Characteristics of Soda Pulp from Distilled Vetiver Root

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Abstract

Cellulose was commonly extracted from wood and other lignocellulosic materials such as leaf, straw, bast, or grass. There is no report found on extraction of cellulose from root plant yet. Industrially, the root of vetiver is distilled to obtain its essential oil. In this study, the distilled vetiver root was soda pulped and the resulted pulp was characterized by the use of X-ray diffraction and FT-IR spectroscopic methods. Response surface methodology with central composite design was used to investigate the influence of delignification on the chemical properties of pulp. Soda pulping was carried out at 160 – 180 ^{o}C for 1 – 3 hrs with 20 – 40% of alkali charge. Severe process conditions were required to achieve a significant degree of delignification. Pulping at 180 ^{o}C for 3 hours with alkali charge of 40% decreased the lignin content of pulp from 39.53% to 4.47%.

Keywords: FT-IR analysis, soda pulping, vetiver root, X-ray diffraction

Abstrak

Umumnya, selulosa diekstrak dari kayu atau bahan ber-lignoselulosa, seperti daun, kulit batang atau rumput. Laporan mengenai selulosa yang diekstrak dari bagian akar tanaman masih terbatas. Akar tanaman akarwangi (*Vetiveria zizanioides* L.) mengandung minyak atsiri. yang diperoleh dengan cara distilasi uap dan menyisakan ampas akarwangi. Pada penelitian ini ampas akarwangi diolah menjadi pulp menggunakan proses soda. Pulp soda ampas akarwangi kemudian dikarakterisasi kristalinitas dan gugus fungsionalnya menggunakan difraksi sinar X and FT-IR. Metode statistik Respon Permukaan dengan desain komposit terpusat digunakan untuk mengetahui pengaruh kondisi proses delignifikasi (suhu 160-180^{o}C, waktu 1-3 jam dan alkali aktif 20-40%) selama proses pulping terhadap sifat kimia pulp soda ampas akarwangi. Untuk mendapatkan memperoleh tingkat delignifikasi yang nyata, dibutuhkan kondisi pulping yang cukup ekstrim. Setelah proses pulping pada suhu 180^{o}C, alkali aktif 40%, selama 3 jam, kandungan lignin dalam pulp soda ampas akarwangi berkurang dari 39,53% menjadi 4,47%.

Kata kunci: akarwangi, analisis FT-IR, difraksi sinar X, pulping soda.

Introduction

Indonesia is a producer of essential oil from vetiver root (*Vetiver zizaniodes*). The distillation process of vetiver roots set aside a large quantities of distilled vetiver root. Based on 2,316 hectare of vetiver plantations in Garut Regency (center of vetiver plantation in Indonesia), productivity of 10 tonnes vetiver root/ha/yr and vetiver oil yield of 0.7%, there would be approximately 23,017 tonnes/yr of distilled vetiver root. These distilled vetiver roots are lignocellulosic materials that contain 30.33% of cellulose (Syamani *et al.* 2013).

In the cell wall of lignocellulosic plant, cellulose is the main constituent and is organized into fibrils, which are surrounded by a matrix of lignin and

hemicellulose. This material is a linear polymer of anhydroglucose units, in form of alpha-cellulose, beta-cellulose and gamma-cellulose, based on its degree of polymerization (Horvath 2006). An aqueous solution of acetic acid and sodium chlorite (acid-chlorite delignification) is the most popular and established laboratory method for the removal of lignin from biomass (Hubbell & Ragauskas 2010). Nevertheless, the organochlorite that was produced during delignification contaminated environment. Many researchers are trying to employ less harmfull chemical in delignification process and studying the extraction of cellulose fibers from wood and other lignocellulosic materials such as leaf, straw, bast, or grass (Hubbell & Ragauskas 2010, Cherian *et al.* 2010, Zaini *et al.* 2013, Nuruddin *et al.* 2011, Rosli *et al.* 2013). There is no report on cellulose extracted from root plant, yet.

In this study, we investigated delignification of distilled vetiver root by soda pulping and characterized soda pulp of vetiver root by using X-ray diffraction and FT-IR spectra.

Materials and Methods

Distilled vetiver roots were obtained from essential oil industry in Garut Regency, West Java, Provence of Indonesia. The vetiver roots were washed several times, sun-dried and cut into ± 2 cm length, then cooked in digester to produce vetiver pulp. The cross section and element of undistilled and distilled vetiver root were analyzed by scanning electron microscope/energy dispersive spectroscope (SEM/EDS) JEOL JSM 6510, operated at 15 kV. Samples were coated with gold using a vacuum sputter-coater to improve conductivity of the samples and thus the quality of the SEM images.

