ANALYSIS OF THE CHANGES IN CHEMICAL PROPERTIES OF DISSOLVING PULP DURING THE BLEACHING PROCESS USING PIECEWISE LINEAR REGRESSION MODELS

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Dissolving wood pulp is a chemically bleached wood pulp that has a cellulose content of more than 90%. Such pulp has certain properties of industrial value according to the products it can be used for. Raw pulp, which comes after acid bisulphite pulping, goes through a number of bleaching processing stages, each with a specific role, to produce dissolving pulp. These processing stages have different effects on the pulp depending on the type of wood genotype that is being processed. The bleaching processing stages are considered as time points for repeated measurements of the following chemical properties viz., viscosity, lignin, γ-cellulose, α-cellulose, copper number, glucose and xylose. Piecewise regression models were used to compare the behaviour of the chemical properties of the seven genotypes throughout the bleaching processing stages. In order to cut costs on the chemicals used for processing, it is important to identify species/genotypes that have similar chemical properties under the chemical pulping process in order to mix them together for optimised processing. It was established that when trying to classify different timber species/genotypes for the purpose of finding which ones can be mixed together, viscosity is not an important variable to consider. The other variables viz., lignin, γ-cellulose, α-cellulose, copper number, glucose and xylose should be used for classification as they were found to be important for that purpose. It is suggested that these properties can also be used in multivariate classification procedures.

Keywords: dissolving pulp, piecewise linear regression, lignin, viscosity, γ-cellulose, α-cellulose, copper numbers, glucose and xylose

INTRODUCTION

Dissolving wood pulp is a bleached pulp with more than 90% pure cellulose fibre.[1] Cellulose is the fibre component in wood that is obtained through pulping and bleaching processes. This pulp has a high level of brightness and uniform molecular weight distribution and it is used to make products such as viscose, rayon, acetate textile fibres, cellophane and many other chemical products.[2] Delignification through pulping and bleaching removes lignin, hemicellulose and other impurities and results in high purity α-cellulose pulp fibre, which can be used in the manufacture of the above mentioned products. Sharma and Shukla[3] state that the delignification process aids in the removal of the structural polymer lignin from wood pulp, resulting in higher purity cellulose. Bleaching follows after the delignification process to further remove residual lignin from the pulp. During the process of extracting lignin through delignification and bleaching, other chemical properties are also altered, namely pulp viscosity, glucose level, degraded celluloses, hemicelluloses, and other chemical properties of which some are discussed in this study.

The process of chemical pulping to produce dissolving pulp has a very low solid matter yield (30% to 35%).[4] Chemical pulping takes place in a high temperature and pressure environment with chemicals added to dissolve lignin and hemicelluloses, which are then washed away.[5] The partial dissolution of lignin, which glues the wood fibres together, results in the cellulose

fibres separating from each other. Lignin removal is important because its presence imparts a yellowish brown colour to the pulp. This is an undesirable property of the dissolving pulp since a high level of brightness is important in the production of cellulose based products, such as viscose and acetate fibres.

Since the chemicals used in pulp processing are costly, it is necessary to optimise the usage of such chemicals by identifying and combining wood species/genotypes with similar chemical properties under the chemical pulping process. This study tries to identify such species/genotypes by modeling the chemical properties of dissolving pulp at all the processing stages using piecewise linear regression models. Piecewise linear regression models are deemed appropriate for these data, since there are three known sub-processes, in series, in the chemical processing of dissolving pulp, namely, delignification, bleaching and finishing. Species/genotypes with similar rates of change (or slopes) in the chemical property under consideration during the three sub-processes will be mixed together during processing in the future if economic quantities cannot be achieved with just one species/genotype. Species/genotypes that differ significantly in the way they respond to the processing stages would better be processed separately. It is expected that each of the three sub-processes will have a different effect on the response variables, hence the resultant models are three segment, piecewise linear regression models. In this study, the response variables are seven important chemical properties of dissolving pulp and the independent variable is the stage of processing.

The main objective in the processing of dissolving pulp is to remove lignin, retaining α-cellulose, while at the same time maintaining other properties like viscosity within certain product specified limits. The modeling, for each species/genotype, of how lignin, viscosity, γ-cellulose, copper number, and xylose content decrease over the processing stages and of how α-cellulose and glucose increase will highlight the differences in species/genotype responses to chemical processing of dissolving pulp.

Pulping process

In order to understand the nature of the data, it is necessary to understand the chemical pulping process in detail. In a pulping process, wood is converted into fibres. This can be achieved mechanically, thermally, chemically or through a combination of these techniques.[6] Chemical delignification, an important process during pulping, includes all processes resulting in partial or total removal of lignin from wood by the action of suitable chemicals.[7] The lignin macromolecule is depolymerised through the cleavage of the ether linkages to become dissolved in the pulping liquor. The α-hydroxyl and α-ether groups are readily cleaved under simultaneous formation of benzilium ions.[8] The cleavage of the open α-aryl ether linkages represents the fragmentation of lignin during acid sulphite pulping. The benzilium ions are sulphonated by the attack of hydrated sulphur dioxide or bisulphite ions, resulting in the increased hydrophylic nature of the lignin molecule. The extent of delignification depends on the degree of sulphonation as well as the depolymerisation[8]. In summary, the aim of pulping is to break down the lignin bonds between the fibres using chemicals and heat, enabling easy removal by washing, whilst not destroying the cellulose and hemicellulose components. The removed lignin is a by-product that can be used in water treatment, dye manufacture, agricultural chemicals and in road construction.[9] Different wood species/genotypes have different levels of lignin content and those species/genotypes that contain more lignin would require more reagents to extract the lignin from the cellulose.[10] This means that different wood species/genotypes have different lignin extraction behaviour as they go through the chemical processing stages and it is of interest to investigate this behaviour. The wood species/genotypes with similar physical and chemical characteristics would naturally be put into the same class and may be mixed during processing if larger processing quantities are needed.

Bleaching process

The laboratory bleaching sequence was a scaled down version of the commercial process. The results obtained for the viscosity and lignin content (K-number) at the oxygen delignification (O) stage were used to adjust the bleaching conditions. The chemical pulping and bleaching process considered here consists of six stages, as indicated in Table 1 below. For the purposes of this study, the first stage will be called the O-stage, i.e., the stage where wood is acid bisulphite pulped into raw material for the bleaching stages.

Table 1
Stage classification for statistical analysis purposes

Stage	Process	Description
0	Wood to raw pulp	Delignification
1	O	Delignification
2	D_1	Brightness
3	E_0	Extraction of hemicelluloses and solubilisation of lignin degradation products
4	D_2	Brightness
5	P	Brightness and residual hemicellulose removal

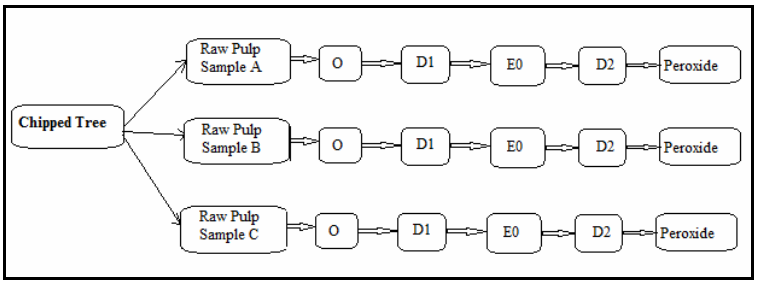

Figure 1: Processing stages and the pulp samples

The aim of adjusting the bleaching conditions was to produce dissolving pulp that would meet the quality control parameters for α-cellulose, viscosity, copper number, glucose (%) and xylose (%) prescribed commercially for the 96α dissolving pulp grade. While it would be reasonable to consider the correlated chemical properties using multivariate techniques, this study looked at a single chemical property individually with the aim of modelling and comparing the behaviour of wood species/genotypes on the same chemical property.

