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Feasibility of Tree Selection for High Pulp Yield, Brightness and Recyclable Paper Production

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Effective utilization of forest resources is demanded toward the construction of efficient carbon loop. For the paper recycle, we have examined the feasibility of tree selection from two plantation sites for high pulp yield, brightness without bleaching and recyclable paper production considered from color reversion by heat treatment. The best *Eucalyptus globulus* tree among utilized 7 trees allowed 372 kg m^{-3} of screened pulp yield, 65.9% ISO of virgin brightness and 64.0% ISO of brightness after 24 h heat exposure by chemithermomechanical process with sodium sulfite, whereas the average of screened pulp yield, virgin brightness and heated brightness were 358 kg m^{-3}, 63.9% ISO and 62.5% ISO, respectively. The significantly high relationship was obtained between pulp properties and wood properties as follows; screened pulp yield and cellulose content (+): virgin brightness and holocellulose content (+). Since the brightness after 24h heat exposure significantly correlated to virgin brightness positively, the tree selection suitable for paper recycle with both high pulp yield and brightness can be performed by wood property determination.
Key words: recycling, paper, tree selection, color reversion, heat exposure

1. INTRODUCTION

Eucalyptus is a widely utilized species for the tree plantation, especially intended for chemical pulp production use [1]. *E. globulus* is one of the fast growing species in a temperate zone with a rotation period of 8-10 years [2]. The tree breeding programs of are aiming to improve growth, pulp yield and strength for the pulp production because the elite tree selection contributes to the reduction of energy, CO_2 emission and pulp cost.

To construct an effective carbon loop, higher pulp yield and paper recycling rate are preferable. The pulp yield of mechanical pulp is higher than that of kraft pulp suitable for this objective. Furthermore, the chemithermomechanical pulp (CTMP), one of the mechanical pulps, has an advantage that the paper strength does not decrease rapidly during recycle. However, the CTMP papers generally have a disadvantage of yellowing occurrence by heat exposure [3]. The degree of yellowing is crucial for recycling because it determines requirement amount of bleaching agents causing pulp fiber damage during bleaching.

In this work, we have examined the feasibility of tree selection of *E. globulus* for high growth rate, pulp yield, brightness and low color reversion by heat exposure for recyclable CTMP paper production using seven individuals from one plantation site.

2. EXPERIMENTAL

2.1 Materials

Seven individuals of *Eucalyptus globulus* trees used in this study were similarly silvicultured and grown in two plantation sites of Manjimup (MJP) and Albany (ABN) in Western Australia (age 9.5). One individual of *Acacia mangium* tree was grown in the plantation site of Kinarut in Malaysia (age 11).

2.2 CTMP

The wood chips were pretreated with 5% sodium sulfite solution of pH 9.9 at 70°C for 1 h following at 20°C for 11 h. The primary refining was conducted at 135°C for 3 min with preheat of 5 min by a defibrator (Metso Defibrator Type D, Helsinki, Finland). The second refining was by a PFI mill (STFI, Stockholm, Sweden) using pulp consistency of 20% at clearance of 0.5 mm. The CTMP was screened by a laboratory flat screen with an 8 cut plate to prepare hand sheets. Hand sheets of CTMP were exposed to dry heat at 105°C for 24 h. The ISO brightness of sheets before and after heat exposure was measured with a spectro whiteness color meter (Suga Test Instruments SC-10W, Tokyo, Japan). Pulp productivity was calculated by screened pulp yield x basic density.

2.3 Wood property determination

The contents of holocellulose, α-cellulose, hemicellulose, lignin, and extractives and

alkali-extractives were quantified by using small-scale method [4]. Basic density was determined by a water immersion method [5] combined with freeze-fracture and -drying, and expressed as dry weight/green volume [kg m^{-3}] [6]. Molar composition of neutral sugars constituting hemicellulose (glucose, xylose, galactose, arabinose and mannose) was determined by hydrolysis of holocellulose with trifluoroacetic acid using high performance liquid chromatography [7].