Experimental design on pulping process

Response surface methodology was utilised to optimise the delignification by pulping process and a central composite design (CCD) was adopted. The central combination for the experimental design was as follows: pulping temperature T=170 ^{o}C, pulping-time-at-temperature t=2 hours and soda concentration or alkali charge (AC) = 30%, with variable of 160 – 180 ^{o}C, 1 to 3 hours and 20 to 40%, respectively.

All pulping trials were carried out in batch rotary digester with 4 ^{o}C min^{-1} of heating rate. The pulping process (cooking) was carried out at liqour-to-material ratio of 8:1. After cooking, the pulps was washed several times until neutralised.

Pulp characterization

The pulp chemical component content was determined following the TAPPI methods as T 204 om-88 for extractive content, T 222 om-88 for lignin content, and T 203 om-93 for alpha cellulose content, with slightly modification. The procedure to determine hollocellulose content was according to Wise's chlorite method.

XRD measurements were performed on a Shimadzu XRD7000 MAXima X-ray diffractometer to analyze pulp crystallinity. The diffracted intensity of Cu Kα radiation (λ= 0.1542 nm; 40 kV and 30.0 mA) was measured in a 2θ range between 10° and 40°.

The FT IR ABB was used to analyze chemical structure of vetiver pulp component. The analysis was run using the KBr pellet technique. The KBr pellets of samples were prepared by mixing 2 ± 0.05 mg of pulp sample with 200 mg KBr (spectroscopy grade) in a

vibratory ball mixer for 20 s. The KBr pellets were prepared under vacuum in a standard device under a pressure of 80 kN cm^{-2} for 3 min to form pellet with diameter and thickness of 13 mm and 0.5 cm, repectively. The spectral resolution was 4 cm^{-1} and the scanning range was from 400 to 4000 cm^{-1}.

Results and Discussion

Cross section morphology of vetiver root fiber

As lignocellulosic materials, vetiver roots contain cellulose, hemicellulose and lignin in its cell wall. The vetiver grass has a long (3–4 m), massive and complex root system. It is grown for soil conservation, water conservation and stabilization. Volatile extracts of vetiver roots are used in the perfume, soap and related industries. After oil extraction, 98% of the starting material remains, leaving huge amounts of residues which are not used as industrial material, but burnt in fields or at the road side (Gaspard 2006).

As shows at Figure 1, vetiver root morphology contructs hollow tube, with cortex and vascular tissue. The two main components of vascular tissue are the xylem and phloem.

Distillation during vetiver oil extraction was done at temperature of 120 °C for 16 hours, caused vetiver fiber cracking (Figure 2). The cracking began from pith of vetiver fiber, then splitted fiber into 4 fragments.

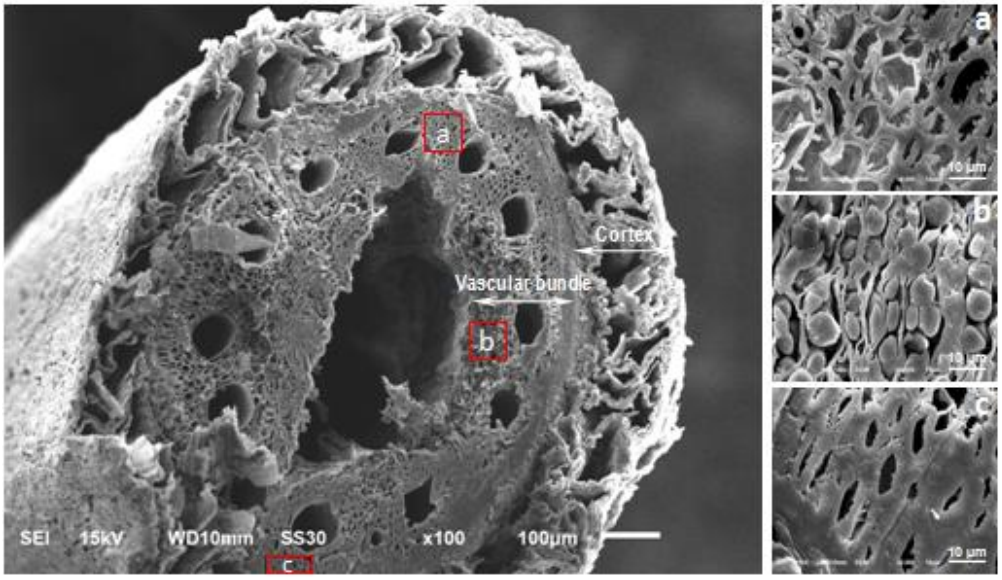

Figure 1 Scanning electron micrographs of vetiver root cross section (100x magnification); (a) xylem, (b) phloem, (c) parenchyma (2000x magnification).

