

DISSOLVING PULP FROM KENAF BY BIO-BLEACHING PROCESS

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Diterima : 10 Juni 2013, Revisi akhir : 14 November 2013, Disetujui terbit : 02 Desember 2013

PULP DISSOLVING DARI KENAF MENGGUNAKAN PROSES BIO-BLEACHING

ABSTRAK

Kenaf berasal dari daerah Jawa Timur Malang - berusia empat sampai lima bulan dan digunakan sebagai bahan baku *dissolving pulp*. Morfologi dan komponen kimia kenaf dianalisis berdasarkan Standar Nasional Indonesia (SNI). Serat kenaf memiliki panjang serat rata-rata 2,59 mm untuk batang dan 3,63 mm untuk kulit pohon, termasuk kedalam kelompok serat panjang dengan panjang serat > 1,60 mm. Kenaf mengandung alpha selulosa sebesar 45,45% untuk kulit dan 39,46% untuk batang. Kenaf dipotong-potong dengan panjang 3 sampai dengan 5 cm. Sebelum pemasakan, dilakukan prahidrolisa menggunakan air dan asam encer (0,4% H₂SO₄) untuk melunakkan serpih kenaf dan membuat ikatan pentosan (hemiselulosa) menjadi lemah, dengan merendamnya dalam air dan 0,4% H₂SO₄ dengan rasio 1 : 5 pada suhu 135°C selama 2 jam. Selanjutnya dilakukan pemasakan dengan proses kraft menggunakan Alkali Aktif (AA) sebesar 16% dan sulfiditas (S) sebesar 28%. Rasio bahan baku dan larutan pemasak adalah 1 : 5 pada suhu 160°C selama 3 jam. Proses pemutihan pulp dilakukan dalam lima tahap terdiri dari XOD₀E₀D₁D₂ (Xilanase, Oksigen delignifikasi, Klorin dioksida, Oksigen Ekstraksi, Klorin dioksida 1, Klorin dioksida 2). Proses pemutihan pada tahap X menggunakan enzim xilanase yang dikenal dengan *bio-bleaching*. Setiap tahap dicuci dengan air panas sampai bersih. Dissolving pulp yang diperoleh dianalisis derajat cerah, kadar selulosa alfa dan komponen kimia lainnya sesuai SNI. Dissolving pulp mempunyai viskositas yang sangat tinggi, ini berarti bahwa proses pemutihan pulp tidak banyak menyebabkan terjadinya degradasi selulosa.

Kata kunci: *bio-bleaching*, *dissolving pulp*, prehidrolisa, kenaf, xilanase

ABSTRACT

The kenaf taken from Malang-East Java was four to five months old and used as the raw material of dissolving pulp. Morphology and chemicals content of kenaf was analyzed based on Indonesian National Standard (SNI). Kenaf fibre has the fibre length average of 2.59 mm for stem and 3.63 mm for bast and it is classified on the long fiber, fibre length > 1.60 mm. It contains alpha cellulose in the amount of 45.45% for bast and 39.46% for stem. Kenaf was cut with the length of 3 to 5 cm to make chips. Before cooking, pre-hydrolyzed using water and dilute acid (0.4% H₂SO₄) was done to remove pentosan (hemicellulose) by soaking chips in water and 0.4% H₂SO₄ in the ratio of 1 : 5 at temperature of 135°C for 2 hours. The results was mixed with cooking liquor which contains Active Alkali (AA) of 16% and Sulfidity (S) of 28%. Ratio of raw material and cooking liquor was 1 : 5 at temperature of 160°C for 3 hours. Bleaching process was done in the five stages consisted of XOD₀E₀D₁D₂ (Xylanase, Oxygen delignification, Chlorine Dioxide, Oxygen Ectraction, Chlorine Dioxide 1st, Chlorine Dioxide 2nd). Bleaching process in the stage of X use xylanase enzyme (*bio-bleaching*). Every stage was washed with hot soft water up to neutral pH. Dissolving pulp was analyzed for brightness, alpha cellulose content and other chemicals content. Pulp viscosity is very high, which means that the pulp bleaching process is not much cause degraded cellulose

