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Environment-Friendly Non-Sulfur Cooking and Totally Chlorine-Free Bleaching for Preparation of Sugarcane Bagasse Cellulose

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Abstract: This study focuses on improving the quality of dissolving pulp (DP) from sugarcane bagasse (SB) prepared by a non-sulfur cooking method and totally chlorine-free (TCF) bleaching sequences. First, the effects of prehydrolysis and soda-anthraquinone (AQ) cooking conditions on brightness and viscosity were studied. Second, a novel five-stage TCF bleaching sequence, which employs oxygen (O) bleaching, peroxymonosulfuric acid (P_{sa}) treatment and alkali extraction with hydrogen peroxide (E_p) in the sequence $O-P_{sa}-E_p-P_{sa}-E_p$ was applied to SB pulps. The maximum brightness and viscosity of unbleached pulp were 46.3% ISO and 34.1 cP, respectively, whereas after the final bleaching stage, the maximum qualities (brightness: 89.1% ISO, viscosity: 6.4 cP, glucan content: 95.7%, and ash content: 0.12%) met the standard requirements. For comparison, the effects of TCF bleaching on oil palm empty fruit bunch pulp were investigated. The proposed TCF bleaching shows a potential as a bleaching method to produce high-quality DP from SB.

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1. Introduction

There is growing interest in the utilization of biomass for the production of biofuels and materials [1, 2]. Dissolving pulp (DP), which has a cellulose purity of more than 90%, is mainly used for rayon production. However, it is also an important material for producing textile fibers, cellulose derivatives, pharmaceuticals, and food additives. Recently, the utilization of non-wood materials has increased owing to deforestation and global warming issues. For instance, the use ratio of non-wood fibers to recovered paper as raw materials for pulp and paper increased from 21% in 1990 to 37% in 2010 [3].

Sugarcane (*Saccharum officinarum*) bagasse (SB) is a cellulosic agro-industrial by-product. In Indonesia, it was reported that 2.6 million ton of crude sugar (cane sugar) was produced from sugarcane (33 million ton) on 0.48 million ha of harvested area in 2014 [4]. Although Statistics Indonesia released no information about the amounts of SB generated, a previous study reported that an annual production of about 33 million

ton of sugarcane resulted in the generation of around 9.9–11.2 million ton (30–34%) of SB per year [5]. Generally, SB is combusted in boiler systems for power generation.

Meanwhile, as the largest oil palm (*Elaeis guineensis*) producer in the world, Indonesia produced 29.3 million ton of crude palm oil (CPO) in 2014 [6]. In oil palm processing, the fruit is separated from the bunch, leaving empty fruit bunches (EFB); about 43.5 million ton of EFB are produced annually. Both SB and EFB are renewable raw materials abundant in Indonesia.

Cotton and wood as agricultural and forestry plantation products are valuable starting materials with very good qualities for producing DP. However, cotton and wood are also excellent starting materials for other important products, including textiles, paper, and boards. Meanwhile, it is well known that good quality paper can be produced from SB, but considerable amounts of SB are not utilized effectively. Therefore, we have focused on the usage of agricultural waste materials, such as SB and EFB.

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Isolation of cellulose from SB has been extensively studied [7–9], but no studies have examined non-sulfur cooking and totally chlorine-free (TCF) bleaching for high-quality DP production from SB.

DP production from SB soda pulp followed by elementary chlorine-free (ECF) bleaching with oxygen (O), chlorine dioxide (D), alkaline extraction with hydrogen peroxide (E_p), and alkaline hydrogen peroxide (P) stages as an O-D- E_p -D-P sequence have been shown in a previous study to achieve an ISO brightness of 88.5% [1]. Meanwhile, the production of DP from oil palm EFB has been reported in many studies [10–14]. Other agricultural waste materials, such as banana plant stems, have also been evaluated as raw materials for DP, and an ISO brightness of 77.9% was achieved after the application of the ECF bleaching process [15]. Matin *et al.* [16] reported that a high ISO brightness of 89% could be obtained after application of a D₀- E_p -D₁- E_p -D₁ bleaching sequence to jute sticks, where D₀ and D₁ indicate different dosages of ClO₂. Meanwhile, bamboo DP prepared using soda-anthraquinone (AQ) cooking and an ECF bleaching sequence had an ISO brightness of 92.4% [17].