Data

The wood species/genotypes analysed in this study are *E.dunnii*, *E.grandis*, *E.nitens*, *E.smithii* and the Eucalyptus clones *E.gc*, *E.guA* and *E.guW*. The variable species/genotype is a fixed effect with seven levels, namely the seven genotypes that are known beforehand. The subjects are the pulp samples taken from pulped wood species/genotypes.

Trees were randomly selected from each of the seven species/genotypes, chipped and raw pulp was produced through acid bisulphite pulping. Independent samples were then taken from the raw pulp and processed. From each sample, measurements of various chemical properties were recorded at the six processing stages described in Table 1, and are shown in Figure 1. The samples were processed using three different bleaching conditions coded as A, B and C. Bleaching condition A is a set of original bleaching conditions, whereas bleaching conditions B and C are revised sets of bleaching conditions specially set to 'fine tune' non-conforming final pulps. If the chemical properties of the final product do not fall within prescribed limits, then the product will not be put on the market. This, in a way, produced a controlled response variable, especially at the final stage of production. The bleaching conditions were found not to be significantly different, hence they are not a prominent part of this study. The pulp samples are random effects, as trees were chosen at random from a large number of possible trees.

EXPERIMENTAL

The six stages in the chemical process fall under three sub-processes, namely, delignification, bleaching and finishing and these were carried out under laboratory conditions as described below.

Delignification: acid bisulphite pulping

The cooking liquor was prepared from acid bisulphite by bubbling SO_2 MgO slurry and circulated in the digester with wood chips. The temperature was ramped to 140 °C and maintained for a period of time. The pressure in the digester was kept at 8.5 bars during the cooking process. At the end of the cooking period, the reaction mixture was allowed to cool down to room

temperature. After pulping, an oxygen delignification step was included in a rotating digester. Pulp charge was 800 g (oven dry); consistency 11%; temperature 100 °C; time at 100 °C = 80 min (96α pulp).

Laboratory bleaching and finishing

The oxygen delignified pulp samples were bleached to target 96α grade using the following bleaching process: D_1 stage (ClO_2 treatment), E stage (NaOH treatment), D_2 stage (ClO_2 treatment), and a peroxide stage.

Wet Chemistry analysis – chemical properties

In the current study, the quality control parameters were measured during each step of processing, as described below.

Cellulose content

Low molecular weight carbohydrates (hemicellulose and degraded cellulose) can be extracted from pulp samples using sodium hydroxide. The solubility of a pulp in alkali thus provides information on the degradation of cellulose and loss or retention of hemicellulose during the pulping and bleaching processes. Thus, it gives an indication of the amount of degraded cellulose/short chain glucan and hemicellulose present in the pulp. S_{10} (%) and S_{18} (%) indicate the proportions of low molecular weight carbohydrates that are soluble in 10% and 18% sodium hydroxide, respectively. The former alkali solubility gives an indication of the total extractable material, that is, degraded cellulose/short chain glucan and hemicellulose content in a pulp sample, while the latter alkali solubility gives an indication of the total hemicellulose content of the pulp sample and is also known as the percentage gamma (γ%) cellulose content of pulp samples.

The quantity of degraded cellulose/short chain glucan, also known as percentage beta (β%) cellulose, was determined by the difference between S_{10} (%) and S_{18} (%) alkali solubilities, that is,

Degraded cellulose/short chain glucan = S_{10} (%) – S_{18} (%).

The α-cellulose content is given by the following equation:

$$\alpha\text{-cellulose} = 100 - \left(\frac{S_{10}\,\% + S_{18}\,\%}{2} \right) \quad (1)$$

S_{10} (%) and S_{18} (%) alkali solubilities were determined according to TAPPI method T235 OM-60.[11] The principle of the method is based on the extraction of carbohydrates with sodium hydroxide followed by oxidation with potassium dichromate. The procedure for S_{10} (%) alkali solubilities determination is as follows: 1.6 g of the pulp sample is placed in 100 mL of 10% sodium hydroxide (18% sodium hydroxide for S_{18} (%) determination). The pulp and solution are stirred for a period of 3 minutes and thereafter left at 20 ºC for a period of an hour. The pulp sample is filtered under vacuum using a sintered glass crucible (G3). Ten millilitres of 0.4N potassium dichromate and 30 mL of concentrated sulphuric acid are added to 10 mL of the filtrate. Thereafter 500 mL of deionised water is added and the solution is cooled. Approximately 20 mL of 10% potassium iodide is added to the cool solution and 5 minutes thereafter the solution is titrated with 0.1N sodium thiosulphate. A blank, without pulp sample, is also titrated to give a blank titre. The alkali solubility is given by the following equation:

$$\text{Alkali solubility} = \frac{(Blank\ titre - Sample\ titre) \times 0.685\%}{Weight\ of\ pulp\ sample} \quad (2)$$

Viscosity

The viscosity of a pulp sample provides an estimate of the degree of polymerisation (DP) of the cellulose chain. Viscosity determination of pulp is one of the most informative procedures, which are carried out to characterise a polymer, i.e., this test gives an indication of the degree of degradation (decrease in molecular weight of the polymer, i.e. cellulose) resulting from the pulping and bleaching processes. The viscosity measure involves dispersing 1 g of dissolving pulp sample (cellulose I) in a mixture of (15 mL) sodium hydroxide and (80 mL) cuprammonium solution (concentration of ammonia 166 g/L and concentration of copper sulphate 94 g/L) for a period of 1 hour. The dispersed cellulose I is allowed to equilibrate at 20 ºC for 1 hour and is then siphoned into an Ostwald viscometer. The time taken for it to flow between two measured points is recorded and the viscosity is calculated using the specific viscometer coefficient at the corresponding temperature according to a TAPPI method.[12]

Lignin content (k-number)

The permanganate number (k-number method) was used to assess the lignin content after each stage of processing. The principle of the method is based on the direct oxidation of lignin in pulp by standard potassium permanganate and back-titrating the excess permanganate with ferrous ammonium sulphate (Mohr's salt) standard solution.[13] The procedure for permanganate number determination is as follows: approximately 20 mL of 10% sulphuric acid and 180 mL of water are added to 1 g of pulp sample in a conical flask. The mixture is then stirred using a magnetic stirrer. Twenty five millilitres of 0.1N potassium permanganate is added and after 3 minutes 25 mL of 0.1N ferrous ammonium sulphate is added, followed by 10 drops of N-phenyl anthranilic acid indicator. The excess is back titrated with 0.1N potassium permanganate. A blank is also carried out with the exception of the pulp sample. The following calculation is used for permanganate number determination:

Permanganate number = (Sample titre – Blank titre) x 0.355

The data were modelled using piecewise linear regression models that represented the three sub-processes, namely delignification, bleaching and finishing.