The characterization of lignin structure including syringyl/guaiacyl (S/G) ratio was determined by pyrolysis according to a previous report as follows [8]. A vertical microfurnace pyrolyzer (Frontier Lab PY2010D, Koriyama, Japan) was directly attached to a GC (Shimadzu GC17A, Kyoto, Japan) with a flame ionization detector (FID). About 100 μg of the cryo-milled samples were pyrolyzed at 450°C under a flow of helium carrier gas. A metal capillary column (Frontier Lab Ultra-Alloy PY1, 30 m×0.25 mm i.d., coated with 0.25 mm of polydimetylsiloxane through chemical cross-linking) was used. The 50 ml min^{-1} helium carrier gas flow rate at the pyrolyzer was reduced to 1.0 ml min^{-1} at the capillary column by a splitter (split ratio 1:25). The column temperature was programmed from 50-280°C at 5°C min^{-1}, and finally held for 10 min. The peak identification was carried out by a GC (Hewlett-Packard 6890, Avondale, PA, USA) / MS (Jeol Automass Sun 200, Tokyo, Japan) with an electron ionization source (70 eV), to which the pyrolyzer was also directly attached. The examined lignin fragments were the following; guaiacol, 4-methylguaiacol, vinylguaiacol, syringol, eugenol, vanillin, *cis*-isoeugenol, methylsyringol, homovanillin, *trans*-isoeugenol, acetoguaiacone, guaiacylacetone, vinylsyringol, allylsyringol, syringaldehyde, *cis*-propenylsyringol, *cis*-coniferyl alcohol, homosyringaldehyde, *trans*-propenylsyringol, *trans*-coniferaldehyde, acetosyringone, *trans*-coniferyl alcohol, syringylacetone, *cis*-sinapyl alcohol, *trans*-sinapaldehyde and *trans*-sinapyl alcohol.

Fiber morphology (length, diameter, lumen diameter and wall thickness) was assessed by the calibrations created by Raman spectroscopy modifying previous reports as follows [9, 10]. Raman spectra were collected using a Nicolet Raman 960 spectrometer (Nicolet Instrument, Madison, WI, USA) equipped with an InGaAs detector, and an Nd: YAG laser operating at 1064 nm. Tree samples (20 mesh - 0.840 mm opening - pass) were packed into nuclear magnetic resonance tubes and spectra were collected using 180°backscattering at 500 mW, 4 cm^{-1} resolution and 256 scans under 22°C using a thermal box [11]. Spectra of 100-1800 cm^{-1} Raman shift were used. The 1st derivative transformation and the multiplicative scatter correction of Raman spectroscopic data, and the partial least squares (PLS) regression were performed by using the software of Unscrambler 7.5 (Camo AS, Trondheim, Norway). The number of factors used in the PLS calibration model was decided by full-cross-validation method and useful frequencies were selected by Jack-knifing method [12]. A total of 226 samples for calibration sets were utilized from various parts in the trunk of two individual each of *E. globulus* and *E. camaldulensis* used in the previous studies [9, 10].

2.4 Statistical analysis

Correlation coefficients between CTMP and wood properties were calculated by the analysis of variance using a statistical computer software, SPSS 11.0.1J (SPSS Inc., IL, USA).

3. RESULTS AND DISCUSSION

3.1 Tree selection by pulp property (conventional method)

The tree data of *E. globulus* and elite tree candidates were summarized in Table I.

Table I Tree data.

Property	Volume (m^3)	Pulp productivity ($kg \cdot m^{-3}$)	Virgin brightness (%ISO)	Heated brightness (%ISO)
MJP1	0.258	302	65.2	63.5
MJP4	0.312	372	65.9	64.0
ABN38	0.242	396	67.9	64.9
Acacia	-	-	30.2	-
Min	0.231	302	60.3	57.8
Ave	0.262	358	65.0	62.5
Max	0.312	405	68.5	65.1