To prevent pollution at the bleaching stage, the pulp and paper industry started using ECF bleaching instead of chlorine bleaching. However, organochlorine compounds produced at the bleaching stage and by wastewater treatment are still discharged during ECF bleaching [18]. Therefore, TCF bleaching, in which hydrogen peroxide (E_p , P), oxygen (O), ozone (Z), and peroxymonosulfuric acid (P_{sa}) stages are used instead of ClO₂ (D) stage, has been proposed as a solution [19]. TCF bleaching will diminish adsorbable organic halogen (AOX) emissions, as well as the amount of discharged organochlorine substances. Several studies have applied TCF bleaching sequences on non-wood materials for DP production. Harsono *et al.* [11] showed that the application of both TCF and ECF bleaching sequences after soda-AQ cooking of EFB could be used to produce DP with a high ISO brightness (81.6% and 90.7%, respectively). Hedjazi *et al.* [20] reported that the application of a TCF bleaching sequence with chelate treatment (Q) and oxygen with peroxide (OP) stages (O-Q-(OP) and O-Q-(OP)-P sequences) to SB achieved ISO brightness of 78.5% and 83.5%, respectively. Another study applied a TCF bleaching sequence (Q-O/P-Q-P) to SB pulp to achieve an ISO brightness of 76.9% [8]. According to the Indonesian National Standard [21], a minimum ISO brightness of

88%, a viscosity greater than 6.2 cP, a minimum α -cellulose content of 94%, and a maximum ash content of 0.15% are required for DP. However, no previous study has demonstrated that the application of TCF bleaching to SB pulp can achieve the high grade of DP required to meet these standards. While there are various environmentally friendly pulp and paper production technologies available [22], in order to meet the Indonesian National Standard, we have focused on non-sulfur cooking and TCF bleaching.

Soda-AQ cooking was chosen in this study because it is more environmentally friendly than kraft cooking. Alaejos *et al.* [23] compared soda-AQ and kraft pulping of holm oak, revealing that a lower kappa number, higher brightness level, and slightly lower viscosity are obtained for soda-AQ pulp. Moreover, the use of soda-AQ cooking eliminates the risk of environmental damage caused by sulfur emissions. There are two methods of dealing with the waste liquor from soda-AQ cooking processes. The first involves recovery, concentration, and combustion, which is the conventional recovery process used in kraft cooking. The second is lignin separation and lignin derivative utilization [24]. As a potential biorefinery process, the latter method is attractive, and 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.

Therefore, the objectives of this study were to investigate suitable conditions for preparing SB unbleached pulp with optimum brightness and viscosity using a combination of prehydrolysis and soda-AQ cooking, and to clarify the effect of the TCF bleaching sequence on the pulp using a combination of oxygen, peroxymonosulfuric acid, and peroxide stages to enhance the qualities of DP and meet the Indonesian National Standard requirements.

2. Materials and Methods

2.1. Raw materials and analysis of chemical composition

SB was collected from PG Madukismo, a sugar mill in Yogyakarta province, Indonesia. EFB was collected from PT Condong, an oil palm plantation in Garut region, West Java province, Indonesia. The SB fiber fragments of 5–10 cm were further cut to lengths of between 0.5 and 1 cm, and small particles

containing the inner portion (called pith) were removed by fractionation. The EFB fibers of 10–15 cm were cut to lengths of between 0.5 and 1 cm after washing and sun drying.

The SB and EFB materials were milled, and particles (40–80 mesh size) were used for analysis. The extractive content was determined according to TAPPI Test Method [25] using Soxhlet extraction with hexane and acetone. The acid-insoluble lignin (Klason lignin) was analyzed according to the method of Yoshihara *et al.* [26] with modifications by Ohi *et al.* [27] as follows: 0.5 g of oven-dried milled material was hydrolyzed with 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 separated using a glass filter (1 GP 16) to obtain a residue and filtrate. The weight of the residue was taken as the amount of acid-insoluble lignin. The amount of acid-soluble lignin was determined from the UV absorbance of the filtrate at 205 nm using a spectrophotometer [28]. Using a Dionex ICS 3000 ion chromatograph (Dionex, Sunnyvale, CA, USA; Thermo Fisher Scientific, Japan), the monosaccharides in the filtrate were determined following 1000-times dilution [29]. The ion chromatograph system consisted of an electrochemical detector (ED), single pump (SP-1), CarboPac PA 1 column ($\phi 4$ mm $\times$ 250 mm), CarboPac PA 1 guard column ($\phi 4$ mm $\times$ 50 mm), and an autosampler (AS). The ash content was determined according to TAPPI Test Method [30] by incinerating the material at 575 °C for 4 h.

Nitrobenzene oxidation of lignin in the SB and EFB materials was performed according to the method reported by Chen [31] with some modifications. The oxidation products vanillin (V_a) and syringaldehyde (S_a) were determined by gas chromatography (GC). The net yield of the aromatic aldehydes (V_a and S_a) is indicated as mmol per gram of acid-insoluble lignin (mmol/g lignin) and used as an index for uncondensed-type lignin structures. Conditions for GC were as follows: GC system, GC-17 A (Shimadzu, Japan); column, DB-1 (30 m $\times$ 0.25 mm; film thickness: 0.25 μ m) with helium gas as a carrier. Temperature profile for analysis: 15 min at 110 °C, 110–160 °C (5 °C/min), 160–280 °C (20 °C/min) and 7 min at 280 °C.

The hexenuronic acid (HexA) content of unbleached pulp was determined from the contents of 2-furancarboxylic acid and 5-formyl-2-furancarboxylic acid after formic acid hydrolysis at pH 2.5 and 120 °C

for 3h, using high-performance liquid chromatography with 4:1 acetonitrile–water (pH 2.5) as the eluent and a detection wavelength of 265 nm, according to the method reported by Takahashi *et al.* [32].

