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RANDOM COEFFICIENT MODEL FOR CHANGES IN VISCOSITY IN DISSOLVING PULP

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ABSTRACT

In this study the properties of viscosity for seven hardwood genotypes are analysed using random coefficient models. The main purpose was to profile the viscosity behavior of the seven genotypes under study in order to make comparisons amongst them. Such comparisons are useful when it comes to mixing different genotypes in the chemical pulping process or when determining if genotypes with certain natural properties require particular chemical concentrations for processing. It is a plausible generalization that genotypes with similar behavior under chemical pulping are deemed to have similar requirements as far as the processing chemicals and costs are concerned. The study evaluated the effects that the processing stages have on the viscosity of dissolving pulp from seven genotypes of timber under different bleaching conditions. The processing stages are considered as time points for repeated measurements of the chemical reactivity variable considered that is viscosity. The viscosity results indicate that those genotypes that start with high viscosity levels have higher viscosity reduction rates than genotypes with low raw stage viscosities. There is a high negative correlation (r=-0.858) between initial viscosity and the rate of viscosity reduction over the processing stages. This implies that chemicals are used less efficiently in those genotypes that have low viscosities at the raw stage of the chemical pulping process.

KEYWORDS: Pulp viscosity, random coefficients model, genotype.

INTRODUCTION

Dissolving wood pulp is bleached pulp with more than 90 % pure cellulose fibre with a high level of brightness and uniform molecular weight distribution (Patrick 2011). It is used to make products such as rayon and acetate textile fibres, cellophane and other chemical products. The quality of dissolving wood pulp depends on the quality of the raw wood material and the pulp processing itself Jahan et al. (2008) and different variables are used to measure this raw wood

quality, viscosity being one of them.

Chemical pulping and bleaching removes lignin, hemicellulose and other impurities through dissolution followed by washing. This process results in high purity α-cellulose pulp fibre which can be used in the manufacture of the products mentioned above. Cellulose can also be made into cellulose powder which has many industrial uses. During the process of extracting lignin through bleaching, other chemical properties are also altered, namely pulp viscosity, glucose level, degraded celluloses or hemicelluloses, sugars and other chemical properties. The process of chemical pulping has a very low solid matter yield (40-50 %) since lignin constitutes a large part of the raw wood pulp and in general most of the lignin and hemicelluloses are removed (Biermann 1993).

The chemicals used in pulp bleaching are costly hence effort must not be spared in trying to optimize the process. Viscosity is an important chemical properties of dissolving pulp and in this study the levels of viscosity at all the processing stages is investigated and comparisons made on the seven genotypes under study.

The pulping process and the data

The pulping process

Chemical pulping removes lignin and other impurities from pulped wood to leave α-cellulose as the main product. There are three types of celluloses: α-cellulose, the target product; β-cellulose, the portion that dissolves and then precipitates upon acidification; and γ-cellulose, the portion of cellulose that dissolves but does not precipitate. In paper production α-cellulose is the main product and the other celluloses, lignin and sugars are by-products of the production process and must be removed prior to further derivatisation. The measurements taken for α–cellulose, β–cellulose and γ–cellulose are percentages of the total volume of pulp while lignin levels are measured by k-numbers. The k-number is the volume (in milliliters) of 0.1 N potassium permanganate solution consumed by one gram of moisture-free pulp with some corrections depending on the conditions of the pulp (Tasman and Berzins 1957). Lignin is a by-product that can be used in water treatment, dye manufacture, agricultural chemicals and in road construction (Sundstrom et al. 1983).

Tree species have different levels of lignin content and those species that contains more lignin would require more reagents to extract the lignin from the cellulose (Casey 1983). This means that different tree species have different lignin extraction behaviour as they go through the chemical processing stages. Viscosity is not a substance but a condition of dissolving pulp that must be within certain product specific thresholds at the end of the process.

The tree species with similar physical and chemical characteristics would naturally be put into the same class and may be mixed if economic processing quantities are needed. The chemical pulping process is designed to have the effect of decreasing viscosity, which starts off very high, to the desired levels.

The chemical process considered here consists of six stages, three of which are bleaching stages. For the purposes of this study the first stage will be called the 0-stage which is the stage were wood is acid bi-sulphite pulped into the raw material for the bleaching stages. The other processing stages are as outlined in Tab. 1.

Tab. 1: Stage classification for statistical analysis purposes.