Copper number (Cu number)

Pulping and bleaching are known to affect cellulose structure by the generation of oxidised positions and subsequent chain cleavage in pulp samples.[14] The copper number gives an indication of the reducing end groups in a pulp sample. The copper number is a measure of the reducing properties of the pulp and is defined as the number of grams of metallic copper reduced from the cupric (Cu++) to cuprous (Cu+) state in alkaline solution by 100 g cellulose under standard conditions. The copper number is inversely proportional to the viscosity of the pulp samples, that is, with a decrease in viscosity there is increased chain cleavage and hence more reducing end groups. The copper number also serves as an index of reducing impurities in pulp, such as oxycellulose, hydrocellulose, lignin and monosaccharides, which possess reducing power. The procedure for determining copper number is as follows: 2.5 g of disintegrated pulp is mixed with a carbonate/bicarbonate (2.6/1, w/w) and 0.4N copper sulphate solution (95/5, v/v) for exactly 3 hours. Thereafter the pulp is filtered and washed with 5% sodium carbonate followed by hot deionised water. Cuprous acid is dissolved by treating the cellulose on the filter with 45 mL of 0.2N ferric ammonium sulphate. This is left for 10 minutes then filtered off. The pulp is then washed with 250 mL of 2N sulphuric acid. The filtrate is then titrated with 0.04N KMnO4. The blank is subtracted from the titre value to yield the number of grams of reduced copper in the pulp sample.[15]

Glucose and xylose

The polysaccharides were measured after their conversion to monosaccharides (glucose and xylose) via a two-step hydrolysis procedure with 72% sulphuric acid. The first step in the hydrolysis process is the addition of 3 mL of sulphuric acid to 0.2 g of oven dried pulp in a test tube with stirring. The contents of the test tube are then quantitatively transferred into a Schott bottle with 84 mL of water. The second step in the hydrolysis process involves placing the Schott bottle in an autoclave set at a temperature of 121 ºC and pressure of 103 kPa for 1 hour. The contents are then allowed to cool and then filtered using a 0.45 µm filter. The filtrate is then transferred to a 200 mL volumetric flask and diluted to the mark. 50 µl of the sample is placed in a vial and diluted with 500 µl of water. Twenty microlitres of 1 mg/ml fucose (internal standard) is added using the autosampler. The monosaccharide constituents (glucose, mannose, xylose, arabinose etc.) were analysed using high performance liquid chromatography coupled with pulsed amperometric detection.[16] Reference standards of glucose and xylose were prepared. The standards were treated in the same way as the sample and analysed using high performance liquid chromatography coupled with pulsed amperometric detection. The concentrations of the monosaccharide constituents were obtained from the calibration curves of the standards.

RESULTS AND DISCUSSION

Graphical presentation of chemical properties over processing stages

Figure 2 shows the percentage content of α-cellulose as the processing stages unfold. It is apparently clear from Figure 2 that the change in α-cellulose percentages increase from the first to the last stage for all species/genotypes. Generally, stage D_1 has the effect of slightly reducing the α-cellulose level for all species/genotypes.

The relationship between α-cellulose content and processing stage is not easy to generalize for all species/genotypes, hence the statistical method discussed in this study seeks to describe the patterns in the data. Different species/genotypes are expected to have varying model parameters for the piecewise linear regression model. Species/genotypes with parameters that do not differ significantly can be classified as having similar response profiles to the processing stages of the chemical pulping process and such species/genotypes will require similar amounts of chemicals in each of the six processing stages.

Figure 3 shows how γ-cellulose levels for different species/genotypes evolve over the processing stages. The graph for γ-cellulose (Figure 3) is more of an inverted version of the graph of α-cellulose (Figure 2). This is due to the fact that α-cellulose is closely associated with γ-cellulose and degraded cellulose.

The viscosity profiles for the various species/genotypes as shown in Figure 4 indicate a general declining trend over the processing stages. The process is designed to reduce the viscosity of the product until ideal characteristics are achieved. A final product with pulp characteristics outside the product specific margins is discarded. For the 96α pulp, the pulp characteristics should be within the limits outlined in Table 2.

Lignin content for all species/genotypes under study decreases over the processing stages, as shown in Figure 5.

The decrease in lignin is not linear over the six stages, but can be piecewise linear if the stages

are grouped into sub-processes, namely delignification, bleaching and finishing.

Figure 6 shows that copper numbers decrease with each processing stage with the O_2 and E_0 stages, accounting, to a greater extent, for the decrease in copper numbers. It is also clear from this graph that the species/genotypes do not vary much in their copper numbers as the lines are very close together.

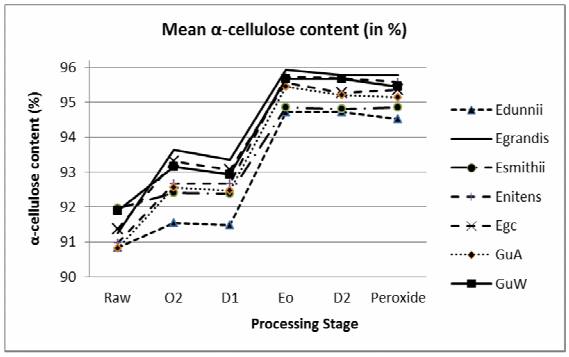

Figure 2: Mean α-cellulose content (in %) by stage for different genotypes

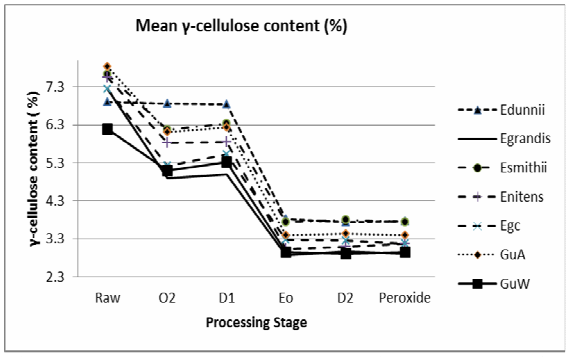

Figure 3: Mean γ-cellulose content (in %) by stage for different genotypes

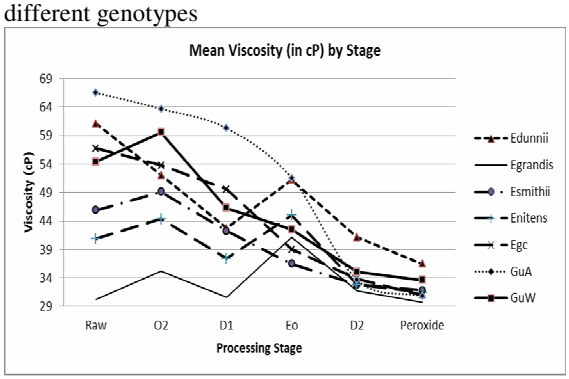

Figure 4: Mean viscosities (centipoise (cP)) by stage for different genotypes

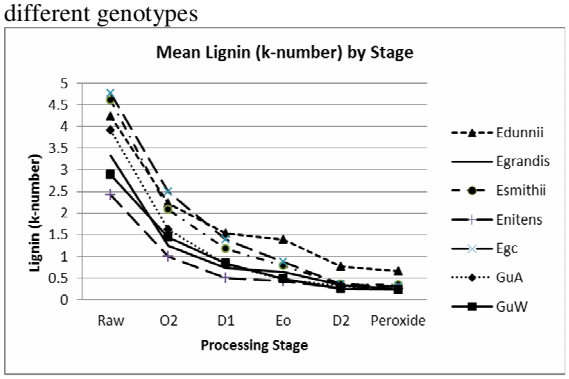

Figure 5: Mean lignin content (k-number) by stage for different genotypes

Table 2
Ideal pulp characteristics for 96α pulp

Final pulp characteristic	Ideal levels
Viscosity (cP)	28 - 35
Copper Number	0.43 - 0.54
S_{10}	6.4 - 7.0
S_{18}	2.7 - 3.3
S_{10}-S_{18}	3.7
α-cellulose	>95.3
K-number	0.25

Mean glucose levels, as indicated in Figure 7, increase as the processing stages unfold with *E.grandis* and *GuW* having higher glucose levels across the stages than the other five species/genotypes.

Figure 8 shows the changes in xylose over the processing stages. It was observed that mean xylose levels decrease as the processing stages unfold with *E.grandis* and *GuW* having closer and lower means by stage.

These two species/genotypes also had very similar α-cellulose, γ-cellulose, lignin and copper numbers levels. Based on this similarity, the two genotypes can be deemed mixable during processing.