Keywords: *bio-bleaching*, *dissolving pulp*, pre-hydrolyzed, kenaf, xylanase

INTRODUCTION

Wood demand from industrial forest plantations for pulpraw material is still not fulfilled yet due to the shrinking of the industrial forest plantations areas of and decreased productivity as well as the wood converted into woodworking raw materials (Sudomo et al., 2007). Seeing this reality, there is alternative which is very possible to fill the shortage of pulp raw material by using kenaf plants (*Hibiscus cannabinus L.*). Kenaf plants is one of long fiber sources of non-wood having advantages compared to forest wood such as very short age between 4 - 5 months. It can be planted at least twice a year (Sudjindro, 2001). Kenaf can be used as a substitute NUKP (Needle Unbleached Kraft Pulp) or NBKP (Needle Bleached Kraft Pulp) in the paper making (Rosli et al., 2009; Mosello et al., 2009). Based on its fibre morphology and chemical composition, kenaf is a good raw material for pulp. Kenaf stem consists of two distinct parts i.e. bast and wood core core. Bast of kenaf contains fibre ropes as many as 35 - 40% by weight. Whereas section wood core containing short fibre as many as 60 - 65%. Kenaf can be processed using whole stalk producing pulp with the quality similar as pulp made from leaf wood. Bleached pulp made from kenaf stems cooked with the soda-anthraquinone process with Active Alkali (AA) of 17% and Anthraquinone (aq) 0.1% can meet all the requirements for NBKP (Pratiwi et al., 2002).

Dissolving pulp is a high-grade cellulose pulp, with low contents of hemicellulose, lignin and resin. This very clean pulp is well suited as a raw material for different kinds of cellulose products, such as viscose. Production of dissolving pulp is today mainly done by acid sulfite and pre-hydrolysis kraft processes (Al-Dajani and Tschirner, 2008; Li et al., 2010). The pulping process has to dissolve the main bulk of the lignin and modify the residual lignin for successful bleaching. Bleaching then has to remove this residual and increase the pulp brightness and cleanliness. The final result should be cellulose as free as possible from lignin and hemicelluloses as well as extractible.

During kraft pulping, the presence of hydrogen sulfide ions greatly facilitates delignification because of their strong nucleophilicity in comparison with hydroxyl ions. For this reason, lignin undergoes more or less drastic degradation reactions resulting from the liberation of phenolic

hydroxyl groups in the simultaneous increase in hydrophilicity of lignin fragments. Most of these depolymerized fragments are thus water-soluble and dissolved in the cooking liquor as sodium phenolates. The term "kraft lignin" (in the case of soda pulping, "alkali lignin") is usually referred to as the soluble lignin degradation products in black liquor, and their structures markedly differ from those of the native lignin and the respective residual pulp lignin ("residual lignin").

Delignification in modern bleaching sequences is conducted in the form of ECF processes by application of chlorine dioxide followed by alkaline extraction. In pulp bleaching, bleaching chemicals are a key process to any pulp mill in order to get bleached pulp. This process use Elemental Chlorine Free (chlorine dioxide/ ClO_2) to pulp bleaching process. Unfortunately, chemicals bleaching react with organic carbon compounds producing toxic compounds of chlorinated hydrocarbons released into environment with the wastewater from the pulp mill if use chlorine (Cl_2) to bleached pulp. These chlorinated hydrocarbons compounds, such as dioxin, is highly toxic chemicals called organo-chlorines, which are basically poisons.