Stage	Process	
0.	Raw Pulp	Wood is chemically converted into pulp
1.	O_2	Delignification stage, mainly targets lignin removal
2.	D_1	Bleaching and removal of γ-cellulose, lignin also removed
3.	E_0	Bleaching and removal of γ-cellulose, lignin also removed
4.	D_2	Bleaching and removal of γ-cellulose, lignin also removed
5.	*P/H*	Finishing, that is chemical peeling or cutting of α-cellulose. In this stage either peroxide (P) or hydroxide (H) is used.

At each stage the different chemical properties are measured. This study looked at changes in viscosity for the seven genotypes under study over the processing stages

The data

The timber genotypes to be analysed in this study are *E.dunnii, E.grandis, E.nitens, E.smithii*, GCG, GUA and GUW thus the variable genotype is a fixed effect with seven levels. The study focuses of comparing these seven genotypes hence they are considered as the only genotypes of interest hence they are fixed effects. The subjects are the pulp samples taken from pulped trees from the various genotypes.

Trees are selected at random from each genotype and broken into wood chips that are then pulped. Samples are then taken from these pulps and processed hence the samples are random effects. From each sample, measurements of various chemical properties are recorded at the six processing stages as shown in Fig. 1 below. The samples were processed using three different bleaching conditions namely *A, B* and *C*. Bleaching condition *A* is a set of the original bleaching conditions, whereas bleaching conditions *B* and *C* are revised sets of bleaching conditions especially set to fine tune non-conforming final results. 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 pulp samples are random effects as trees are chosen at random from a large number of trees.

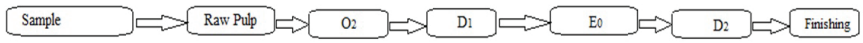

Fig. 1: Processing stages.

MATERIAL AND METHODS

The three sub-processes, delignification, bleaching and finishing were carried out under laboratory conditions and the data were collected from these laboratory experiments which are described in section 3.1 below.

Laboratory conditions

Delignification: Acid bisulphite pulping

The cooking liquor was prepared by bubbling SO_2MgO slurry and circulated in the digester with wood chips. Temperature was ramped to 140°C and was 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 O_2 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 minutes for the 96 αpulp (96 % α-cellulose).

Bleaching and finishing

The O_2 delignified pulp samples were bleached to target the 96α grade using the bleaching process: D1 stage (ClO_2 treatment), E stage (NaOH treatment), D_2 stage (ClO_2 treatment), and a peroxide stage.

Wet chemistry analysis – 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 that is carried out to characterise a polymer, that is, this test gives an indication of the degree of degradation (decrease in molecular weight of the polymer, that is 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°C 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 viscosity constant at the corresponding temperature. Viscosity in this study was determined according to (TAPPI method, T230 om-94) (Tappi T230, 1994).

The data was modelled using the random coefficient. Fig. 2 is a graph of the mean viscosities for each genotype at each stage. Viscosity exhibits a linear trend over the processing stages thus a linear random coefficient model will be fitted to the data. Different genotypes are expected to have varying model parameters and 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 genotypes will require similar processing conditions.

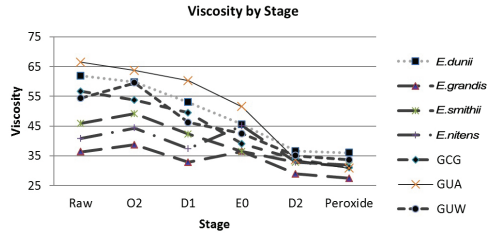

Fig. 2: Mean viscosities by stage for different Genotypes.

The linear mixed model for repeated measures and the random coefficient model

The linear mixed model for repeated measures (longitudinal data) for the pulp data has genotype, processing stage and bleaching condition as fixed effects and the pulp samples as random effects on which repeated measurements are taken. The model can be expressed as

$$= f_{ij} + \tau_t + I_{ijt} + e_{ijlt} \quad (1)$$

where: f_{ij} - the part of the model that is due to the fixed effects and this can be expressed as

$f_{ij} = \mu + \alpha_i + \beta_j + C_{ij}$

where: μ - the overall mean,
α_i - the genotype effect,
β_j - the bleaching condition effect,
C_{ij} - the interaction effect between genotype and bleaching condition.