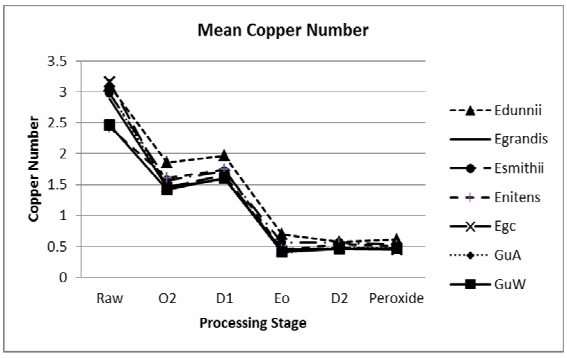

Figure 6: Mean copper numbers by stage for different genotypes

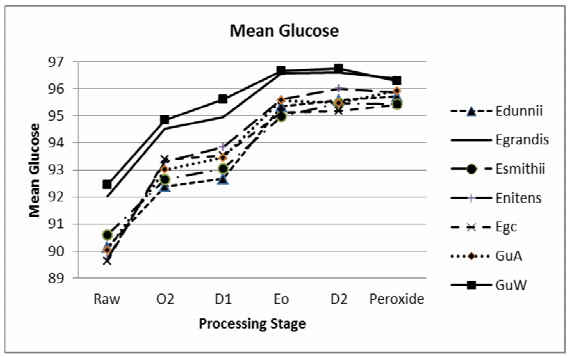

Figure 7: Mean glucose by stage for different genotypes

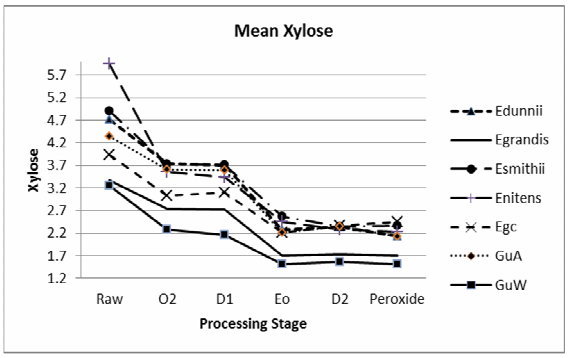

Figure 8: Mean xylose by stage for different genotypes

Piecewise linear regression

The data representations in Figures 2 to 8 show that there is a degree of non-linearity in the data. The piecewise linear regression approach is a useful method to model such data using two or more piecewise linear splines.[17] It is more appropriate to use this method for the pulp processing data, since there are three basic sub-processes in the whole chemical pulping process and there will be a spline for each of these sub-processes in the model. The transition points or knots are points where the parameters of the model change from one spline to the other giving the model a broken stick appearance.[18] The three sub-processes are:

(i) delignification,
(ii) bleaching and
(iii) finishing (peroxide stage)

The delignification sub-process is activated at the O stage followed by the bleaching sub-process spanning stages D_1, E_o and D_2, and the finishing sub-process, which is activated at the last stage (where peroxide is used). The variable t_1 is used to represent the delignification sub-process, t_2 for the bleaching and t_3 for the finishing sub-processes. The values of t_1, t_2 and t_3 for each sub-process are as defined in Table 3. The whole process can be described in terms of t_1, t_2 and t_3 by equation (3) below:

$$Y=\begin{cases}\beta_0+\beta_1 t_1+e & \text{delignification}\\ (\beta_0+\beta_1)+\beta_2 t_2+e & \text{bleaching}\\ (\beta_0+\beta_1+3\beta_2)+\beta_3 t_3+e & \text{final}\end{cases} \quad (3)$$

where the values of t_1, t_2 and t_3 are as shown in Table 3. The response variable Y is the pulp characteristic of interest, seven of which are modelled independently in this study, viz., viscosity, lignin, γ-cellulose, α-cellulose, copper

numbers, glucose and xylose. It is assumed that the error terms (*e*'s) within each pulp sample are correlated at different processing stages according to a suitable covariance structure, which will be determined by choosing one with the lowest AIC value.[19]

Chemical pulp processing is a continuous process, and measurements on the seven chemical properties under study were taken at six time points or stages (see Table 1). The knots of the piecewise regression model are set as the stages at which a different sub-process starts. This is so because each sub-process has a different effect on the chemical properties. There are two knots that separate the three sub-process and these are stages 2 and 5, as indicated in Table 1. Instead of fitting the piecewise linear regression model with one covariate (stage as indicated in Table 1) together with two indicator variables for the two knots, time or stage is recoded into three time variates. Each of the new time variates is set to zero when the sub-process it represents begins.

In equation (3) above, β_1, β_2 and β_3 are rates of change of the response variable due to delignification, bleaching and the finishing stage, respectively. Since delignification occurs at the raw pulp and the O stages, to be followed by bleaching thereafter, we let t_1=0 for the raw stage and t_1=1 from the O stage up to the finishing stage as the delignification sub-process ends at the O stage. The bleaching sub-process begins at stage D_1 (t_2=1) and continues in stages E_0 (t_2=2) and D_2 (t_2=3). In the finishing stage, there is no bleaching occurring so t_2 remains unchanged at t_2=3. A value of t_i=0 for i=1, 2 or 3, indicates that chemical sub-process t_i has not been activated and if t_i remains constant for subsequent stages then the chemical sub-process ascribed to t_i has stopped. For example t_1 remains at t_1=1 for stages O, D_1, E_o, D_2 and the finishing stage because it is activated only at stage O and does not occur in subsequent stages.

The intercept of the delignification sub-process is β_0 with slope parameter β_1 and the intercept of the bleaching sub-process is (β_0+β_1), since these are the predicted values of the response variable when delignification and bleaching start, respectively. In the same way the intercept of the finishing sub-process is $\beta_0 + \beta_1 + 3\beta_2$. Equation (3) together with the values of t_1, t_2 and t_3, as outlined in Table 3, can be generalised as:

$$E(Y) = \beta_0 + \beta_1 t_1 + \beta_2 t_2 + \beta_3 t_3 \qquad (4)$$

where β_0 (the delignification intercept) is the initial value of the response variable in the raw stage. The parameters β_1, β_2 and β_3 can be compared for different species/genotypes to see which species/genotypes have the same response rates to the three sub-processes in the chemical pulp processing.

Analysis of the chemical pulp properties data for the 96α pulp

The SAS procedure Proc Mixed[20] was used to analyse the data and the results are presented in the sections that follow. The procedure Proc Mixed in SAS has the versatility to be used for the computation of parameter estimates for various models that include repeated measures models, such as random coefficient models and piecewise regression models.[21]

Piecewise regression models were fitted to the data for viscosity, lignin, α-cellulose, γ-cellulose, copper number, glucose and xylose in order to compare the response patterns of the seven species/genotypes.

Table 3
Values of *t* for the three main chemical sub-processes in dissolving pulp

Stage	t_1 (Delignification)	t_2 (Bleaching)	t_3 (Finishing)
Raw	0	0	0
O	1	0	0
D_1	1	1	0
E_0	1	2	0
D_2	1	3	0
Finishing (P)	1	3	1

Table 4
AIC values for different covariance structures for the piecewise regression models

Covariance structure	Number of parameters	Wet chemistry property (AIC values)						
		Viscosity	Lignin	α-cellulose	γ-cellulose	Copper number	Glucose	Xylose
Unstructured	7	**863.7***	**67.3***	**372.4***	**284.9***	**65.2***	**276.5***	**173.5***
ANTE(1)	6	869.6	-	398.0	314.8	99.3	281.5	179.5
AR(1)	3	885.2	107.7	394.2	313.5	97.3	283.3	190.3
ARMA(1,1)	4	887.2	109.7	396.2	313.5	99.3	283.0	189.1
CS	3	886.0	107.7	394.2	313.5	93.8	283.3	190.3
Toeplitz	4	887.2	108.8	394.9	314.4	96.5	282.1	186.4
SP(Pow)	3	888.7	107.7	394.2	313.5	97.3	283.3	190.3
SP(Gau)	3	888.7	107.7	394.2	316.4	97.3	287.1	196.7