Biotechnology can play a major role in establishing the new, technologically advanced and effective processes (Kumar et al., 2009; Russomanno dan Sarkanen, 1998). Xylanase has been found to be effective in reducing chlorine dosage requirement in pre-bleaching process of kraft pulp (Raghukumar et al., 2005). Other applications proposed for xylanase include debarking, refining pulp fibers and preparing dissolving pulps (Christov et al., 1996; Ibarra et al., 2010). If kraft pulps are pre-bleached with xylanase, the ClO_2 required to achieve a given degree of bleaching on the delignification of unbleached softwood and hardwood kraft pulps is lower, which reduce organo-chlorines discharges (Saleem dan Akhtar, 2002; Tremblay dan Archibald, 1993; Viikari et al., 1994). The pulp and paper industry is modifying its pulping, bleaching and effluent treatment technologies to reduce the environmental impact of mill effluents (Tremblay dan Archibald, 1993).

The use of kenaf wood from industrial forest plantations is generally used for the manufacture of paper pulp type. To diversify the use of kenaf wood, conditions optimization of dissolving pulp making is necessary. Effect of acid and water use in the pre-hydrolysis process of kenaf and

effect the use of xylanase in bleaching process of unbleached pulp to the quality of dissolving pulp produced is also presented.

MATERIALS AND METHOD

Kenaf used in the making of dissolving pulp is taken from plantation at Malang district, East Java. Dissolving pulp process making is consisted of:

1. Raw material preparation
Kenaf was cut to the length of 3 - 5 cm and was dried in the open air to maintain a uniform moisture content.
2. Pre-hydrolysis process
Pre-hydrolysis experiments of kenaf were conducted in two pre-hydrolysis conditions that are by using water and 0.4% H_2SO_4 solution. Pre-hydrolysis process of kenaf was carried out in an autoclave by immersing approximately 400 grams of wood chip in water and 0.4% H_2SO_4 solution with the ratio of each ingredient with a pre-hydrolysis solution of 1 to 4 at a temperature of 135°C for 2 hours. After completing of pre-hydrolysis, the remaining water and the solution were removed by filtering and the pre-hydrolysis product was then cooked.
3. Cooking process
Cooking process of kenaf chip is done by using active alkali (AA) of 16%, sulfidity (S) of 28% with a ratio of 1 to 5 at the temperature of 160°C for 3 hours. During cooking, both temperatures in the autoclave and in the digester room were controlled. After cooking, the pulp was washed on the flat screen and the pulp fibres were refined in pin shredder. Unbleached pulp produced was then pressed and was determined the Kappa number and the yield.

4. Bleaching process

Bleaching of unbleached pulp was performed without the use of chlorine with five stages, namely $XOD_0E_0D_1D_2$ (xylanase, oxygen delignification, chlorine dioxide, oxygen extraction, 1st chlorine dioxide, 2nd chlorine dioxide). Pulp from each bleaching stage was washed with hot soft water until the neutral pH. Bleaching process conditions is shown in Table 1.

Morphology of kenaf was analyzed by the method of procedure Franklin U.S. Forest Products Research Laboratory, Department of Agriculture and the Indonesian National Standard. Chemical properties of kenaf were analyzed by Indonesian National Standard (SNI). Unbleached and bleached dissolving pulp produced was analyzed by Indonesian National Standard (SNI 0938-1989-A).

RESULTS AND DISCUSSION

Raw Materials and Characterization

Kenaf plants (Figure 1a) is one of long fiber sources of non-wood having advantages compared to forest wood such as very short age between 4 - 5 months. It can be planted at least twice a year (Sudjindro, 2001). Kenaf stem (Figure 1b) consists of two distinct parts i.e. bast and wood core. Bast of kenaf contains fibre ropes as many as 35 - 40% by weight. Kenaf plants used in the investigation of dissolving pulp making in the cooking laboratory of Center for Pulp and Paper (CPP) is one of superior type of kenaf obtained in the form of stem from kenaf farmers located at Malang district, East Java.