2.2. Prehydrolysis and cooking

The SB (or EFB) material (35 g, oven-dried weight) was prehydrolyzed with 245 mL of distilled water at 150 °C for 3 h in a 300 mL steel reactor. In some cases, sulfuric acid (0.1% of material weight) was added during prehydrolysis to determine the effects of acid-catalyzed prehydrolysis. After removal of 160 mL prehydrolyzate (PHL), the wet solid residue of SB was subjected to soda-AQ cooking at 150 °C for 2 h with 12–19% active alkali (AA) dosage (as Na_2O) and 0.1% of AQ (as 1,4-dihydro-9,10-dihydroxyanthracene sodium salt, SAQ; provided by Kawasaki Kasei Chemicals Ltd.), at a liquor-to-solid ratio of 7. Meanwhile, the EFB residue was subjected to cooking at 160 °C for 3 h with 20% AA dosage (as Na_2O) and 0.1% of AQ, at a liquor-to-material ratio of 7.

2.3. Bleaching sequences

In this study, a combination of oxygen bleaching (O), peroxymonosulfuric acid (H_2SO_5) treatment (P_{sa}), and alkali extraction with hydrogen peroxide (E_p) stages were used in the TCF bleaching sequence of $\text{O-P}_{\text{sa}}\text{-E}_\text{p}\text{-P}_{\text{sa}}\text{-E}_\text{p}$. Prehydrolyzed soda-AQ pulp (10 g, oven-dried weight) was oxygen bleached at a pulp consistency (PC) of 25% with 1–2% NaOH, 0–0.2% MgSO_4 , and an oxygen pressure of 0.5 MPa at 115 °C for 60 min. Various combinations of NaOH and MgSO_4 doses were used in the oxygen bleaching stage to improve the brightness and viscosity, and the obtained pulps were named SB1–SB5, EFB1, and EFB2. These bleaching conditions of O stage are shown in Table 4.

H_2SO_5 was prepared according to the procedure of Rizaluddin *et al.* [33] by dropping 95% sulfuric acid (Wako Pure Chemical Industries, Ltd.) into 45% hydrogen peroxide aqueous solution (Mitsubishi Gas Chemical Company, Inc.) at 70 °C. The obtained solution contained 0.19 mmol/L H_2SO_5 , 0.81 mmol/L H_2SO_4 , and 0.14 mmol/L H_2O_2 , and the H_2O_2 to H_2SO_5 ratio was 38.4–61.6% (s.d. of ± 4.1 , $n = 4$). The first and second P_{sa} stages were carried out at a PC of 10% with 0.1% H_2SO_5 at pH 3 for 70 min at 70 °C for SB1–SB5 and EFB1–EFB2. The first and second E_p stages were carried out at a PC of 10% with 0.7% NaOH, 0.1% MgSO_4 , and 1% H_2O_2 for 60 min at 70 °C for SB1–SB5 and EFB1–EFB2. For comparison with TCF bleaching, ECF bleaching with the sequence $\text{O-P}_{\text{sa}}\text{-E}_\text{p}\text{-D}$ was

carried out on prehydrolyzed soda-AQ SB pulp. The D bleaching stage was carried out in a bag made of polyvinylidene chloride sheets at a PC of 10% with 0.7% ClO₂ at pH 3.3 for 60 min at 70 °C.

2.4. Evaluation of pulp qualities

The kappa number, viscosity, and α -cellulose content were determined using TAPPI Test Method [34–36], respectively. The ISO brightness was measured based on TAPPI Test Method [37] using a digital color meter (TC-1500 SX, Tokyo-Denshoku). The amounts of acid-insoluble lignin and acid-soluble lignin, and the carbohydrate composition of the pulp were determined using the methods described in section 2.1.

2.5. Molecular weight distribution of SB bleached pulp

SB bleached pulp or filter paper (Advantec, qualitative No. 1) as a control was dissolved in *N,N*-dimethylacetamide (DMAc) according to a procedure previously reported by Dupont [38]. SB bleached pulp (0.05 g) was twice dispersed in 10 mL of water at 40 °C for 1 h, and then, it was twice dispersed in 8 mL of methanol at room temperature for 45 min after water was removed without drying. After removing most of the methanol by using an aspirator, the pulp was immersed in 8 mL of DMAc at room temperature for 45 min and then filtered. The pulp was immersed again in 8 mL of DMAc and mixed with a magnetic stirrer at room temperature for 24 h and then filtered. Finally, 5 mL of DMAc containing 8 wt% of LiCl (8% LiCl/DMAc) was added to the pulp containing a small amount of DMAc (approximately 0.2 g). The pulp was mixed with a magnetic stirrer at room temperature for 24 h until complete dissolution in the 8% LiCl/DMAc.

