TOOLS TO PREDICT THE EUCALYPTUS KRAFT PULP YIELD

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SUMMARY

Indicative wood characteristics and reliable analytical methods to predict the pulping behavior were studied with six selected *Eucalyptus grandis* clones. Clear correlations between the chemical composition (the contents of carbohydrates, lignin, and extractives) of the raw material and pulp yield were found. The data obtained by pyrolysis-GC/MS, *i.e.* the total content of lignin and syringyl/guaiacyl (S/G) ratio, correlated well with the pulping behavior of the clones. In this case, a high S/G ratio was not beneficial to pulp yield, but correlated with high lignin content. In this respect, the content of lignin was more critical to pulp yield than lignin structure. Near infrared (NIR) spectroscopy seemed to be a potential method to screen rapidly large number of wood samples for selecting optimal clones. After a proper calibration this method is a fast and simple tool to be used even at mills or plantations.

Keywords: *Eucalyptus grandis*, pulp yield, kraft cooking, NIR spectroscopy, pyrolysis

RESUMO

Estudaram-se características sintomáticas e métodos analíticos confiáveis para a previsão do comportamento do processo de produção de pasta com seis clones selecionados de *Eucalyptus grandis*. Foram observadas correlações claras entre a composição química (teores de carboidratos, lignina e extrativos) da matéria-prima e o rendimento em pasta. Os dados obtidos por Py-GC/MS, ou seja, o teor total de lignina e a relação siringila/guaiacila (S/G), demonstraram boa correlação com o comportamento dos clones no processo de produção de pasta. No caso, uma razão S/G alta não se mostrou benéfica para o rendimento em pasta, mas correlacionou-se com alto teor de lignina. Desse ponto de vista, o teor de lignina comprovou-se mais essencial para o rendimento da pasta do que a estrutura da lignina. O método de espectroscopia de infravermelho próximo (NIR) pareceu ter bom potencial para a rápida triagem de grandes quantidades de amostras de madeira na seleção de clones ótimos. Depois da calibração adequada, esse método é uma ferramenta ágil e simples que pode ser usada mesmo em moinhos ou plantações.

Palavras-chave: *Eucalyptus grandis*, rendimento em pasta, cozimento kraft, espectroscopia NIR, pirólise

INTRODUCTION

High cooking yields and wood densities are required to minimize the wood consumption and to maximize the cost efficiency of both kraft pulping process and wood production in eucalyptus plantations. High density increases the wood production per unit area, and high pulping yield reduces wood consumption. The latter is affected both by cooking conditions and wood raw material. For selection and development of optimal eucalyptus species and clones for pulping, it is important to identify the chemical and physical characteristics of wood raw material correlating with pulp yield. This provides means to predict the pulping yield also in cases where gravimetric yield determination by laboratory cooking experiments is not possible, *e.g.* due to small amount of eucalyptus wood clones in the early phase of breeding.

A lot of data on the effect of eucalyptus wood chemistry on pulping and pulp utilization is available, and *e.g.* correlations of chemical composition and lignin structure to the pulp yield have been reported [1, 2, 3]. In generally, high carbohydrates/cellulose content, and low extractives and lignin contents are favorable to the efficient pulping process and high yield. Although lignin with a high syringyl/guaiacyl (S/G) ratio is known to be more advantageous to pulping [4], contradictory results on the effect of S/G ratio on pulp yield have been obtained. In many cases, eucalyptus trees with a high S/G ratio result in a high pulping yield [1, 5], whereas only a moderate or poor correlation to pulp yield has been shown with some other eucalyptus species [3]. In addition, the age of trees is also a factor affecting pulping yield. Wood density, extractives content and fiber coarseness increase with age, but the correlations of wood age to pulp yield have been controversial depending on eucalyptus species [1].