Before cooking, the size of kenaf chip was classified by using a vibrating sieve which

Table 1. Bleaching Process Condition

Parameter	X	O	D ₀	E ₀	D ₁	D ₂
ClO ₂ (%)	-	-	22 KN	-	1	0.2
O ₂ (psig)	-	87	-	29	-	-
NaOH (%)	-	1.5	-	1	-	-
H ₂ SO ₄ (%)	-	-	0.7	-	-	-
Xylanase (%)	1	-	-	-	-	-
Consistency (%)	10	10	8	8	10	10
Temperature (°C)	25	95	60	75	75	75



a). Plants of *kenaf*



b). Stem of *kenaf*

Figure 1. Plants and Stem of Kenaf

has 5 class sizes. Kenaf chip used for cooking experiment is that retained in the screen of stage 2 and 3 with the chip size of around the length of 30 – 50 mm as shown in Figure 2.



Figure 2. Kenaf Chips

Uniformity of the chip wood size that will be cooked is intended in order that in the cooking time and temperature applied could produce pulp with a homogeneous level of maturity (Casey, 1980). When the size of kenaf chip is smaller, it will cause the pulp produced is quite mature. Conversely, if the size of kenaf chips is larger, it can cause some chip is immature (Casey, 1980). Results of analysis of fibre morphology and chemical components of kenaf can be seen in Table 2 and Table 3, respectively.

Data obtained an experimental result of two replications. Felting power, stiffness, muhlstep ratio and runkel numbers are fibre properties to identify the extent of fibre able to be modified such as spun, untwisted fibre, and woven sheets made. If the value of runkel number is more than 1 (one), it indicates that types of non-wood fibres have thick walls, so the possibility of requiring

greater energy milling or hard to be fibrillated. While kenaf fibre has the fibre length average of 2.59 mm for stem and 3.63 mm for bast and it is classified as the long fiber, fibre length > 1.60 mm (Casey, 1980).

From Table 3, it can be seen that holocellulose content of kenaf is 77.60% and 75.57% for bast and stem, respectively. Holocellulose is part of the fibre-free extractive and lignin, composed of cellulose and hemicelluloses, white to yellowish colour. Holocellulose content is the total carbohydrate or polysaccharides content in the raw materials. While the alpha cellulose content is 45.56% for bast and 39.46% for stem. This alpha cellulose content is high enough and it will produce high pulp yield (Casey, 1980).

Table 2 . Fibre Morphology of Kenaf

No	Parameter	Stem	Bast
Fibre length (mm):			
1.	- minimum	0.84	2.07
	- maximum	6.22	6.81
	- average	2.59	3.63
Diameter (µm):			
2.	- outer	28.44	23.78
	- in	10.58	8.24
3.	Wall thickness	8.93	7.77
4.	Runkel number	1.69	1.89
5.	Slimness	91.07	152
6.	Stiffness	0.31	0.33
7.	Flexibility	0.37	0.35
8.	Muhlstep ratio (%)	68.16	87.99

Cellulose is a linear polysaccharide composed of units with ties anhydro-glucose 1-4 b glucosidic that the hydrolysis in acidic conditions produces D-glucose. Cellulose is divided into three parts, namely α cellulose having a high molecular weight which is the part that stayed after the other cellulose dissolved on treatment with sodium hydroxide of 9.45%. Dissolution will be developed with 17.5% sodium hydroxide, addition of 9.45% sodium hydroxide will produce soluble cellulose in the form of β -cellulose and γ -cellulose (Casey, 1980).

Table 3. Chemical Analysis of Kenaf

No.	Parameter	Bast	Stem
1.	Ash (%)	4.59	3.50
2.	Lignin (%)	10.16	16.88
3.	Extractive (%)	2.00	2.47
4.	Holocellulose (%)	77.60	75.57
5.	α -cellulose (%)	45.56	39.46
6.	Pentosan (%)	16.92	22.65
7.	Solubility in cold water (%)	8.92	7.84
8.	Solubility in hot water (%)	6.72	6.93
9.	Solubility in NaOH (%)	25.36	28.51

Extractive content contained in the raw materials are generally composed of fatty acids, resin, wax, gum and the other are volatile materials and un-volatile materials. Extractive (alcohol-benzene extract) is a substance in wood or pulp extracted by alcohol-benzene as a solvent, performed at the boiling point of solvent within a certain time. In general, non-wood containing low extractive will produce a clean pulp (Casey, 1980). Scanning Electron Microscope (SEM) picture of kenaf and their components that are inside can be seen in Figure 3. Figure 3 shows that the organic carbon component in the kenaf wood is 73.43% and the remaining is the other components.