Samples were subjected to gel permeation chromatography (GPC). The system consisted of a refractive index (RI) detector and Shodex KD-806M column (Showa Denko, Japan; ϕ 8 mm $\times$ length 300 mm, 2 series). As the eluent, 0.5% LiCl/DMAc was used, and pullulan was used as an internal standard ($\log_{10}M_w = -0.00442 t + 12.30$, t : second) with a flow rate of 0.6 mL/min.

2.6. X-ray diffraction

The crystallinity of the SB raw material, SB unbleached pulp, SB bleached pulp, and cellulose powder (Toyo Roshi Kaisha, Ltd., Tokyo) as a standard were determined by X-ray diffraction (XRD) analysis by using a D8 ADVANCE diffractometer (Bruker AXS GmbH, Karlsruhe, Germany). Radiation

with a Cu tube (0.154 nm) at a voltage of 40 kV and current of 40 mA was employed. Scan type was θ -2 θ , and the sample angle range (2 θ) was 10 to 30 ° with a scan time of 348 s (6000 steps and 0.05 s/step). Crystallinity index (*CrI*) was calculated based on the following equation: $[(I_{\max} - I_{\min})/I_{\max}] \times 100$.

3. Results and Discussion

3.1. Chemical characteristics of SB and EFB raw materials

The chemical compositions of SB and EFB are shown in Table 1. The total lignin content of the SB raw material (26.0%) was lower than that of EFB (30.2%), whereas the cellulose content of SB (39.3%) was higher than that of EFB (31.5%). Meanwhile, the EFB material contained much more ash and extractive compounds than the SB material.

3.2. Prehydrolysis and soda-AQ cooking

Prehydrolysis was applied to the SB and EFB materials prior to soda-AQ cooking, and the PHL was collected and freeze-dried. The xylan content in the PHL of both SB and EFB (4.0% and 1.6%, respectively) was higher than the glucan content (0.8% and 0.4%, respectively) (Table 1). Moreover, small amounts of lignin in SB and EFB (1.0% and 1.1%, respectively) were also removed during prehydrolysis. The remaining unidentified substances in the PHL mainly include hydrophilic organic compounds like acetic acid, uronic acids, furfural, and polyphenols. As a next step, we will analyze these materials and products according to previously reported methods [39, 40].

As reported in Table 1, the kappa number and yield of prehydrolyzed soda-AQ SB pulp (7.1 and 35.8%, respectively) were lower than those of soda-AQ SB pulp (10.8 and 52.5%, respectively). Similar behavior was also observed for EFB pulp. These results suggest that prehydrolysis may decrease the linkages between lignin and carbohydrates, as reported by Ma *et al.* [41], which will make lignin removal easier. The ash content of SB decreased significantly from 1.8% (raw material) to 0.1% in the prehydrolyzed soda-AQ pulp. The ash content of EFB decreased from 3.4% (raw material) to 0.6% (pulp).

The EFB material treated with an AA dosage of 20% at 160 °C for 3 h had a higher kappa number (10.1) than the SB pulp (7.1) after treatment with an AA dosage 16% at 150 °C for 2 h. When higher AA dosages, higher cooking temperatures, and longer cooking times were applied, the SB pulp was of better

Table 1 Chemical composition of sugarcane bagasse (SB) and oil palm empty fruit bunch (EFB) raw materials, prehydrolyzates (PHLs), and unbleached pulps.

	SB		EFB	
	Raw material	PHL	Raw material	PHL
Acid-insoluble lignin (%)	23.7 ± 0.2	0.2 ± 0.1	27.4 ± 0.5	0.3 ± 0.1
Acid-soluble lignin (%)	2.3 ± 0.1	0.8 ± 0.1	2.8 ± 0.1	0.8 ± 0.1
Glucan (%)	39.3 ± 1.4	0.8 ± 0.1	31.5 ± 1.1	0.4 ± 0.1
Xylan (%)	18.0 ± 0.8	4.0 ± 0.1	17.5 ± 0.6	1.6 ± 0.1
Other sugars (%)	2.6 ± 0.1	0.6 ± 0.1	1.2 ± 0.1	0.5 ± 0.1
Extractives (%)	2.0 ± 0.1	–	5.9 ± 0.7	–
Ash (%)	1.8 ± 0.1	1.1 ± 0.1	3.4 ± 0.1	2.2 ± 0.1
Unknown (%)	10.3 ± 0.4	4.0 ± 0.1	10.3 ± 0.4	2.5 ± 0.1
Yield (%)	100	11.4 ± 0.1	100	8.3 ± 0.1
V _a and S _a yield by NBO ^a (mmol/g lignin)	1.40 ± 0.39	–	1.31 ± 0.13	–
	Soda-AQ pulp ^b	Prehydrolyzed ^c soda-AQ pulp ^b	Soda-AQ pulp ^d	Prehydrolyzed ^c soda-AQ pulp ^d
Kappa number	10.8 ± 0.4	7.1 ± 0.2	19.0 ± 0.2	10.1 ± 0.4
Pulp yield (%)	52.5 ± 1.1	35.8 ± 0.4	49.2 ± 0.8	37.6 ± 0.2
Acid-insoluble lignin (%)	1.0 ± 0.1	0.5 ± 0.1	2.0 ± 0.1	0.9 ± 0.1
Acid-soluble lignin (%)	0.5 ± 0.1	0.3 ± 0.1	0.5 ± 0.1	0.4 ± 0.1
Glucan (%)	30.8 ± 0.3	25.9 ± 0.3	27.3 ± 0.3	24.4 ± 0.2
Xylan (%)	10.7 ± 0.1	1.7 ± 0.1	8.9 ± 0.1	6.5 ± 0.1
Other sugars (%)	0.9 ± 0.1	0.4 ± 0.1	0.5 ± 0.1	0.2 ± 0.1
Ash (%)	0.6 ± 0.1	0.1 ± 0.1	1.4 ± 0.1	0.6 ± 0.1
Unknown (%)	8.0 ± 0.3	6.9 ± 0.1	8.6 ± 0.2	4.6 ± 0.1
Viscosity (cP)	–	34.1 ± 0.6	–	18.8 ± 0.5
HexA content (mmol/kg pulp)	–	0.23 ± 0.03	–	14.4 ± 0.2