For the screening of large number of trees, easy and reliable analytical methods allowing the prediction of pulping yield on the bases of wood chemical characteristics are required. Wallis *et al.* [2, 3] have found a good correlation between the total content of wood carbohydrates and pulp yield, and have suggested carbohydrate analyses of eucalyptus wood raw material as a method to predict their pulping yield and papermaking properties. Pyrolysis could also be a convenient method to evaluate pulping yield through the wood lignin content and lignin structure, *e.g.* the S/G ratio [5, 6, 7,]. Contrary to the traditional wet chemical methods, pyrolysis is applicable to a very small sample amount without any laborious pretreatments. The near infrared spectroscopy (NIRS) has also been tested for the prediction of pulping yield [8, 9, 10]. It is fast, non-destructive, and simple method, but requires the development of calibration models combining the spectral data with the pulp yield and/or chemical characteristics determined by the traditional methods. After calibration, the laborious laboratory cooking experiments or chemical analysis could, however, be avoided.

The main target of this work was to establish a procedure to predict the cooking yield on the bases of the chemical analysis of wood raw material, and also to find out proper methods being applicable also at the mill site and plantations for the selection of optimal wood species and clones for pulping. For this purposes, six *Eucalyptus grandis* clones were cooked to different delignification degrees, and the gravimetric yields interpolated to the kappa level of 18 were correlated with the wood density, chemical composition (lignin content, carbohydrate composition, and extractives content), and lignin structure (S/G ratio). The pyrolysis-GC/MS was used for the characterization of lignin structure directly from wood or pulp. The potential of NIRS combined with principal component analysis was tested as a very fast and simple tool to predict the cooking yield and/or the characteristics of wood raw material, such as density.

EXPERIMENTAL

Sampling of the wood raw material

Six *Eucalyptus grandis* clones (clones A to F) representing different growth locations and conditions were selected for the study. The age of the clones was 5 years, only clone A was harvested at the age of 8 years. Of each clone, 6-20 trees were selected and a log of 0.5 m was cut from the chest height. For cooking experiments and density measurements, 4 cm thick disks were cut from the middle of each log, providing 6-20 discs and density values of each clone. The discs were manually chipped with a constant length of 4 cm and a thickness of 4 mm but variable width.

Laboratory cooks

The chips were cooked in 1-liter rotating stainless steel autoclaves (air heated) to the kappa levels of 25-14 using H-factors 250, 300, 350 and 400. Alkali charge of 5 mol NaOH/kg wood and sulphidity of 35 % were used. Liquor to wood ratio was 4 l/kg and cooking temperature 155 °C. After cooking, the pulps were screened (slot 0.25 mm) and dried. Gravimetric pulp yield and the amount of reject were determined.

Wood characterization

Wood density was determined according to SCAN CM 43:95. Standardized methods were also used for the determination of extractives content (SCAN CM 49:35), and total lignin content as gravimetric Klason and acid-soluble lignin (Tappi T 222 om-02). Carbohydrate composition was determined according to the modified Tappi T 249 cm-00 standard after acid hydrolysis, and monosaccharides were quantified by HPAEC-PAD [11]. Polysaccharide compositions were calculated according to Janson [12], using constants given for birch. The total content of carbohydrates in pulps was calculated by subtracting the contents of lignin and extractives from 100%.

For Py-GC/MS analyses, air-dried pulp and wood samples were Wiley milled and washed with tap water to remove the possible sodium ion residues [13]. Samples were pyrolyzed at 580 °C using a filament pulse pyrolyzer Pyrola2000 (Pyrola AB, Sweden), as described previously [7]. All peak areas were normalized to the weighed sample amounts, and the S/G ratios were calculated from the sum of peak areas assigned to the syringyl and quaiacyl type phenols.

The NIR measurements were performed by a Nicolet Antaris Near-IR Analyzer (1000-2500 nm, 2 nm resolution, 64 scans) for wood chips and wood meal using the Fiber Optic Sampling technique. Air dry chips were milled with a Cyclotec 1093 Mill having a 1-mm screen. Three parallel millings were performed for each clone. Analyst software was used for multivariate analysis to create the PLS-regression based calibration models combining the spectral data with the corresponding pulp yields and wood characteristics determined by other methods. Untreated NIR-spectra and their second derivatives were used for modeling.

RESULTS AND DISCUSSION

Cooking yield and wood density

Interpolated pulp yields together with the densities of clones A-F are given in Table 1. Screened pulp yields of the clones varied from 49.6 % to 52.6 %, and in each case the amount of reject was very low. Average wood densities varied within 385-461 kg/m^3. With respect to the specific wood consumption, a high wood density is beneficial, but no correlation to pulp yield was found. This finding is consistent with the results of Colodette *et al.* [1].

