You T-T, Zhang L-M, Zhou S-K, Xu F. Structural elucidation of lignin–carbohydrate complex (LCC) preparations and lignin from Arundo donax Linn. Industrial Crops and Products. 2015; 71:65–74.

[2] Giummarella N. Fundamental Aspects of Lignin Carbohydrate Complexes (LCC) : Mechanisms, Recalcitrance and Material concepts. TRITA-CBH-FOU NV - 2018:18. [Wood Chemistry and Pulp Technology, Fibre- and Polymer Technology, School of Engineering Sciences i Chemistry, Biotechnology and Health (CBH), KTH]: KTH Royal Institute of Technology; 2018.

[3] Sjöström E. Wood Chemistry: Fundamentals and Applications. In: SJÖSTRÖM E, editor. Wood Chemistry (Second Edition). Second Edi. San Diego: Academic Press; 1993. p. 1–248.

[4] Guadix-Montero S, Sankar M. Review on Catalytic Cleavage of C–C Inter-unit Linkages in Lignin Model Compounds: Towards Lignin Depolymerisation. Topics in Catalysis. 2018; 61(3):183–98.

[5] Jiang Z, Zhang H, He T, Lv X, Yi J, Li J-M, et al. Understanding the cleavage of inter- and intramolecular linkages in corncob residue for utilization of lignin to produce monophenols. Green Chemistry. 2016 Jul 11;18(14).

[6] Solomon K. Chlorine in the Bleaching of Pulp and Paper. Pure and Applied Chemistry - PURE APPL CHEM. 1996 Sep 1;68(9):1721–30.

[7] Mira M, Ghasemian A, Resalati H, Zeinaly F. Total Chlorine-Free Bleaching of Populus deltoides Kraft Pulp by Oxone. Vliegenthart JF, editor. International Journal of Carbohydrate Chemistry. Hindawi Publishing Corporation; 2015;2015:381242.

[8] Loureiro P, Domingues E, Evtuguin D, Graça M, Carvalho MG. ECF bleaching with a final hydrogen peroxide stage: Impact of the chemical composition of Eucalyptus globulus kraft pulps. BioResources. 2010;5(4):2567–80.

[9] Valchev I, Tsekova P. Xylanase post-treatment as a progress in bleaching processes. Appita Journal. 2010;63(1):45–52.

[10] Wikanaji D. Potential of xylanase enzymes for boosting the ECF bleaching of several harwood pulps. Asian Institute of Thechnology, Thailand; 2003.

[11] Brogdon B. Optimization of elemental chlorine-free bleaching for a softwood kraft pulp (I): Impact of oxidative extraction on chlorine dioxide stoichiometry. Tappi Journal. 2010;9:27.

[12] Hart PW. Pulp bleaching. In: Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley and Son, Inc; 2019. p. 1–30.

[13] Karim MR, Islam MN, Malinen RO. Response of Eucalyptus camaldulensis and Acacia mangium kraft pulp in different ECF bleaching options. Wood Science and Technology. 2011; 45(3):473–85.

[14] Rizaluddin A, Salaghi A, Ohi H, Nakamata K. Peroxymonosulfuric Acid Treatment as an Alternative to Ozone for Totally Chlorine-free and Elementary Chlorine-free Bleaching of Hardwoods Prehydrolysis-kraft Pulp. JAPAN TAPPI JOURNAL. 2016;7(7):724–33.

[15] Gustavsson C, Al-Dajani W. Influence of cooking conditions on the degradation of hexenuronic acid, xylan, glucomannan and cellulose during kraft pulping of softwood. Nordic Pulp and Paper Research Journal. 2000 Jun 1;15(2):160–7.

[16] Chakar FS, Allison L, Ragauskas AJ, McDonough TJ. Influence of Hexenuronic Acids on Kraft Bleaching. Tappi Journal. 2000;83.

[17] Njamela S, Vena P, Briemzo M, Görgens J, Tyhoda L. The effect of hemicelluloses pre-extraction on the lignin-carbohydrate complex structure of sugarcane bagasse pulp. TAPPSA Journal. 2013;6:2013.

[18] Yoon K, Homma M, Tanifuji K, Ohi H, Nakamata K. Pulp Yield and Hexenuronic Acid Content in Pre-hydrolysis Polysulfide-anthraquinone Cooking of Plantation Hardwood. In: International
Symposium on Resource Efficiency in Pulp and Paper Technology. Bandung, Indonesia; 2012. p. 103–5.

[19] Garriga M, Almaraz M, Marchiaro A. Determination of reducing sugars in extracts of Undaria pinnatifida (harvey) algae by UV-visible spectrophotometry (DNS method). Actas de Ingenieria. 2017;3:173–9.

[20] Ragnar M, Lindström M. A comparison of emerging technologies: Hot chlorine dioxide bleaching versus hot acid treatment. Paperi ja Puu/Paper and Timber. 2004 Jan 1;86(1):39–44.

[21] Jeffries TW. Biodegradation of lignin-carbohydrate complex. Biodegradation. 1990;1:163–76.

[22] Ratledge C. Biochemistry of microbial degradation. Ratledge C, editor. Springer Netherlands; 1994.

[23] Nishimura H, Kamiya A, Nagata T, Katahira M, Watanabe T. Direct evidence for α ether linkage between lignin and carbohydrates in wood cell walls. Vol. 8, Scientific Reports. 2018.

[24] Tarasov D, Leitch M, Fatehi P. Lignin–carbohydrate complexes: properties, applications, analyses, and methods of extraction: a review. Biotechnology for Biofuels. 2018;11(1):269.

[25] Vaaler DAG. Yield-increasing additives in kraft pulping: Effect on carbohydrate retention, composition and handsheet properties. Norwegian University of Science and Technology; 2008.

[26] Giummarella N, Pu Y, Ragauskas AJ, Lawoko M. A critical review on the analysis of lignin carbohydrate bonds. Green Chemistry. The Royal Society of Chemistry; 2019;21(7):1573–95.