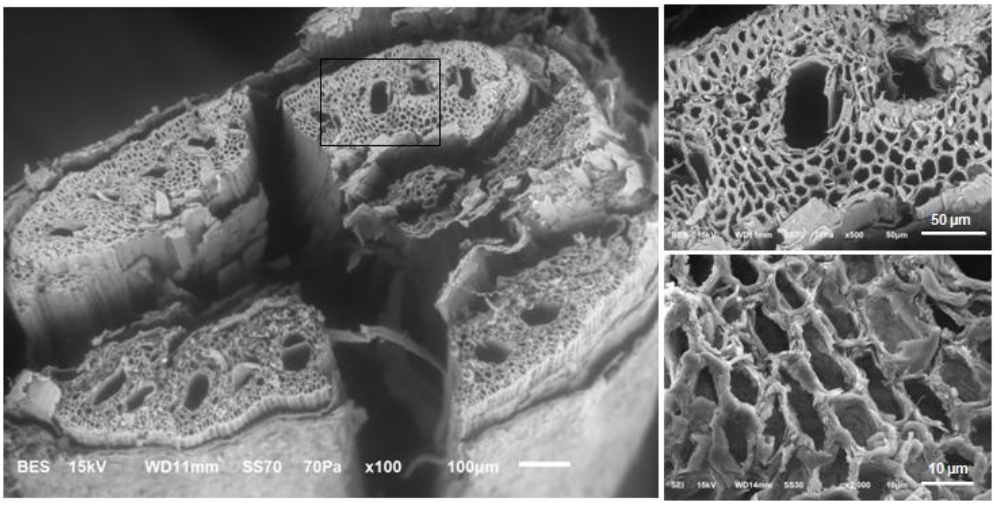

Figure 2 Scanning electron micrographs of distilled vetiver root fiber cross section.

Vetiver root can uptake and accumulate Pb up to 3000 mg kg^{-1} dry weight without affecting its growth (Andra *et al.* 2010). Vetiver root from Garut Regency in West Java, Indonesia contained 8.35% of Pb element or 15.96% of PbO (Table 1). In vetiver root, Pb was deposited in cortex and pith (Andra *et al.* 2009) and did not chemically attached to vetiver component. During distillation, Pb was taken out from vetiver root. It confirmed by EDS analysis that distilled vetiver did not contain Pb in form of element or compound.

Chemical analysis of vetiver pulp

Delignification of vetiver roots was done by studying the responses of pulp properties to the process variables. Lignin dissolved during delignification. In that case, the chemical agent used in this study (NaOH) was the only variable that has direct impact on the chemical properties of resulting pulp. The results for soda pulping of vetiver roots are summarized in Table 2.

Table 1 Component and oxide compound in vetiver fiber

	Element	% Mass	Oxide compound	% Mass
Undistilled vetiver	C	44.61		
	O	45.51		
	K	1.51	K_2O	16.09
	Pb	8.36	PbO	15.96
Distilled vetiver	C	53.48		
	O	41.94		
	Al	4.15	Al_2O_3	14.02
	Si	0.43	SiO_2	1.49

Table 2 Lignocelulosic component of vetiver pulp

No	Pulping variables			Responses			
	Temperature	Time	Alkali Charge	Extractive	Holocellulose	Lignin	Cellulose
	(°C)	(min)	(%)	(%)	(%)	(%)	(%)
1	160	60	20	1.93	61.34	32.05	52.87
2	180	60	20	1.96	68.67	27.56	61.44
3	160	180	20	2.01	81.28	13.81	72.18
4	180	180	20	1.96	69.40	25.54	61.35
5	160	60	40	1.48	85.71	11.73	75.70
6	180	60	40	1.94	93.76	9.25	84.68
7	160	180	40	1.72	90.56	6.32	79.12
8	180	180	40	1.96	91.89	4.47	82.56
9	153	120	30	1.66	76.85	19.20	58.33
10	187	120	30	2.20	91.68	5.29	81.11
11	170	19	30	1.48	84.04	13.24	73.36
12	170	221	30	1.79	89.38	8.36	80.04
13	170	120	13	2.81	51.49	40.49	44.76
14	170	120	47	1.87	91.82	4.74	81.93
15	170	120	30	2.44	90.79	5.96	81.82
16	170	120	30	1.50	89.13	8.71	78.56
17	170	120	30	1.62	89.47	8.88	79.35