Table 5
Tests for the effects of delignification, bleaching and finishing on genotype

Effect		Viscosity	Lignin	γ-cellulose	α-cellulose	Copper number	Glucose	Xylose
Intercept by genotype	F	205.55	808.21	329.67	23411.40	279.41	72851.0	480.62
	p-value	0.000*	0.000*	0.000*	0.000*	0.000*	0.000*	0.000*
Delignification by genotype	F	0.22	70.14	6.78	2.52	28.04	38.01	14.01
	p-value	0.976	0.000*	0.001*	0.056	0.000*	0.000*	0.000*
Bleaching by genotype	F	1.53	15.32	29.05	15.29	31.350	41.01	26.57
	p-value	0.224	0.000*	0.000*	0.000*	0.000*	0.000*	0.000*
Finishing by genotype	F	0.80	0.190	0.21	0.21	0.160	0.57	0.13
	p-value	0.595	0.983	0.980	0.980	0.990	0.768	0.995

Degrees of freedom for numerator=7 for all cases
Degrees of freedom for denominator=65 for intercept and 17 for delignification, bleaching and finishing

The purpose of fitting these models is to analyse the effects of each of the three main sub-processes, namely delignification, bleaching and finishing (peroxide stage) on the dissolving pulp chemical properties mentioned above. The choice of the covariance structure for the six processing stages was done after considering a few commonly used covariance structures, the results of which are presented in Table 4. Table 5 is a summary of Analysis of Variance (ANOVA) tests carried out to evaluate if the various species/genotypes have significantly different initial values and response characteristics to delignification, bleaching and finishing.

The rate of change in a chemical property due to any stage of a sub-process is represented by the slope parameter estimate of the sub-process. In this study, β_0 is the intercept or raw stage value, β_1 is the rate of change of a chemical property due to delignification, β_2 is the rate of change due to bleaching and β_3 is the rate of change due to the finishing sub-process. The rates of change of the seven chemical properties discussed in this study are presented in Tables 6 to 12.

Viscosity data

For viscosity, the unstructured covariance structure had the lowest AIC value (Table 4: AIC=863.7). In fact, the unstructured covariance structure was fitted for all the chemical properties studied, as it had the lowest AIC values for all chemical properties.

The seven species/genotypes had significantly different raw pulp viscosities (Table 5: F=205.55, df1=7, df2=65, p-value<0.000), but had no significantly different delignification slopes for viscosity (Table 5: F=0.22, df1=7, df2=17, p-value=0.976). The seven species/genotypes did not have significantly different bleaching slopes for viscosity (Table 5: F=1.53, df1=7, df2=17, p-value<0.224) and they also did not have significantly different finishing stage viscosity slopes (Table 5: F=0.80, df1=7, df2=17, p-value=0.595). This means that viscosity cannot be

used as a classifying variable for the species/genotypes. The trajectory of viscosity values are shown in Figure 5.

The parameter estimates for the piecewise linear regression models for the 96α viscosity data for the seven species/genotypes are obtained from Table 5 as:

E.dunnii: $\hat{Y}$=61.083-10.681t_1-2.427t_2-6.647t_3
E.grandis: $\hat{Y}$=*30.183*+4.501t_1-0.019t_2-5.028t_3
E.smithii: $\hat{Y}$=45.883-2.473t_1-5.471t_2-0.100t_3
E.nitens: $\hat{Y}$=40.882+3.062t_1-2.696t_2-4.440t_3
E.gc: $\hat{Y}$=56.713-2.143t_1-7.016t_2-2.516t_3
E.guA: $\hat{Y}$=66.517+0.592t_1-9.878t_2-6.687t_3
E.guW: $\hat{Y}$=54.413+2.986t_1-7.718t_2-0.630t_3

From these model estimates, the viscosity levels can be estimated at each processing stage by substituting the values of t_1, t_2 and t_3 as defined in Table 2. The *t*-tests, as indicated by the *p*-values, which are all greater than 5% for delignification, bleaching and finishing, are not significant (Table 6: *p*-values>0.050). This indicates that no specific sub-process reduces viscosity significantly for all seven species/genotypes, which means that viscosity is reduced steadily across the three sub-processes without any particular sub-process reducing viscosity significantly.

Lignin data

For the lignin data, the unstructured covariance structure had the lowest AIC value (Table 4: AIC=67.3) hence it was fitted to the data. The rate of lignin decrease by species/genotype over the sub-processes can be used to highlight the differences in the response patterns of the seven species/genotypes to the three sub-processes. Ideally, most of the lignin must be removed in the delignification stage, but this does not remove all the lignin to product specified levels. The species/genotypes have significantly different raw stage lignin levels (Table 5: F=808.21, df1=7, df2=17, *p*-value=0.000). The results in Table 4 also show that the seven genotypes have significantly different slopes for lignin at delignification (Table 5: F=70.14. df1=7, df2=17, *p*-value=0.000) and bleaching (Table 5: F=15.32, df1=7, df2=17, *p*-value=0.000). There are no significant differences among species/genotypes in lignin content due to the finishing sub-process (Table 5: F=0.190. df1=7, df2=17, *p*-value=0.983). The results above mean that lignin levels in the raw, delignification and bleaching stages can be used to classify species/genotypes according to their slope parameters.

Table 6
Piecewise linear regression model parameter estimates and *t*-tests for viscosity (96α)

Genotype	β_0		β_1		β_2		β_3	
	Parameter (Std Dev)	*t*-test (df=65) p-value	Parameter (Std Dev)	*t*-test (df=17) p-value	Parameter (Std Dev)	*t*-test (df=17) p-value	Parameter (Std Dev)	*t*-test (df=17) p-value
E.dunnii	61.083 (3.832)	15.94 0.000*	-10.681 (10.516)	-1.02 0.320	-2.427 (5.114)	-0.47 0.641	-6.647 (4.996)	-1.33 0.201
E.grandis	30.183 (3.832)	7.88 0.000*	4.501 (10.516)	0.43 0.674	0.019 (5.114)	0.00 0.997	-5.028 (4.996)	-1.01 0.328
E.smithii	45.883 (2.710)	16.93 0.000*	2.473 (7.436)	0.33 0.744	-5.471 (3.616)	-1.51 0.149	-0.100 (3.533)	-0.03 0.978
E.nitens	40.882 (3.832)	10.67 0.000*	3.062 (10.516)	0.29 0.774	-2.696 (5.114)	-0.53 0.605	-4.440 (4.996)	-0.89 0.387
E.gc	56.713 (3.832)	14.80 0.000*	-2.143 (10.516)	-0.20 0.841	-7.016 (5.114)	-1.37 0.188	-2.516 (4.996)	-0.50 0.621
E.guA	66.517 (3.832)	17.36 0.000*	0.592 (10.516)	0.06 0.956	-9.878 (5.114)	-1.93 0.070	-6.687 (4.996)	-1.34 0.198
E.guW	54.413 (3.832)	14.20 0.000*	2.986 (10.516)	0.28 0.780	-7.718 (5.114)	-1.51 0.150	-0.630 (4.996)	-0.13 0.901

*significant parameters at the 5% significance level

Table 7
Piecewise linear regression model parameter estimates and *t*-tests for lignin (96α)