Table 1. Screened and total pulp yields at an interpolated kappa number of 18 together with the density values of the *E. grandis* clones studied.

Clone	**Screened yield,** %	**Total yield,** %	**Wood density,** kg/m^3
Clone A	49.6	49.7	461
Clone B	50.7	50.7	423
Clone C	50.7	51.0	385
Clone D	50.9	50.9	456
Clone E	51.7	51.8	457
Clone F	52.6	52.7	436

Chemical composition of wood raw material

As also shown previously [1-3], the chemical composition of wood raw material correlated reasonably well with pulp yield (Figures 1-4). High carbohydrates or cellulose contents and low lignin and extractives contents were beneficial to pulp yield. Although the content of cellulose gave nearly as good result as that of the total carbohydrates, the amount of hemicelluloses or the individual xylan and glucomannan contents showed no correlation to pulp yield. Roughly 1 %-unit higher cellulose or 1 %-unit lower lignin content resulted in a similar increase in pulp yield.

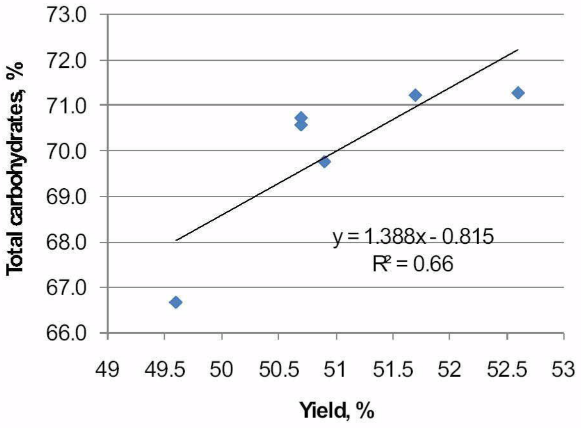

Figure 1. The total content of carbohydrates (100% - Lignin-w% - Extractives-w%) in *E. grandis* clones as a function of the pulp yield interpolated to the kappa number of 18.

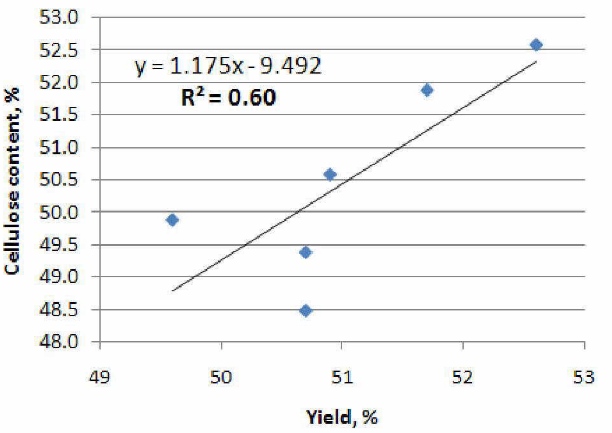

Figure 2. The content of cellulose in *E. grandis* clones as a function of the pulp yield interpolated to the kappa number of 18.

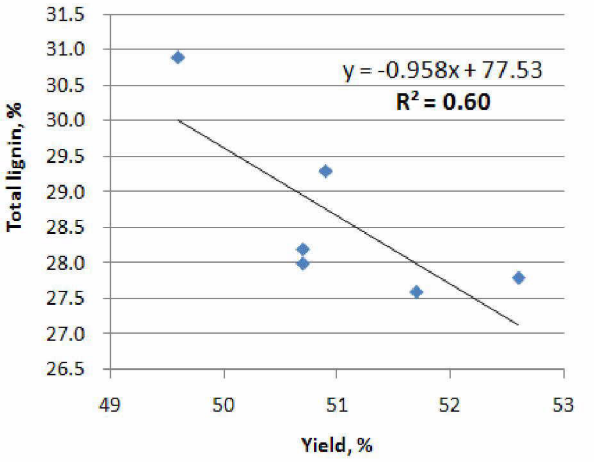

Figure 3. The total content of lignin in *E. grandis* clones as a function of the pulp yield interpolated to the kappa number of 18.