Pulp Making Process

Data obtained from an experimental result of three replications. The initial phase of dissolving pulp making is the process of pre-hydrolysis of kenaf chip. This pre-hydrolysis process helps to facilitate the separation of cellulose fibres from lignin. kenaf pulp

produced is still brown (unbleached). The results of the cooking non-wood of each pre-hydrolysis process can be seen in Table 4.

Table 4 shows that pre-hydrolysis with water followed by the cooking process produce almost similar yield than that of pre-hydrolysis with acid. But the Kappa number is slightly higher than that of the pre-hydrolysis with acid.

Table 4. Result of Cooking Process

No	Pre-hydrolysis	Kappa number	Yield (%)
1.	Water	22.81	50.03
2.	H ₂ SO ₄	19.81	50.00

Pulp Bleaching Process

Bleaching of pulp was done by XOD₀E₀D₁D₂. Bleaching pulp at the stage of X using xylanase enzyme is known as bio-bleaching. Bio-bleaching can reduce chemical of bleaching so that it can reduce content of pollutants from pulp effluents (Noorbach et al., 2009; Rosli et al., 2005; Saleem et al., 2002). Pulp bleaching results are shown in Table 5 and Table 6.

The experimental results showed that the bleaching of kenaf pulp produce bleaching yield > 96%. In this case, there is not much degraded cellulose by using xylanase enzymes (bio-bleaching). The brightness degree of dissolving pulp produced by the bleaching stage of XOD₀E₀D₁D₂ result is quite high i.e. above 86% ISO. This value is above the specifications of dissolving pulp for rayon grade (> 85% ISO) (SNI 0938-1989-A). Data obtained from an experimental result of three replications.

The chemical analysis results of dissolving pulp can be seen in Table 6. It shows that the dissolving pulp pre-hydrolyzed by acid and water has α -cellulose content higher than 86% and it is a little bit lower than the specifications as a raw material for the making of cellulose derivatives (SNI 0938-1989). Brightness and cellulose can be increased by reducing the content of pentosan. Pulp viscosity is very high, which means that the pulp bleaching process is not much cause degraded cellulose. Ash content in the bleached pulp is still quite high. To lower the ash content can be done by depithing process on its kenaf feedstock.

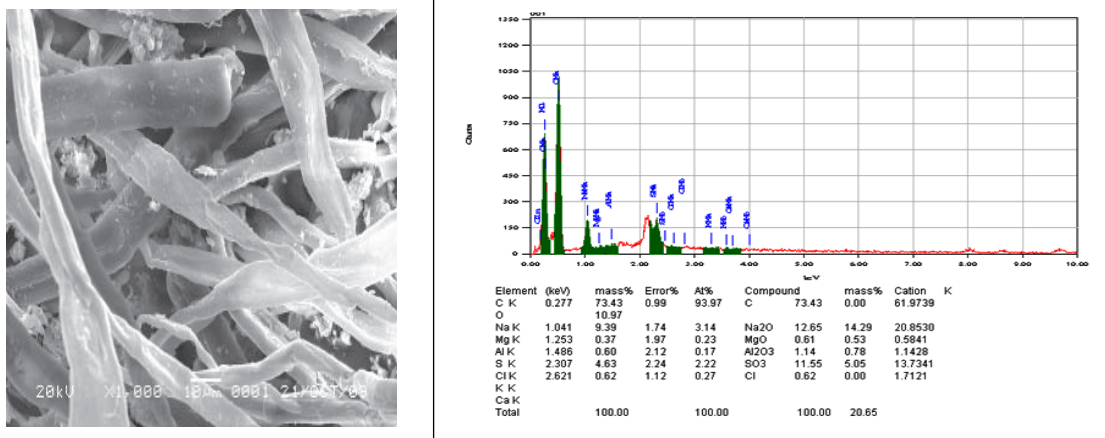


Figure 3. SEM Micrograph of Kenaf

Table 5. Result of Bleached Pulp

No	Prehydrolysis	Yield (%)	Kappa Number after O ₂	Brightness (% ISO)	Brightness of rayon grade pulp
1.	Water	96.92	9.58	86.23	> 85% ISO
2.	H ₂ SO ₄	98.73	8.69	86.27	