Genotype	β_0		β_1		β_2		β_3	
	Parameter (Std Dev)	*t*-test (df=65) p-value	Parameter (Std Dev)	*t*-test (df=17) p-value	Parameter (Std Dev)	*t*-test (df=17) p-value	Parameter (Std Dev)	*t*-test (df=17) p-value
E.dunnii	4.230 (0.148)	28.62 0.000*	-2.073 (0.286)	-7.26 0.000*	-0.449 (0.128)	-3.50 0.003*	-0.141 (0.193)	-0.73 0.473
E.grandis	3.319 (0.148)	22.46 0.000*	-2.157 (0.286)	-7.55 0.000*	-0.284 (0.128)	-2.21 0.041*	-0.062 (0.193)	-0.32 0.751
E.smithii	4.609 (0.105)	44.10 0.000*	-2.673 (0.202)	-13.24 0.000*	-0.556 (0.091)	-6.12 0.000*	0.074 (0.136)	0.54 0.593
E.nitens	2.414 (0.148)	16.33 0.000*	-1.520 (0.286)	-5.32 0.000*	-0.227 (0.128)	-1.77 0.095	0.036 (0.193)	0.19 0.854
E.gc	4.763 (0.148)	32.22 0.000*	-2.453 (0.286)	-8.59 0.000*	-0.690 (0.128)	-5.37 0.000*	0.062 (0.193)	0.32 0.753
E.guA	3.917 (0.148)	26.50 0.000*	-2.467 (0.286)	-8.64 0.000*	-0.428 (0.128)	-3.34 0.004*	0.066 (0.192)	0.34 0.737
E.guW	2.887 (0.148)	19.54 0.000*	-1.538 (0.286)	-5.39 0.000*	-0.396 (0.128)	-3.09 0.007*	0.077 (0.193)	0.40 0.695

*significant parameters at the 5% significance level

The piecewise linear regression parameters estimates of lignin are summarized in Table 7, which shows the estimates, their standard deviations and the corresponding *t*-tests.

The piecewise linear regression models built from Table 7 are given as follows:

E.dunnii: $\hat{Y}=4.230-2.073t_1-0.449t_2-0.141t_3$
E.grandis: $\hat{Y}=3.319-2.157t_1-0.284t_2-0.062t_3$
E.smithii: $\hat{Y}=4.609-2.673t_1-0.556t_2+0.074t_3$
E.nitens: $\hat{Y}=2.414-1.520t_1-0.227t_2+0.036t_3$
E.gc: $\hat{Y}=4.763-2.453t_1-0.6909t_2+0.062t_3$
E.guA: $\hat{Y}=3.917-2.467t_1-0.428t_2+0.066t_3$
E.guW: $\hat{Y}=2.887-1.538t_1-0.396t_2+0.077t_3$

Lignin levels can thus be estimated by substituting the appropriate values of t_1, t_2 and t_3 for any stage of the process for each species/genotype, where t_1, t_2 and t_3 are as defined in Table 2. The small but positive slopes for all genotypes in the finishing stage indicate that the finishing sub-processes slightly increase lignin levels. However, this lignin increase in the finishing stage is not significant as shown by the *p*-values of β_3, which are not significant for all species/genotypes (Table 7).

γ-Cellulose data

For the γ-cellulose data, the unstructured covariance structure had the lowest AIC value (Table 4: AIC=284.9), hence it was used in the analysis. As with viscosity and lignin, the finishing stage had no significant effect on γ-cellulose (Table 5: F=0.21, df1=7, df2=17, *p*-value=0.980). However, there were significant differences in the changes in γ-cellulose levels among the seven species/genotypes due to delignification (Table 5: F=6.78, df1=7, df2=17, *p*-value=0.001) and bleaching (Table 5: F=29.05, df1=7, df2=17, *p*-value=0.000) sub-processes. This means that γ-cellulose is an important classifying variable for the seven species/genotypes.

The piecewise linear regression model parameters estimates for γ-cellulose are summarized in Table 8. The results in Table 8 show that *E.dunnii* does not have a significant reduction of γ-cellulose due to delignification (Table 8: $\beta_1=0.283$, $t=0.51$, df=17, *p*-value=0.619). It is the only genotype that has this behaviour out of the seven genotypes studied. The other species/genotypes had significant reductions in γ-cellulose levels during both delignification and bleaching.

The corresponding piecewise linear regression models derived from Table 8 for the seven species/genotypes are as follows:

E.dunnii: $\hat{Y}=6.896+0.283t_1-1.240t_2+0.296t_3$
E.grandis: $\hat{Y}=7.244-2.117t_1-0.795t_2+0.179t_3$
E.smithii: $\hat{Y}=7.635-1.170t_1-0.970t_2+0.195t_3$
E.nitens: $\hat{Y}=7.553-1.466t_1-1.103t_2+0.382t_3$
E.gc: $\hat{Y}=7.256-1.707t_1-0.816t_2+0.072t_3$
E.guA: $\hat{Y}=7.826-1.401t_1-1.086t_2+0.235t_3$
E.guW: $\hat{Y}=6.198-0.794t_1-0.894t_2+0.222t_3$

The levels of γ-cellulose can be estimated in a similar way as described above for viscosity and lignin.

α-Cellulose data

The covariance structure with the smallest AIC value for the α-cellulose data is the unstructured one (Table 4: AIC=372.4) and this was fitted to the data. The seven species/genotypes start with significantly different α-cellulose levels in the raw stage (Table 5: F=23411.40, df1=7, df2=65, p-value=0.000) and the sub-process of delignification does not produce significantly different rates of change in α-cellulose across the seven species/genotypes (Table 5: F=2.52, df1=7, df2=17, p-value=0.056). The sub-process of bleaching affects the rates of change of α-cellulose levels of the different species/genotypes in a significantly different manner (Table 5: F=15.29, df1=7, df2=17, p-value=0.000). As with the other chemical properties discussed above, the effects of the finishing sub-process do not differ significantly across the seven species/genotypes (Table 5: F=0.21, df1=7, df2=17, p-value=0.980). Since the rates of change in α-cellulose levels differ among the seven species/genotypes during the bleaching sub-process, α-cellulose can be used as a classifying variable.

The piecewise linear regression model parameter estimates are presented in Table 9.

The piecewise linear regression models, which can be used to predict the α-cellulose levels of each genotype at each processing stage, are derived from Table 9 and presented below:

E.dunnii: $\hat{Y}=90.846+0.361t_1+1.271t_2-0.508t_3$
E.grandis: $\hat{Y}=91.256+2.074t_1+0.899t_2-0.238t_3$
E.smithii: $\hat{Y}=91.965+0.202t_1+0.964t_2-0.202t_3$
E.nitens: $\hat{Y}=90.976+1.393t_1+1.216t_2-0.432t_3$
E.gc: $\hat{Y}=91.375+1.663t_1+0.843t_2-0.200t_3$
E.guA: $\hat{Y}=90.808+1.474t_1+1.094t_2-0.416t_3$
E.guW: $\hat{Y}=91.890+0.923t_1+1.031t_2-0.451t_3$

Copper number

The unstructured covariance structure had the best fit to the copper numbers data (Table 4: AIC=65.2). The delignification and bleaching rates of change in copper numbers were found to be significantly, different among the seven species/genotypes (Table 5: F=28.04, df1=7, df2=17, p-value=0.000; and Table 5: F=31.35, df1=7, df2=17, p-value=0.000, respectively). The finishing sub-process as with the other chemical properties did not produce significantly different rates of change in copper numbers (Table 5: F=0.16, df1=7, df2=17, p-value=0.980). In addition, the seven species/genotypes start off with significantly different copper numbers (Table 5: F=279.41, df1=7, df2=65, p-value=0.000). This means that copper number is an important chemical property that can be used in classifying the seven species/genotypes.

The copper numbers' piecewise linear regression model parameter estimates for the seven species/genotypes are presented in Table 10.