^a Vanillin and syringaldehyde yield by nitrobenzene oxidation

^b Cooking conditions: 150 °C and 2 h, active alkali dosage of 16%

^c Prehydrolysis conditions: 150 °C and 3 h

^d Cooking conditions: 160 °C and 3 h, active alkali dosage of 20%

quality. These results show the advantages and potential for utilization of SB compared with EFB.

Table 1 shows that the V_a and S_a yield of SB (1.40 mmol/g lignin) was higher than that of EFB (1.31 mmol/g lignin). Uncondensed-type lignin structures with β-aryl ethers are expected to decompose faster under alkaline cooking conditions than condensed-type lignin structures with β-5 and 5-5 carbon-carbon bonds [31]. Therefore, the kappa number and lignin content of SB unbleached pulp were lower than those of EFB unbleached pulp, even though a lower AA dosage was applied during cooking. Moreover, the higher lignin content of the EFB material with more condensed-type lignin structures should inhibit lignin decomposition during cooking. However, the influence of the lignin structure on the delignification rate of these materials needs to be studied further.

3.3. Effects of active alkali dosage and acid-catalyzed prehydrolysis

The optimum conditions to obtain high brightness and viscosity were studied by increasing the AA dosage from 12% to 19% (Table 2). The kappa number and yield decreased with increasing AA dosage. In contrast, the brightness was increased by increasing the AA dosage from 12% to 16%. Increasing the AA dosage will increase lignin removal, resulting in increased brightness of the pulp. However, further increasing the AA dosage decreased the brightness. At higher AA dosages, the fiber becomes soft, which likely decreases the light scattering coefficient [42]. Meanwhile, the viscosity showed no specific tendency with increasing AA dosage from 12% to 16%, with the highest viscosity observed at an AA dosage of 16%. However, increasing the AA dosage further (17% to 19%)

Table 2 Effects of active alkali dosage on the properties of SB pulp prepared by prehydrolysis and soda-AQ cooking^a.

Active alkali (%)	Yield (%)	Kappa number	Brightness (% ISO)	Viscosity (cP)
19	33.9 ± 0.2	5.3 ± 0.1	43.7 ± 0.6	29.7 ± 0.4
18	34.3 ± 0.2	5.6 ± 0.1	42.9 ± 0.6	30.1 ± 0.6
17	34.7 ± 0.3	5.7 ± 0.1	44.1 ± 0.6	32.4 ± 0.6
16	35.8 ± 0.2	7.1 ± 0.1	46.3 ± 0.6	34.1 ± 0.6
15	35.9 ± 0.3	7.2 ± 0.1	46.0 ± 0.8	29.5 ± 0.1
14	36.7 ± 0.3	8.6 ± 0.2	42.7 ± 0.9	29.1 ± 0.3
13	36.9 ± 0.2	13.3 ± 0.2	36.6 ± 0.7	28.4 ± 0.5
12	38.1 ± 0.4	28.6 ± 0.2	30.4 ± 0.6	30.8 ± 0.3

^a Prehydrolysis conditions: 150 °C and 3 h, Cooking conditions: 150 °C and 2 h, liquor-to-material ratio: 7, SAQ dosage: 0.1%

Table 3 Effects of acid-catalyzed prehydrolysis on the properties of SB pulp prepared by prehydrolysis and soda-AQ cooking.

H ₂ SO ₄ dose (%)	Temp. ^a (°C)	Prehyd. ^b time (h)	AA ^c (%)	Cooking time (h)	Yield (%)	Kappa number	Brightness (% ISO)	Viscosity (cP)
0	150	3	18	1.5	38.8 ± 1.1	6.0 ± 0.2	48.5 ± 0.6	33.4 ± 0.4
0.1	150	3	18	1.5	38.1 ± 0.2	5.2 ± 0.2	49.9 ± 0.9	31.6 ± 0.4
0.1	120	10	18	10	47.1 ± 0.2	9.2 ± 0.2	48.9 ± 0.1	31.3 ± 0.2

^a Prehydrolysis and cooking temperature

^b Prehydrolysis

^c Active alkali

resulted in a decrease in the viscosity. This result was probably caused by further degradation of cellulose at higher AA dosages.