The effect of stage (or time) t is denoted by τ_t. The term I_{ijt} of model (1) is the interaction between processing stage and the two treatment factors such that

$I_{ijt} = D_{it} + E_{jt} + F_{ijt}$,

where: D_{it} - the two-way interaction between processing stage and genotype,
E_{it} - the two-way interaction between processing stage and bleaching condition,
F_{ijt} - the three-way interaction between processing stage, genotype and bleaching condition.

The term e_{ijtl} is the random effect part of the model which is the random error associated with subject l under the $(ij)^{th}$ treatment at stage t. Model (1) can also be written as

$$Y_{ijk} = \mu + \alpha_i + \beta_j + C_{ij} + \tau_t + I_{ijt} + e_{ijlt} \quad (2)$$

The subjects (pulp samples) are assumed to be independent while the observations of each pulp sample over the processing stages are correlated according to some suitable covariance structure. If the complete set of observations is put into a single vector $\boldsymbol{Y}$, noting that there are L subjects in total and T processing stages, the covariance matrix of Y can be written as

$Var(\boldsymbol{Y}) = \boldsymbol{I}_L \otimes \boldsymbol{\Sigma}_T$

where: the covariance matrix $\boldsymbol{\Sigma}_T$ shows how the values of a single subject at different stages are related to each other. The matrix I_L is an L×L identity matrix while $\boldsymbol{\Sigma}_T$ has one of the many possible covariance structures. The best fitting covariance structure is determined by considering known covariance structures and choosing one with the best fit according to the Akaike information criteria (*AIC*) Burnhan and Anderson (2004). A correct choice of a covariance structure for $\boldsymbol{\Sigma}_T$ will greatly affect the quality of the model parameters obtained (Littell et al. 2006). The covariance matrix of the observations on each subject over all the time periods can also be decomposed into

$$\boldsymbol{\Sigma_T} = \sigma_T^2 \boldsymbol{J} + \boldsymbol{R}$$

where: $\sigma_T^2 \boldsymbol{J}$ - the part of variation due to the subject,
$\boldsymbol{R}$ - the covariance matrix of observations within the same subject due to the different stages.

Having identified an appropriate covariance structure the model parameters can be estimated either using the Maximum Likelihood (ML) or the Restricted Maximum Likelihood (REML) method.

According to Swamy (1970), the random coefficient regression model is similar to the linear mixed model for repeated measures. Such a model has also been described by Bollen and Curran (2006) as a latent curve model. Under this model each genotype and bleaching condition combination (or treatment) has its parameters estimated separately to form a family of parameters which have overall mean parameters for all treatments. The parameters for all treatments can then be used to compare the performances of the different genotype/bleaching condition combinations.

The effect of time on the treatments can be linear or any form suggested by the graph of the response variable over time. As an example, a quadratic random coefficient regression model is of the form:

$$Y_{gbi} = \alpha_{0gb} + \alpha_{1gb}t + \alpha_{2gb}t^2 + \varepsilon_{gbi} \quad (3)$$

where: α_{0gb} - the initial value of the response variable Y at time $t=0$ (or raw pulp stage) of genotype g under bleaching condition b,
α_{1gb}- the overall linear slope of samples under genotype g and bleaching condition b over.

The parameters are treated as variables affected by genotype and bleaching condition and they can be expressed as $\alpha_{0gb} = (\beta_0 + b_{0gb})$, $\alpha_{1gb} = (\beta_1 + b_{1gb})$ and $\alpha_{2gb} = (\beta_2 + b_{2gb})$. The quantities β_0, β_1 and β_2 are the overall intercept, slope and curvature parameters respectively and b_{0gb}~N(0, σ_0^2), b_{1gb}~N(0, σ_1^2) and b_{2gb}~N(0, σ_2^2) are genotype/bleaching condition specific variables. Substituting α_{0gb}, α_{1gb} and α_{2gb} in (3) gives

$$Y_{gbi} = (\beta_0+b_{0gb}) + (\beta_1+b_{1gb})t + (\beta_2+b_{2gb})\, t^2+\varepsilon_{gbi} \quad (4)$$

where: $E(Y_{gbi}) = \beta_0 + \beta_1 t + \beta_2 t^2$ - the population growth model for all genotype/ bleaching condition combinations.