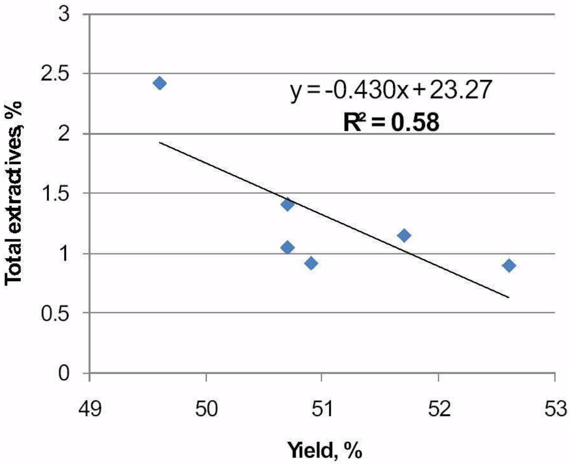

Figure 4. The total content of extractives in *E. grandis* clones as a function of the pulp yield interpolated to the kappa number of 18.

The results indicate that the chemical composition of wood clones, especially the total contents of lignin and extractives could provide valuable data for the prediction of pulping yield. It was also evident that the carbohydrate analysis alone is not a sufficient measurement for this reason. The monosaccharide composition as such showed no correlation to pulp yield, and the total contents of lignin and extractives were required to calculate the total amounts of carbohydrates/cellulose. In any case, more accuracy for the selection of the best clones for pulping can be obtained, if all three standardized measurements, *i.e.* the determination of carbohydrates, lignin and extractives, are performed. However, as a disadvantage, the sample amounts required are several grams, and all three measurement procedures are laborious to carry out.

Lignin content and structure by pyrolysis

The content and structure of lignin in the *E. grandis* clones were investigated by pyrolysis. As shown in Figure 5, the total area of aromatic degradation products after pyrolysis correlated well with the total lignin contents determined by the standard method. For this reason, pyrolysis can be used for the prediction of pulping behavior and only very small sample amounts without any other sample pretreatment than milling to homogenize the sample are needed. As an additional benefit, information on the S/G ratio known to affect lignin reactivity can be obtained.

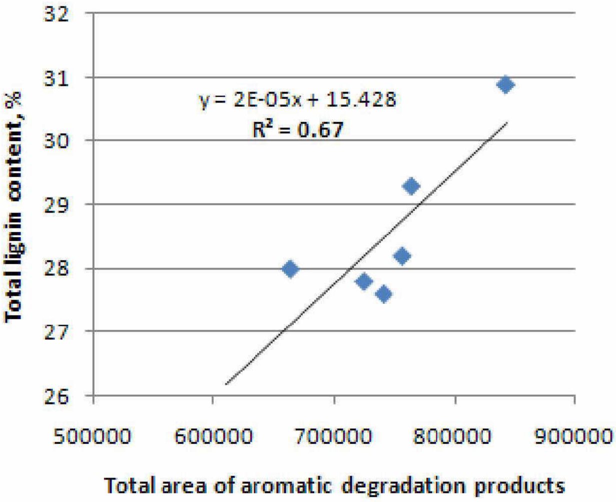

Figure 5. Correlation between the total signal area of aromatic decradation products after pyrolysis and the total content of lignin in the *E. grandis* clones.

As shown in Figure 6, a good correlation between the pulp yield and the lignin S/G ratio was also found. However, unlike expected a high S/G ratio was not favorable to pulp yield in this case. Wood clones with a high S/G ratio also had a high lignin content, which seemed to be more critical to pulp yield than lignin structure (Figure 7). According to Figure 8, the amount of G units remained nearly constant, but the amount of S units increased with an increasing lignin content. In all cases, the S/G ratio decreased during cooking (S/G below 2 after cooking), suggesting the higher reactivity of syringyl lignin.