Based on these results, an AA dosage of 16% was chosen as the optimum condition, giving SB unbleached pulp with an ISO brightness of 46.3% and viscosity of 34.1 cP (Table 2).

The effects of acid-catalyzed prehydrolysis were studied by adding dilute sulfuric acid (0.1% of material weight). The addition of acid increased the ISO brightness of SB unbleached pulp from 48.5% to 49.9%; however, the viscosity decreased from 33.4 to 31.6 cP and the kappa number also decreased from 6.0 to 5.2 (Table 3). These phenomena can be explained by increased removal of hemicelluloses and lignin with addition of acid during prehydrolysis. Increasing hemicellulose and lignin removal makes purification of cellulose easier and higher brightness can be achieved. A previous study showed that the addition of dilute acid during prehydrolysis increased the accessible surface area, hemicellulose removal, and lignin structure alteration [2]. Similar brightness and viscosity were obtained during prolonged acid-catalyzed prehydrolysis at a lower temperature of 120 °C (Table 3).

3.4. Effect of bleaching sequences

The SB pulp with a kappa number of 7.1, ISO brightness of 46.3%, and viscosity of 34.1 cP (Table 1) was treated with multistage TCF bleaching (SB1, SB3) and ECF bleaching (SB2). Further, SB pulp prepared using acid-catalyzed prehydrolysis with a kappa number of 5.2, ISO brightness of 49.9%, and viscosity of 31.6 cP (Table 3) was subjected to TCF bleaching (SB4, SB5). For comparison, EFB pulp with a kappa number of 10.1, ISO brightness of 44.7%, and viscosity of 18.8 cP (Table 1) was treated with TCF bleaching (EFB1, EFB2).

As shown in Table 4, the kappa number of the prehydrolyzed soda-AQ SB pulp decreased from 7.1 to 1.6–2.3 after the oxygen bleaching stage (SB1–SB3). Meanwhile, the SB pulp prepared by acid-catalyzed prehydrolysis had final kappa numbers of 2.2 and 1.8 (SB4 and SB5, respectively). In contrast, after oxygen bleaching, the EFB pulp (EFB1 and EFB2) had considerably higher kappa numbers (6.7 and 5.5, respectively) than the SB pulps.

The effect of MgSO₄ addition on oxygen bleaching can be observed by comparing samples SB1 and SB2. The addition of MgSO₄ to SB pulp increased the viscosity from 21.7 to 22.9 cP but decreased the ISO brightness slightly from 69.6% to 67.5%.

Table 4 Effects of NaOH and MgSO₄ addition on oxygen bleaching of SB and EFB pulps.

Material	Chemical addition at oxygen bleaching			Before oxygen bleaching			After oxygen bleaching		
	Sample name	NaOH (%)	MgSO ₄ (%)	Kappa number	Brightness (% ISO)	Viscosity (cP)	Kappa number	Brightness (% ISO)	Viscosity (cP)
SB	SB 1	1	0	7.1 ± 0.1	46.3 ± 0.6	34.1 ± 0.6	2.2 ± 0.1	69.6 ± 0.7	21.7 ± 0.1
	SB 2	1	0.2	7.1 ± 0.1	46.3 ± 0.6	34.1 ± 0.6	2.3 ± 0.1	67.5 ± 0.7	22.9 ± 0.2
	SB 3	2	0.2	7.1 ± 0.1	46.3 ± 0.6	34.1 ± 0.6	1.6 ± 0.2	70.0 ± 0.7	19.3 ± 0.1
	SB 4	1	0	5.2 ± 0.2	49.9 ± 0.9	31.6 ± 0.4	2.2 ± 0.2	72.1 ± 0.4	21.7 ± 0.2
	SB 5	2	0.2	5.2 ± 0.2	49.9 ± 0.9	31.6 ± 0.4	1.8 ± 0.1	72.8 ± 0.3	15.5 ± 0.1
EFB	EFB 1	1	0	10.1 ± 0.2	44.7 ± 0.4	18.8 ± 0.2	6.7 ± 0.1	59.7 ± 0.1	13.7 ± 0.2
	EFB 2	2	0.2	10.1 ± 0.2	44.7 ± 0.4	18.8 ± 0.2	5.5 ± 0.2	62.5 ± 0.1	11.3 ± 0.2

Meanwhile, the effect of NaOH dosage can be observed by comparing samples SB2 and SB3. Increasing the NaOH dosage clearly increased the ISO brightness from 67.5% to 70.0% and decreased the viscosity from 22.9 to 19.3 cP. Although the behavior of the EFB pulps and SB pulps was similar when NaOH dosage increased, the EFB pulps had higher kappa numbers, lower brightness, and lower viscosities than the SB pulps.