Lignin content in distilled vetiver root was 39.53% (Syamani *et al.* 2013). After pulping with alkali charge of 40% for 180 min at 180° C, lignin content decreased to 4.47%. Statistical analysis on the pulping variables interaction shows that temperature or time of pulping had no significant effect on the pulp lignin content at all levels of alkali charge.

FTIR analysis

IR spectroscope has been employed to determine delignification of vetiver soda pulp. Natural lignin contain the following functional groups: metoxyl, phenolic hydroxyl, primary and secondary aliphatic hydroxyl, ketone and aldehyde groups. Depending on method of isolation and chemical treatment, new functional groups that are not present in natural lignin, may appear (Bykov 2008).

The infrared spectra of lignin present peaks in the range 1200-1300 cm^{-1} corresponding to the aromatic skeletal vibration. In addition, due to the presence of functional groups such as methoxyl-O-CH_3, C-O-C and aromatic C=C, peaks in the region between 1830 cm^{-1} and 1730 cm^{-1} were also observed. The peak presents at 1730-1740 cm^{-1} in the spectrum corresponding to the presence of C=O lingkage, which is a characteristic of lignin groups (Owen & Thomas 1989).

The enhanced carbonyl absorption peak at 1735 cm^{-1} (C=O ester), C–H absorption at 1381 cm^{-1} (–C–CH3), and –C–O– stretching band at 1242 cm^{-1} confirmed the formation of ester bonds. Also, it is evidenced an increase in the intensity of OH in plane bending vibration at 1385 cm^{-1} band specific to the wood components, cellulose and hemicelluloses (Bykov 2008).

Every lignin IR spectrum has a strong wide band between 3000-3500 cm^{-1} assigned to OH stretching vibrations. This band is caused by presence of alcoholic and phenolic hydroxyl groups involved in hydrogen bonds (Bykov 2008).

The enhanced O–H absorption band at 3348 cm^{-1} and 2901 cm^{-1} (Figure 3) were

observed, indicated that the hydroxyl group contents in vetiver soda pulp were increased after pulping reaction.

Peak at 2361 cm^{-1} was observed on spectra from vetiver soda pulp produced by pulping at alkali charge 20% though with different pulping temperature 160°C (pulp a) and 180° C (pulp c), then was disappeared on spectra of vetiver soda pulp produced at alkali charge 40% (pulp b and pulp d). The band in the 2700 – 2200 cm^{-1} region is the ammonium band (Silverstein *et al.* 2005). In particular, the peak of 2361 cm-1 corresponds to a azide bond, which is the anion with formula NH_3^- (Kshirsagar *et al.* 2013). The root of vetiver absorp some nitrogen compounds from fertilizer and detected in vetiver pulp which was cooked at alkali charge of 20%. While vetiver pulp from pulping process at alkali charge of 40% has no nitrogen element anymore.

X-ray diffraction analysis

X-ray diffraction analysis was conducted to determine vetiver soda pulp crystallinity. Vetiver soda pulp that was produced by pulping at temperature 160 °C for 60 min and alkali charge of 20% and 40%, indicated crystallinity of 32.58 -47.55%, respectively. While vetiver soda pulp that was produced by pulping at temperature 180 °C for 60 min and alkali charge of 20% and 40%, showed crystallinity of 34.83%, 49.00%, respectively.

Temperature of pulping had no significant effect on the pulp crystallinity. However, alkali charge of pulping had significant effect. Vetiver soda pulp crystallinity was higher at higher alkali charge of pulping. The higher alkali charge of pulping, the more lignin dissolved from vetiver root and delivered the more cellulose and thus pulp crystallinity.