Table 8
Piecewise linear regression model parameter estimates and *t*-tests for γ-cellulose (96α)

Genotype	β_0		β_1		β_2		β_3	
	Parameter (Std Dev)	*t*-test (df=65) p-value	Parameter (Std Dev)	*t*-test (df=17) p-value	Parameter (Std Dev)	*t*-test (df=17) p-value	Parameter (Std Dev)	*t*-test (df=17) p-value
E.dunnii	6.896 (0.430)	16.05 0.000*	0.283 (0.560)	0.51 0.619	-1.240 (0.197)	-6.28 0.000*	0.296 (0.560)	0.53 0.604
E.grandis	7.244 (0.430)	16.86 0.000*	-2.117 (0.560)	-3.78 0.002*	-0.795 (0.197)	-4.03 0.001*	0.179 (0.560)	0.32 0.754
E.smithii	7.635 (0.304)	25.13 0.000*	-1.170 (0.396)	-2.95 0.009*	-0.970 (0.140)	-6.96 0.000*	0.195 (0.396)	0.49 0.628
E.nitens	7.553 (0.430)	17.58 0.000*	-1.446 (0.560)	-2.58 0.019*	-1.103 (0.197)	-5.59 0.000*	0.382 (0.560)	0.68 0.504
E.gc	7.256 (0.433)	16.89 0.000*	-1.707 (0.560)	-3.05 0.007*	-0.816 (0.197)	-4.14 0.001*	0.072 (0.560)	0.13 0.899
E.guA	7.826 (0.430)	18.22 0.000*	-1.401 (0.560)	-2.50 0.023*	-1.086 (0.197)	-5.51 0.000*	0.235 (0.560)	0.42 0.680
EguW	6.198 (0.430)	14.43 0.000*	-0.794 (0.560)	-1.42 0.175	-0.894 (0.197)	-4.53 0.000*	0.222 (0.560)	0.40 0.697

*significant parameters at the 5% significance level

Table 9
Piecewise linear regression model parameter estimates and *t*-tests for α-cellulose (96α)

Genotype	β_0		β_1		β_2		β_3	
	Parameter (Std Dev)	*t*-test (df=65) p-value	Parameter (Std Dev)	*t*-test (df=17) p-value	Parameter (Std Dev)	*t*-test (df=17) p-value	Parameter (Std Dev)	*t*-test (df=17) p-value
E.dunnii	90.846 (0.639)	142.28 0.000*	0.361 (0.833)	0.43 0.670	1.271 (0.286)	4.45 0.000*	-0.508 (0.833)	-0.61 0.550
E.grandis	91.256 (0.639)	142.92 0.000*	2.074 (0.833)	2.49 0.023*	0.899 (0.286)	3.15 0.006*	-0.238 (0.833)	-0.29 0.778
E.smithii	91.965 (0.452)	203.69 0.000*	0.202 (0.589)	0.34 0.735	0.964 (0.202)	4.77 0.000*	-0.202 (0.589)	-0.34 0.735
E.nitens	90.976 (0.639)	142.48 0.000*	1.393 (0.833)	1.67 0.113	1.216 (0.286)	4.26 0.001*	-0.432 (0.833)	-0.52 0.611
E.gc	91.375 (0.639)	143.11 0.000*	1.663 (0.833)	2.00 0.062	0.843 (0.286)	2.95 0.009*	-0.200 (0.833)	-0.24 0.813
E.guA	90.808 (0.639)	142.22 0.000*	1.474 (0.833)	1.77 0.095	1.094 (0.286)	3.83 0.001*	-0.416 (0.833)	-0.50 0.624
E.guW	91.890 (0.639)	143.91 0.000*	0.923 (0.833)	1.11 0.283	1.031 (0.286)	3.61 0.002*	-0.451 (0.833)	-0.54 0.595

*significant parameters at the 5% significance level

Table 10
Piecewise linear regression model parameter estimates and *t*-tests for copper number (96α)

Genotype	β_0		β_1		β_2		β_3	
	Parameter (Std Dev)	*t*-test (df=65) p-value	Parameter (Std Dev)	*t*-test (df=17) p-value	Parameter (Std Dev)	*t*-test (df=17) p-value	Parameter (Std Dev)	*t*-test (df=17) p-value
E.dunnii	3.107 (0.185)	16.83 0.000*	-1.064 (0.241)	-4.42 0.000*	-0.514 (0.083)	-6.22 0.000*	0.104 (0.241)	0.43 0.669
E.grandis	2.886 (0.185)	15.63 0.000*	-1.277 (0.241)	-5.30 0.000*	-0.414 (0.083)	-5.01 0.001*	0.083 (0.241)	0.34 0.736
E.smithii	2.974 (0.131)	22.78 0.000*	-1.245 (0.170)	-7.32 0.000*	-0.417 (0.058)	-7.14 0.000*	0.063 (0.170)	0.37 0.714
E.nitens	2.423 (0.185)	13.12 0.000*	-0.657 (0.241)	-2.73 0.014*	-0.452 (0.083)	-5.47 0.000*	0.105 (0.241)	0.44 0.669
E.gc	3.168 (0.185)	17.16 0.000*	-1.534 (0.241)	-6.37 0.000*	-0.418 (0.083)	-5.07 0.001*	0.075 (0.241)	0.31 0.759
E.guA	2.999 (0.185)	16.24 0.000*	-1.397 (0.241)	-5.80 0.000*	-0.410 (0.083)	-4.97 0.000*	0.102 (0.241)	0.42 0.678
E.guW	2.472 (0.430)	13.39 0.000*	-0.881 (0.241)	-3.66 0.002*	-0.408 (0.083)	-4.94 0.000*	0.112 (0.241)	0.47 0.647

*significant parameters at the 5% significance level

All rates of change of copper numbers due to delignification and bleaching are significant for all species/genotypes (Table 10: all *p*-values for t-test<0.05). From Table 10, the piecewise linear regression models for copper numbers can be constructed as:

E.dunnii: $\hat{Y}=3.107-1.064t_1-0.514t_2+0.104t_3$
E.grandis: $\hat{Y}=2.886-1.277t_1-0.414t_2+0.083t_3$
E.smithii: $\hat{Y}=2.974-1.245t_1-0.417t_2+0.063t_3$
E.nitens: $\hat{Y}=2.423-0.657t_1-0.452t_2+0.105t_3$
E.gc: $\hat{Y}=3.168-1.534t1-0.418t_2+0.075t_3$
E.guA: $\hat{Y}=2.999-1.397t_1-0.410t_2+0.102t_3$
E.guW: $\hat{Y}=2.472-0.881t_1-0.408t_2+0.112t_3$

The piecewise regression models can be used to estimate copper numbers for the seven species/genotypes at each stage by substituting the values of t_1, t_2 and t_3 that were described in Table 2. The correlation between the percentage of γ-cellulose at the beginning (raw pulp stage) and at the end of processing was found to be r=0.766. This means that there is a strong

relationship between the initial and final percentage levels of γ-cellulose.

Glucose data

Having the lowest AIC value, the unstructured covariance structure was fitted to the glucose data (Table 4: AIC=276.5). The effects of delignification and bleaching were significantly different on the rates of change of glucose for the seven species/genotypes (Table 5: F=38.01, df1=7, df2=17, p-value=0.000; and Table 5: F=41.01, df1=7, df2=17, p-value=0.000, respectively). In general, glucose had significant rates of change during delignification and bleaching for all genotypes (Table 11: β_1's>0 and β_2's>0 with *p*-values for *t*-tests<0.05 for all genotypes). The changes in glucose due to the finishing stage were not significant for all species/genotypes.

The piecewise linear regression model parameter estimates derived from Table 11 are shown below and these models can be used to estimate glucose levels at each stage of chemical processing using the values of t_1, t_2 and t_3 defined in Table 2 above.