After oxygen bleaching, the pulps were subjected to a P_{sa}-E_p-P_{sa}-E_p bleaching sequence. P_{sa} was chosen because a previous study revealed that P_{sa} increased HexA decomposition [43]. One of the causes of the yellowing effect is HexA in the pulp. Therefore, by removing HexA, brightness reversion can be avoided. Moreover, Rizaluddin *et al.* [33] reported that P_{sa} treatment resulted in larger reduction of kappa number per unit of viscosity (better selectivity) than ozone bleaching. In this study, bleaching of SB pulps with 0.1% P_{sa} resulted in a 2.3–3.7% increase in ISO brightness and a decrease in viscosity by 3.0–6.6 cP (Fig. 1).

During the E_p stage, 0.1% MgSO₄ was added to maintain the viscosity. A previous study clarified that the beneficial effect of MgSO₄ on pulp brightness and viscosity during the E_p stage is the result of stabilization of peroxide and oxygen species by MgSO₄ [44, 45]. In this study, a significant increase in the brightness of both SB and EFB pulps was observed after the E_p stage compared with that after the P_{sa} stage.

Similar multistage TCF bleaching sequences applied to hardwood pulps prepared by prehydrolysis and kraft cooking obtained ISO brightness of 87.3–88.3% after the final stage, but the viscosities of the samples decreased to 5.1–6.0 cP [19]. However, in this study, the ISO brightness of the SB pulps after the

Fig. 1 Brightness and viscosity profile of SB3 pulp during O-P_{sa}-E_p-P_{sa}-E_p bleaching sequence (white bar: brightness; gray bar: viscosity)

final stage of the P_{sa}-E_p-P_{sa}-E_p bleaching sequence reached 88.3–89.6% with viscosities of 5.6–6.9 cP (Table 5). The brightness level of all these samples met the requirements of the Indonesian National Standard; however, sample SB5 did not meet the standard requirement for viscosity (>6.2 cP). The glucan content of each of the SB TCF-bleached pulps was in the range of 95.4–96.4% and the α -cellulose content was 93.6 ± 0.9%, which met the standard requirement (minimum 94%). The ash content analysis revealed that only sample SB3 (0.1%) and sample SB4 (0.1%) met the standard requirement. Therefore, sample SB3, with an ISO brightness of 89.1%, viscosity of 6.4 cP, glucan content of 95.7%, and ash content of 0.12% was chosen as the optimum result.

Table 1 shows that HexA content of SB prehydrolyzed soda-AQ pulp (0.2 mmol/kg) was considerably lower than that of the EFB pulp (14.4 mmol/kg). The higher brightness of the SB pulp after the final bleaching stage should be influenced by the lower HexA content, as H₂SO₅ is consumed in a reaction with HexA [43]. Any H₂SO₅ not consumed in this reaction can effectively degrade residual lignin and colored substances.

During the overall bleaching sequence, the

Table 5 Viscosity, brightness, carbohydrate content, and ash content of TCF (O-P_{sa}-E_p-P_{sa}-E_p) and ECF (O-P_{sa}-E_p-D) bleached pulps.

	Bleaching sequence	Brightness (% ISO)	Viscosity (cP)	Glucan (%)	Xylan (%)	Ash (%)
SB 1	O-P _{sa} -E _p -P _{sa} -E _p	88.9 ± 0.7	6.9 ± 0.1	95.4 ± 0.6	4.1 ± 0.1	0.26 ± 0.05
SB 3	O-P _{sa} -E _p -P _{sa} -E _p	89.1 ± 1.3	6.4 ± 0.1	95.7 ± 0.5	4.0 ± 0.1	0.12 ± 0.02
SB 4	O-P _{sa} -E _p -P _{sa} -E _p	88.3 ± 0.2	6.3 ± 0.1	96.4 ± 0.8	3.5 ± 0.1	0.13 ± 0.02
SB 5	O-P _{sa} -E _p -P _{sa} -E _p	89.6 ± 0.4	5.6 ± 0.1	96.2 ± 0.6	3.6 ± 0.1	0.17 ± 0.05
SB 2	O-P _{sa} -E _p -D	88.8 ± 0.3	8.9 ± 0.1	94.7 ± 0.7	4.4 ± 0.1	0.11 ± 0.02
EFB 1	O-P _{sa} -E _p -P _{sa} -E _p	79.1 ± 0.3	8.9 ± 0.1	80.4 ± 1.6	18.5 ± 0.1	0.83 ± 0.06
EFB 2	O-P _{sa} -E _p -P _{sa} -E _p	81.6 ± 0.2	7.0 ± 0.1	82.4 ± 1.5	16.8 ± 0.1	0.52 ± 0.04

decrease in viscosity for EFB (18.8 to 7.0 cP) was lower than that for SB (34.1 to 6.4 cP). This result shows that EFB pulp fiber is more resistant to bleaching chemicals than SB materials. This finding opens the possibility of increasing the chemical dosage for EFB in future studies. However, for DP production, SB is preferable because of the lower chemical dosage needed to reach the standard. The application of this TCF bleaching sequence to achieve the standard brightness (minimum 88%) can be considered the first report of DP production from SB.