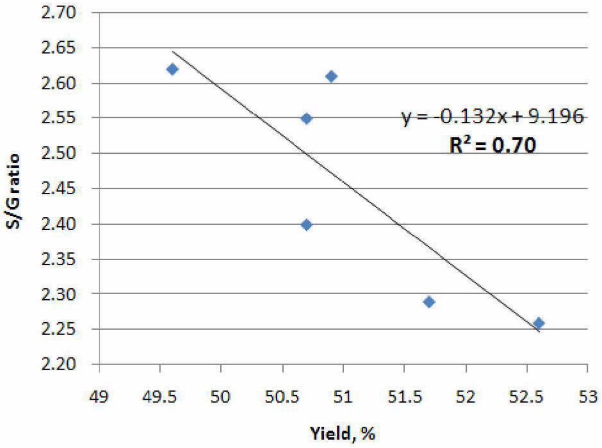

Figure 6. Correlation between the lignin syringyl/guaiasyl (S/G) ratio and the pulp yield of the *E. grandis* clones.

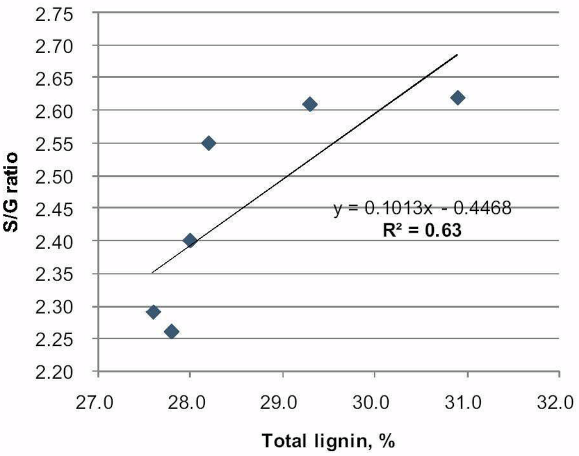

Figure 7. Correlation between the lignin syringyl/guaiacyl (S/G) ratio and the total lignin content of the *E. grandis* clones.

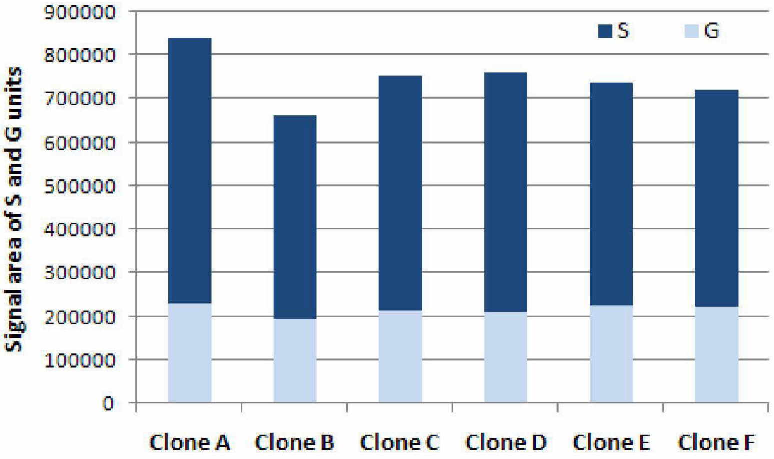

Figure 8. The proportion of syringyl (S) and guaiacyl (G) units of lignin in the *E. grandis* clones.

In general, rather contradictory results on the effects of lignin S/G ratio on pulp yield have been reported [1, 3], and this is probably not a proper way to evaluate the pulping behavior of different wood clones. In contrast to our results, the S/G ratio has been shown to correlate negatively with effective alkali demand and positively with pulping yield of *E. urograndis* [1]. In that case, the eucalyptus wood raw materials with a high lignin content also had low S/G ratios and were hard to process [1]. A positive correlation between pulp yield and S/G ratio was found also with *E. globulus*, even though wood samples with a higher content of lignin had a higher S/G ratio [5]. In both studies [1, 5], higher S/G ratios than in this study were reported; 3.5-6.5 for the *E. globulus* [5] and 2.5-3.1 for *E. urograndis* [1]. It is thus possible that there is a 'threshold', after which the high S/G ratio can affect positively pulp yield. On the other hand, the results may be very much dependent on wood species. Wallis *et al.* [3] have found only a moderate correlation between S/G ratios and pulp yield with *E. globulus*, whereas for *E. nitens* the correlation was poor. Regardless of the high S/G ratios of 3.2-4.4, the results of Wallis *et al.* [3] support our finding that the chemical composition and lignin content is more critical to pulp yield than lignin structure.