Table 6. Chemicals Properties of Bleached Pulp

No	Pre-hydrolysis	Moisture content (%)	Ash (%)	α -cellulose (%)	Pentosan (%)	Viscosity (cP)	Solubility in 10% NaOH	Solubility in 18% NaOH
1.	H ₂ SO ₄	4.92	0.78	86.36	14.97	29.06	10.93	7.65
2.	Water	4.61	0.77	86.71	14.71	27.55	10.34	7.33

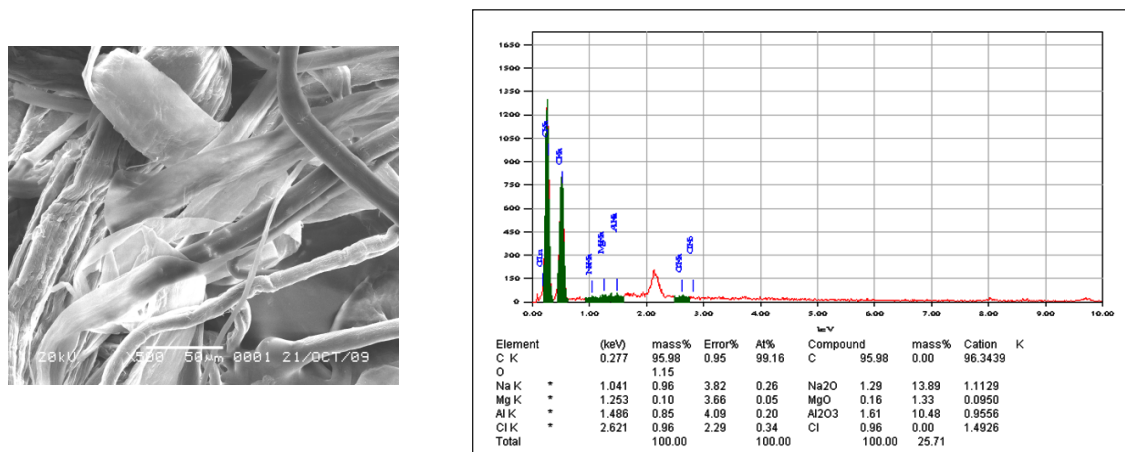


Figure 4. SEM Micrograph of Pulp Pre-Hydrolyzed by Acid

Scanning Electron Microscope (SEM) picture of dissolving pulp pre-hydrolyzed by acids and the components therein can be seen in Figure 4. It shows that the components of organic carbon (C compound) in dissolving pulp made from kenaf is 95.98% and the rest is the other components that are higher than that kenaf itself. It shows that organic carbon (C compound) in dissolving pulp is higher than the raw material.

CONCLUSIONS

Kenaf fibre having an average fibre length of 2.59 to 3.63 mm fibres belonging to the long fibres. Holocellulose content of kenaf is 77.60% and 75.57% for bast and stem. Pre-hydrolysis with acid followed by the cooking process produce higher dissolving pulp yield, brightness, alpha cellulose, viscosity, alkali solubility and lower kappa number compared with pre-hydrolysis with water. Dissolving pulp having yield up to 98%, the degree of brightness higher than 86% ISO, and alpha cellulose higher than 86% could be obtained by the bleaching stage of $XOD_0E_0D_1D_2$. Pulp viscosity is very high which means that the pulp bleaching process is not much cause degraded cellulose.

ACKNOWLEDGEMENTS

The authors are grateful to the colleagues at Center for Pulp and Paper (CPP) Bandung-Indonesia. Ministry of Industry for the support and the encouragement.

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