Figure 2 shows the molecular weight distributions of the SB TCF bleached pulp (SB 3) and ECF bleached pulp (SB 2). The weight-average molecular weight (M_w) and the number-average molecular weight (M_n) of the TCF bleached pulp were 1.59×10^5 g/mol and 5.66×10^4 g/mol, respectively (polydispersity: $M_w/M_n = 2.82$). M_w was slightly lower than that of the ECF bleached pulp ($M_w = 2.44 \times 10^5$ g/mol, $M_w/M_n = 2.95$). These M_w results are higher than the molecular weight calculated from the degree of polymerization (DP) by employing a viscosity method via the TAPPI Test Method. Based on the

correlation $DP^{0.905} = 0.75 - 954 \log(x) - 325$ [46], where x is the viscosity (cP) based on the TAPPI T 230 method, DP for SB TCF and ECF pulps were found to be 613 and 824, respectively. Further, the viscosity-average molecular weights (M_v) of the cellulose in the TCF and ECF pulps were 9.93×10^4 g/mol and 1.33×10^5 , respectively. Pullulan, a polysaccharide composes of maltotriose units (three $\alpha(1 \rightarrow 4)$ linked glucose molecules) in which the units are linked by $\alpha(1 \rightarrow 6)$ glycosidic bonds, has a different polymer backbone with cellulose ($\beta(1 \rightarrow 4)$ linked). It was reported that M_w of methyl cellulose obtained by GPC using pullulan as the standard was overestimated to a greater extent than that determined by the light scattering method [47].

The TCF bleaching chemicals cause a greater degree of de-polymerization of cellulose than the ECF bleaching chemicals, as indicated by the viscosity and M_w of the SB TCF bleached pulp being lower than those of the SB ECF bleached pulp. A previous study [19] reported that the replacement of chlorine dioxide with H_2SO_5 during the bleaching stages caused viscosity loss in hardwood pulp. In addition, the total dosages of H_2O_2 and NaOH during TCF bleaching were 2.0% and 3.4%, respectively, which were two times higher than those in the case of ECF bleaching, and this resulted in the viscosity of the TCF pulp being lower than that of the ECF pulp.

Figure 3 showed that the crystallinity index (CrI) of the SB TCF bleached pulp (SB3) and SB ECF bleached pulp (SB2) increased to 73.6% and 78.8%, respectively, from 46.3% (raw material) and 65.5% (unbleached pulp). The increase in CrI was caused by the removal of amorphous lignin and hemicelluloses after delignification and bleaching [48]. CrI of the SB TCF bleached pulp was slightly lower than that of the SB ECF bleached pulp. NaOH dosages including in the oxygen bleaching stage during TCF bleaching

Fig. 2 Molecular weight distributions of SB TCF bleached pulp (1), SB ECF bleached pulp (2) and filter paper (3)

Fig. 3 XRD spectra of SB raw material (1), SB unbleached pulp (2), SB TCF bleached pulp (3), SB ECF bleached pulp (4) and cellulose powder (5)

was 3.4% (two times higher than that in the case of ECF bleaching). A higher NaOH dosage should remove more lignin and hemicelluloses, resulting in a higher cellulose content. A higher NaOH dosage should also cause more swelling of cellulose under an alkaline condition and decrease cellulose crystallinity.

Four-stage ECF bleaching (O-P_{sa}-E_p-D) of SB pulp resulted in an ISO brightness of 88.8% with a high viscosity of 8.9 cP, a glucan content of 94.7%, and an ash content of 0.1% (Table 5). Thus, ECF bleaching may meet the standard requirements, even if a lower dosage of ClO₂ (0.7%) is applied. However, within the context of environmental issues, TCF bleaching is preferable because no organochlorine substances are discharged. Meanwhile, bleached EFB pulps only achieved ISO brightness of 79.1% and 81.6%, which are below the Indonesian National Standard (minimum 88%).

4. Conclusions

Prehydrolysis is an important step in the production of DP from SB. An ISO brightness of 46.3% and viscosity of 34.1 cP were obtained by prehydrolysis for 3 h at 150 °C and cooking for 2 h at 150 °C with an AA dosage of 16%. The application of a TCF bleaching sequence (P_{sa}-E_p-P_{sa}-E_p; chemical dosages of 0.1, 1.0, 0.1, and 1.0%, respectively) to the oxygen-bleached pulp was successful. The ISO brightness (89.1%), viscosity (6.4 cP), ash content (0.12%), α-cellulose content (93.6%), and glucan content (95.7%) achieved for the bleached pulp met the requirements by Indonesian National Standard.

These results demonstrate not only an approach for reducing dependency on wood as a raw material, but also the potential of an environmentally friendly biorefinery process for the utilization of SB materials to achieve high-quality DP production.

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