E.dunnii: $\hat{Y}=90.146+2.010t_1+1.226t_2-0.116t_3$
E.grandis: $\hat{Y}=92.009+2.467t_1+0.792t_2-0.474t_3$
E.smithii: $\hat{Y}=90.595+1.884t_1+1.035t_2-0.153t_3$
E.nitens: $\hat{Y}=89.712+3.493t_1+0.987t_2-0.298t_3$
E.gc: $\hat{Y}=89.619+3.640t_1+0.701t_2-0.054t_3$
E.guA: $\hat{Y}=90.042+2.908t_1+0.949t_2-0.124t_3$
E.guW: $\hat{Y}=92.454+2.493t_1+0.675t_2-0.672t_3$

Xylose data

With the lowest AIC, the unstructured covariance structure was of best fit to the xylose data (Table 4: AIC=173.5). The rates of change in xylose due to delignification and bleaching differed significantly across the seven species/genotypes (Table 5: F=14.01, df1=7, df2=17, p-value=0.000; and Table 5: F=26.57, df1=7, df2=17, p-value=0.000). This renders xylose an important classification variable for the seven species/genotypes. The finishing sub-process, as with the other chemical properties, did not have a significant effect on the final xylose readings.

There were significant rates of decrease in xylose during the delignification and bleaching processes for most species/genotypes (Table 12: β_1's<0, β_2's<0 with p-values<0.05 for t-tests), except for EguA, which did not have a significant decrease in xylose during delignification (Table 12: β_1=-0.626, t=-1.95, df=17, p-value=0.068). The finishing stage did not have a significant effect on the xylose values just like with the other chemical properties.

Table 11
Piecewise linear regression model parameter estimates and *t*-tests for Glucose (96α)

Genotype	β_0		β_1		β_2		β_3	
	Parameter (Std Dev)	*t*-test (df=65) p-value	Parameter (Std Dev)	*t*-test (df=17) p-value	Parameter (Std Dev)	*t*-test (df=17) p-value	Parameter (Std Dev)	*t*-test (df=17) p-value
E.dunnii	90.146 (0.352)	256.46 0.000*	2.010 (0.461)	4.36 0.000*	1.226 (0.157)	7.80 0.000*	-0.116 (0.458)	-0.25 0.803
E.grandis	92.009 (0.352)	261.76 0.000*	2.467 (0.461)	5.35 0.000*	0.792 (0.157)	5.04 0.001*	-0.474 (0.458)	-1.03 0.315
E.smithii	90.595 (0.272)	332.74 0.000*	1.884 (0.345)	5.47 0.000*	1.035 (0.111)	9.31 0.000*	-0.152 (0.324)	-0.47 0.645
E.nitens	89.712 (0.352)	255.23 0.000*	3.493 (0.461)	7.57 0.014*	0.987 (0.157)	6.28 0.000*	-0.298 (0.458)	-0.65 0.524
E.gc	89.619 (0.352)	254.96 0.000*	3.640 (0.461)	7.89 0.000*	0.701 (0.157)	4.46 0.001*	0.054 (0.458)	0.12 0.908
E.guA	90.042 (0.352)	256.17 0.000*	2.908 (0.461)	6.30 0.000*	0.949 (0.157)	6.04 0.000*	0.124 (0.458)	0.27 0.791
EguW	92.454 (0.352)	263.03 0.000*	2.493 (0.461)	5.41 0.000*	0.675 (0.157)	4.29 0.001*	-0.672 (0.458)	-1.47 0.161

*significant parameters at the 5% significance level

Table 12
Piecewise linear regression model parameter estimates and *t*-tests for xylose (96α)

Genotype	β_0		β_1		β_2		β_3	
	Parameter (Std Dev)	*t*-test (df=65) p-value	Parameter (Std Dev)	*t*-test (df=17) p-value	Parameter (Std Dev)	*t*-test (df=17) p-value	Parameter (Std Dev)	*t*-test (df=17) p-value
E.dunnii	4.714 (0.214)	22.04 0.000*	-0.857 (0.322)	-2.66 0.016*	-0.565 (0.096)	-5.91 0.000*	-0.037 (0.279)	-0.13 0.895
E.grandis	3.367 (0.214)	15.75 0.000*	-0.545 (0.322)	-1.69 0.109*	-0.402 (0.096)	-4.21 0.001*	0.084 (0.279)	0.30 0.766
E.smithii	4.912 (0.166)	29.66 0.000*	-1.032 (0.237)	-4.35 0.000*	-0.528 (0.068)	-7.80 0.000*	0.069 (0.197)	0.35 0.729
E.nitens	5.939 (0.214)	27.77 0.000*	-2.279 (0.322)	-7.09 0.000*	-0.484 (0.096)	-5.06 0.000*	0.017 (0.279)	0.06 0.952
E.gc	3.927 (0.214)	18.37 0.000*	-0.817 (0.322)	-2.54 0.021*	-0.291 (0.096)	-3.04 0.007*	0.218 (0.279)	0.78 0.445
E.guA	4.340 (0.214)	20.29 0.000*	-0.626 (0.322)	-1.95 0.068	-0.516 (0.096)	-5.39 0.000*	-0.046 (0.279)	-0.16 0.871
E.guW	3.244 (0.214)	15.17 0.000*	-0.951 (0.322)	-2.96 0.009*	-0.280 (0.096)	-2.93 0.009*	0.055 (0.279)	0.20 0.846

*significant parameters at the 5% significance level

The parameter estimates for the piecewise linear regression models for xylose derived from Table 12 are presented below:

E.dunnii: $\hat{Y}=4.714-0.857t_1-0.565t_2-0.037t_3$
E.grandis: $\hat{Y}=3.367-0.545t_1-0.402t_2+0.084t_3$
E.smithii: $\hat{Y}=4.912-1.032t_1-0.528t_2+0.069t_3$
E.nitens: $\hat{Y}=5.939-2.279t_1-0.484t_2+0.017t_3$
E.gc: $\hat{Y}=3.927-0.817t_1-0.291t_2+0.218t_3$
E.guA: $\hat{Y}=4.340-0.626t_1-0.516t_2-0.046t_3$
E.guW: $\hat{Y}=3.244-0.951t_1-0.280t_2+0.055t_3$

Although some parameter estimates for the finishing sub-process are negative, most of them are generally positive. It was observed that for all chemical properties, the finishing stage had the general effect of reversing the trend in bleaching, but such reversal is not significant. Glucose is also an important classifying variable for the seven species/genotypes.

CONCLUSION

The piecewise linear regression models had the capability of outlining the effect of each sub-process of chemical pulping on the seven reactivity variables studied. The ability of the model to state, by the model parameters, the effect of each sub-process on the chemical properties is a value addition to the study of chemical pulping processes. This can be extended to other types of pulp processing with known sub-processes i.e. kraft pulping, neutral sulphite pulping.

Based on the results from the piecewise linear regression models, it was established that the six chemical properties lignin, γ-cellulose, α-cellulose, copper numbers, glucose and xylose were important classification variables for species/genotypes, while viscosity, based on the results obtained, was not. This means that when one wants to compare or group wood species/genotypes using their chemical properties for the purpose of deciding which ones are mixable during processing, they do not need to consider viscosity.

Using the coding of the stages as shown in Table 2, the levels of the chemical properties studied can be estimated at each stage using the piecewise linear regression models developed in this study. This is essential to dissolving pulp manufacturers as the model can be used as a predictive tool to assess species/genotype properties without having to carry out the actual bleaching, especially if such models have already been developed for the concerned timber species/genotype. This will reduce the use of costly chemicals, as well as limit the generation of harmful waste. Another advantage of the developed models is that the parameter estimates for the various species/genotypes can be grouped according to their sizes in order to classify the

species/genotypes into groups of mixable species or genotypes during chemical processing. This reduces the trial and error involved in selecting specific clones and species for specific grades of dissolving pulp. The methodology can thus be used for other pulps earmarked for other products in the timber industry.

For further studies, it would of interest to develop a classifying method based on multivariate statistical techniques, such as cluster analysis, classification algorithms and stepwise linear regression.

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