Large tree-to-tree variation was observed in tree volume under the bark and pulp yield even silvicultured and grown similarly. As expected, CTMP yield is higher than kraft pulp [13]. *E. globulus* CTMP gave high brightness without bleaching using chemical agents. The reference data of *A. mangium*, one of the major plantation species, was included in the table and obviously requires bleaching for printing paper production. Surprisingly, the highest brightness level of *E. globulus* CTMP paper is equivalent to a bleached conventional copy paper. The species difference may be derived from the low content of extractives and lignin in *E. globulus* shown in Table II although further studies are expected. In brightness, large tree-to-tree variation was observed similar to volume and pulp yield. This implies that *E. globulus* CTMP from selected trees can produce various types of papers without a bleaching process and minimize the facility of pulp production mill.

Consequently, the elite tree selection is encouraged for the effective utilization of forest resources, minimizing energy and chemical agent consumption and CO_2 emission.

The change of ISO brightness by heat exposure was examined and the results were summarized in Table I. The yellowing of *E. globulus* CTMP by heat exposure was very weak for each individual and the CTMP brightness is very stable against heat exposure. This suggests that the storage of used papers manufactured from *E. globulus* CTMP is permitted under high temperature without light. Furthermore, virgin brightness positively correlated to heated brightness with correlation coefficient of 0.978, which was significant at more than the 1% level although no relationship between screened pulp yield and brightness. The selection of the individual producing brighter virgin

pulp will make the paper more recyclable since severe pulp fiber damage can be avoided by the reduction of bleaching agent amount.

In this study, an individual of MJP4 can be selected as an elite tree providing 1.19 times higher volume (growth), 1.04 higher pulp yield, 1.01 times higher virgin brightness and 1.02 times higher heated brightness compared to the average of utilized seven individuals. The tree selection will contribute to the construction of efficient carbon loop.

3.2 Tree selection by wood property (increment core method)

Tree selection is preferably performed by using an increment core method, which retains the tree for future breeding and propagation. To achieve this, the relationship between pulp and wood properties is critical and examined. The wood property data were summarized in Table II and the relationships for pulp yield and for brightness were shown in Table III.

Screened pulp yield significantly related to cellulose content positively (+) and to hemicellulose content negatively (–), but not to extractives content. This is possibly caused by that extractives content in *E. globulus* is low in about 2-4% compared to other species [13]. The CTMP process is operated to retain chemical compounds as much as possible and the results obtained are reasonable since hemicellulose can be easily solubilized into water and lost during pulping. The hemicellulose composition was extracted as important traits as xylan (–), glucomannan (+) and arabinan (–). These hemicellulose fractions might represent pH difference for lignin synthesis environment, which was proposed to cause the structural difference of lignin synthesized with the polysaccharides as glucomannan is more acidic compared to others and hardly give more conjugated lignin structure digested in the CTMP process [14]. Further studies are required. Many lignin fragments by pyrolysis were also extracted. Almost all of positively related lignin fragments owned benzene ring with a side-chain containing carbonyl group and/or C=C or a side-chain containing C=C with no functional group. They may be derived from not conjugated lignin structures inside the cell wall considered from pyrograms of dehydrogenatively synthesized lignin [15] and of native lignin [8]. They were for both S and G units, which agree with that lignin S/G ratio was not an important trait. On the other hand, negatively related lignin fragments owned benzene ring with no side-chain or a side-chain of propenyl alcohol for S unit only. They may be derived from the reducing end of lignin [8] and can be cleaved by the CTMP process with sodium sulfite.

Virgin brightness significantly related to holocellulose content positively (+) and to arabinan composition in hemicellulose negatively (–). However, in heated brightness, extractives content was extracted negatively. This may imply the residual of extractives in CTMP. The result obtained was similar to a previous report [16].

Consequently, the relationship between pulp and wood properties was significantly high and can be explained reasonably described above. Tree selection for high pulp yield, high virgin brightness and low color reversion by heat exposure can be performed by the analysis of wood properties. Because holocellulose significantly related to all utilized traits positively, only holocellulose analysis may allow the tree selection. Since the representative height of holocellulose can be decided to take an increment core using a radially divided increment core method [13], the elite tree can be retained for its future breeding and propagation.