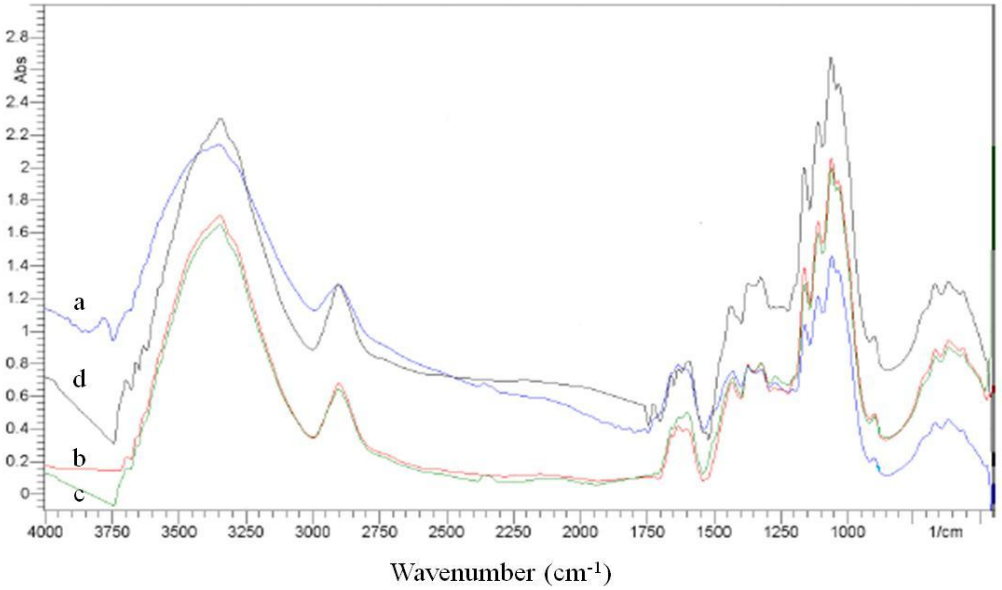

Figure 3 FTIR analysis of vetiver pulp from varied temperature, time and alkali charge pulping condition: (a) 160 °C, 60 min, AC 20%; (b) 160 °C, 60 min, AC 40%; (c) 180 °C, 60 min AC 20%; (d) 180 °C, 60 min, AC 40%.

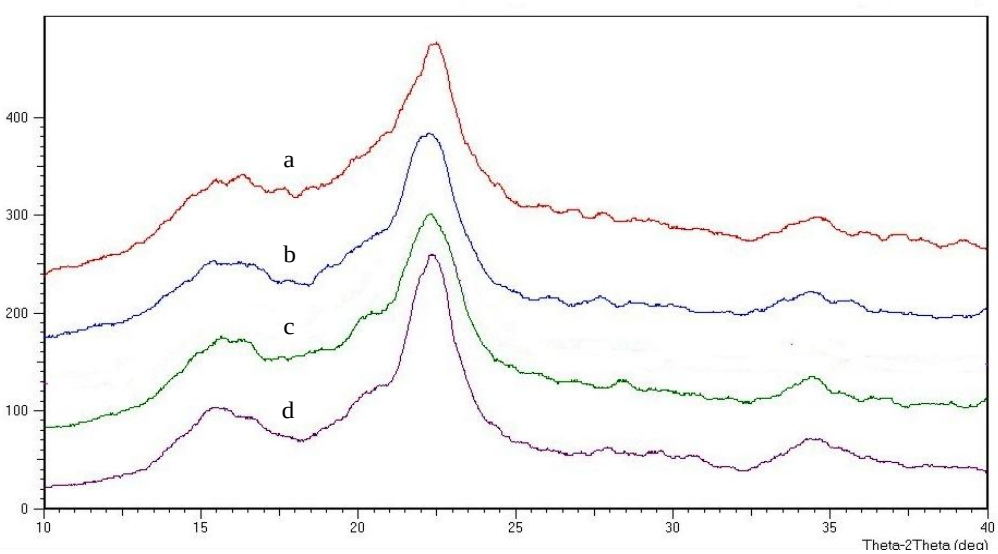

Figure 4 XRD analysis of vetiver pulp from varied temperature, time and alkali charge pulping condition: (a) 160 °C, 60 min, AC 20%; (b) 160 °C, 60 min, AC 40%; (c) 180 °C, 60 min AC 20%; (d) 180 °C, 60 min, AC 40%.

Conclusions

Distillation at 120 °C for 16 hours during vetiver oil extraction caused vetiver fiber cracking and removed Pb out of vetiver root. Statistical analysis on the pulping variables interaction effects shows that NaOH was the only variable that has direct impact on the chemical properties of resulting pulp. Severe pulping condition (180 ^{o}C and alkali charge of 40% for 3 hours) need to be employed for vetiver root delignification from 39.53 - 4.47%. FTIR spectras show chemical compound alteration due to soda pulping. Vetiver soda pulp crystallinity was higher at higher alkali charge pulping.

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