It is obvious that with respect to the prediction of pulping behavior of different clones pyrolysis can provide useful information, even from very small core samples. However, it probably cannot be considered as a routine method to be used at mills and plantations.

NIR spectroscopy

NIR spectra were measured from wood chips without any pretreatment and from wood meal after milling. Multivariate analysis and PLS regression models were created to combine the spectroscopic data with pulp yields and the chemical characteristics of *E. grandis* clones determined by traditional methods. Both the untreated NIR spectra and their second derivatives were tested in the models. The reliability of the models was evaluated according to the correlation coefficients (r^2), standard error of calibration (SEC), and standard error of prediction (SEP).

Models showing best predictability are given in Tables 2 and 3. In general, somewhat better results could be obtained by the measurements of milled wood samples than wood chips. The pulp yield could be predicted this way with a very good accuracy (r^2=0.99). Also the wood chemical characteristics, such as cellulose content, could be reliably predicted (r^2=0.99). In most cases, the use of derivative spectra did not improve the accuracy of the calibration models. However, in the case of wood density, a better correlation was obtained with the derivative spectra (r^2=0.71).

Table 2. The best PLS models in predictions of the chemical characteristics of the *E. grandis* clones and pulp yield by the NIR measurements of wood meal (r^2=correlation coefficient, SEC=standard error of calibration and SEP=standard error of prediction).

Predicted property	Range covered by the model	R^2	SEC	SEP	Number of factors
NIR-PLS models for untreated spectra					
Pulp yield	45-58%	0.99	0.128	0.352	6
Cellulose content	45-55%	0.99	0.328	0.821	6
Extractives content	0.9-2.6%	0.96	0.146	0.183	4
S/G ratio	2-3	0.78	0.091	0.098	2
NIR-PLS models for 2nd derivative spectra					
Lignin content	25-34%	0.7	0.821	1.22	1
Density	350-500 kg/m^3	0.71	19.3	34.3	2

Table 3. The best PLS models for predictions of the chemical characteristics of the *E. grandis* clones and pulp yield by the NIR measurements of wood chips (r^2=correlation coefficient, SEC=standard error of calibration and SEP=standard error of prediction).

Predicted property	Range covered by the model	R^2	SEC	SEP	Number of factors
NIR-PLS models for untreated spectra					
Pulp yield	45-58%	0.98	0.162	0.792	9
		0.79	0.516	0.817	4
Cellulose content	45-55	0.94	0.458	1.420	8
Extractives content	0.9-2.6%	0.86	0.246	0.422	4
S/G ratio	2-3	0.78	0.090	0.100	2
NIR-PLS models for 2nd derivative spectra					
Lignin content	25-34%	0.68	0.76	1.23	1
S/G ratio	2-3	0.93	0.06	0.17	4
Density	350-500 kg/m^3	0.83	14.5	30.7	2

According to the preliminary tests, the NIR spectroscopy proved to be a potential tool to predict both the pulp yield and the chemical characteristics of wood raw material by a single measurement. It is a fast and simple method to be used even at the mills for large sample series. However, prior to the use, it requires more extensive calibration series against pulp yields and/or other structural data. As an additional benefit, the models can be extended to predict also the pulp characteristics and quality.

CONCLUSIONS

Clear correlations between the chemical composition, *i.e.* the contents of carbohydrates, lignin and extractives, of eucalyptus wood and pulp yield were found, as reported also previously. Good correlation between lignin S/G ratio and pulp yield was observed, but unlike expected a high S/G ratio was not beneficial to pulp yield. A low lignin content was more critical to pulp yield than lignin structure. Regarding the methods tested, NIR spectroscopy seemed the most potential method for a fast screening of large number of samples, and could be used even at mill site or plantations to select the most optimal wood clones for pulping. Pyrolysis was also a convenient method to evaluate the pulping behavior of wood clones based on the lignin content. In addition, it is applicable to very small sample amounts without any laborious pretreatments, allowing ranking of the wood clones already in the very early stage of breeding.

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