Table II Wood property data.

Wood property	Min	Ave	Max
Holocellulose (%)	83.2	83.8	84.6
α-Cellulose (%)	43.2	45.1	46.6
Hemicellulose (%)	37.5	38.7	39.9
Lignin (%)	14.9	16.8	18.3
Extractives (%)	1.9	3.0	3.8
Alkali-extractives (%)	14.6	15.9	17.0
Basic density ($kg \cdot m^{-3}$)	495	535	582
Glucose (mol%)	11.4	15.5	18.9
Xylose (mol%)	70.0	74.3	79.8
Galactose (mol%)	5.2	6.0	6.5
Arabinose (mol%)	1.1	1.3	1.4
Mannose (mol%)	2.2	2.9	4.4
Guaiacol (mol%)	5.31	6.00	6.60
4-Methylguaiacol (mol%)	2.13	2.75	3.22
Vinylguaiacol (mol%)	2.06	2.41	2.77
Syringol (mol%)	11.92	12.21	12.63
Eugenol (mol%)	0.41	0.68	1.13
Vanillin (mol%)	1.19	1.31	1.41
cis-Isoeugenol (mol%)	0.12	0.17	0.23
Methylsyringol (mol%)	8.08	8.64	9.45
Homovanillin (mol%)	0.00	0.00	0.00
trans-Isoeugenol (mol%)	1.37	1.64	1.84
Acetoguaiacone (mol%)	0.23	0.30	0.41
Guaiacylacetone (mol%)	0.20	0.36	0.53
Vinylsyringol (mol%)	13.59	14.01	14.60
Allylsyringol (mol%)	2.42	2.83	3.49
Syringaldehyde (mol%)	8.89	9.43	9.95
cis-Propenylsyringol (mol%)	1.01	1.07	1.13
cis-Coniferyl alcohol (mol%)	0.14	0.24	0.33
Homosyringaldehyde (mol%)	3.35	3.75	4.06
trans-Propenylsyringol (mol%)	8.98	9.79	10.30
trans-Coniferaldehyde (mol%)	0.00	0.00	0.00
Acetosyringone (mol%)	4.33	4.73	5.13
trans-Coniferyl alcohol (mol%)	0.45	0.85	1.30
Syringylacetone (mol%)	1.62	1.71	1.86
cis-Sinapyl alcohol (mol%)	2.34	2.84	3.22
trans-Sinapaldehyde (mol%)	9.24	9.94	10.14
trans-Sinapyl alcohol (mol%)	0.42	2.32	4.95
Lignin syringyl / guaiacyl ratio (-)	4.55	5.00	5.45
Fiber length (mm)	0.732	0.822	0.937
Fiber diameter (μm)	12.5	13.1	13.9
Fiber lumen diameter (μm)	7.42	8.19	9.48
Fiber wall thickness (μm)	1.76	2.46	2.87

Table III Correlation coefficient between pulp and wood properties.

Pulp property	Wood property	Correlation coefficient
Screened pulp yield	α-Cellulose	0.905***
	Hemicellulose	−0.718**
	Holocellulose	0.685**
	Xylose	−0.684**
	trans-Sinapaldehyde	0.681**
	Syringol	−0.651*
	Homosyringaldehyde	0.664*
	Glucose	0.643*
	trans-Propenylsyringol	0.640*
	Mannose	0.638*
	trans-Sinapyl alcohol	−0.621*
	Acetoguaiacone	0.620*
	Syringylacetone	0.612*
	cis-Isoeugenol	0.591*
	Arabinose	−0.556*
Virgin brightness	Holocellulose	0.795**
	Arabinose	−0.552*
Heated brightness	Holocellulose	0.670**
	Extractives	−0.595*

*** Significant at 1% level, **Significant at 5% level, * Significant at 10% level

The feasibility of tree selection for effective utilization of forest resources toward the construction of efficient carbon loop was proved. Selected trees are expected to suppress atmospheric CO_2 increase.

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