The quantities b_{0gb}, b_{1gb} and b_{2gb} are the variable parts of the model parameters that depend on genotype and bleaching condition and have zero means with a covariance structure which can be written as:

$$Cov(b_{0gd}, b_{1gb}, b_{2gb}) = \begin{bmatrix} \sigma_0^2 & \sigma_{01} & \sigma_{02} \\ \sigma_{10} & \sigma_1^2 & \sigma_{12} \\ \sigma_{20} & \sigma_{21} & \sigma_2^2 \end{bmatrix} \quad (5)$$

where: σ_i^2 = variance(b_{igb}),$\sigma_{ij} = \sigma_{ji}$=covariance($b_{igb}$,$b_{jgb}$) for i, j = 0, 1, 2. If σ_0^2 = 0, then all the genotype/bleaching condition combinations have identical intercepts (or stage 0 values) equal to β_0. Likewise if σ_1^2= 0 then the linear slopes of all genotype/bleaching condition combinations are identical. The covariance σ_{01} shows the association between the raw stage value (intercept) and the linear slope and σ_{02} shows the association between the intercept and the curvature of the model. The value σ_{12} shows the association between the slope parameter and the curvature of the model. Higher or lower order random coefficient regression models can also be considered depending on the relationship between the response variable and time t (or processing stage in this case).

RESULTS AND DISCUSSION

The SAS procedure Proc MIXED with the RANDOM and REPEATED subcommands were used to fit the random coefficients model to the data using restricted maximum likelihood estimates (REML) (Liu et al. 2007). The results of the data analysis are presented below.

Viscosity data (96α pulp)

The analysis of variance tests for the linear mixed model for repeated measures are shown in Tab. 3 below. The covariance structure selected in modeling the data is the unstructured one as it had the lowest *AIC* value (Tab. 5: *AIC*= 778.2).

The results indicate that the seven genotypes have significantly different viscosity readings in the whole chemical pulping process (Tab. 2: F=4.15, df_1=6, df_2=17, p-value = 0.0095). The six processing stages have significantly different viscosities (Tab. 2: F=67.37, df_1=5, df_2=17, p-value <0.0001). The interaction between genotype and stage is also significant (Tab. 2: F=2.69, df_1=30, df_2=17, p-value = 0.0176), which implies that viscosities for different genotypes differ across the processing stages. Bleaching conditions did not produce significantly different viscosity results throughout the whole process and neither did any interaction between bleaching conditions and stage nor bleaching conditions and genotype).

Tab. 2: Viscosity ANOVA results for the linear mixed model for repeated measures.

Effect	Numerator DF	Denominator DF	F-value	p-value
Genotype	6	17	4.15	0.0095*
Bleaching Condition	2	17	0.65	0.5356
Genotype*Bleaching Conditions	11	17	0.17	0.9978
Stage	5	17	67.37	<0.0001*
Genotype*Stage	30	17	2.69	0.0176*
Bleaching Condition*Stage	10	17	0.33	0.9610
Genotype*Bleaching Condition*Stage	55	17	0.98	0.5432

*=significant at the significance 5 % level

Comparisons of genotype viscosities

The mean viscosities for the seven genotypes by stage are presented in Tab. 3 below. The ranking of the genotypes by viscosity from the lowest to the highest final viscosity is as follows:

1.*E.grandis*, 2.GUA, 3.GCG, 4.*E.nitens*, 5.*E.smithii*, 6.GUW and 7. *E.dunnii*

Genotype *E.dunnii* has the lowest standard error at the final stage hence it has the most consistent final viscosity results while the other genotypes have more or less similar levels of consistency in their final viscosities. The genotypes *E.nitens*, GCG and GUA have similar variability levels which are the highest for the seven genotypes.

Tab. 3: Mean viscosity of genotype by stage.

Genotype	Stage											
	Raw		O_2		D_1		E_0		D_2		Finishing	
	Mean	Std Error	Mean	Std Error	Mean	Std Error	Mean	Std Error	Mean	Std Error	Mean	Std Error
E.dunnii	61.89	4.63	59.59	4.46	52.68	2.76	45.33	2.98	36.53	2.29	35.877	2.23
E.grandis	33.60	8.77	36.87	8.46	32.36	5.23	38.72	5.65	29.92	4.33	28.291	4.23
E.smithii	43.43	7.77	45.17	7.50	40.12	4.63	37.49	5.01	35.15	3.84	33.575	3.75
E.nitens	40.88	9.94	44.34	9.59	37.42	5.93	45.02	6.40	32.82	4.91	31.424	4.79
GCG	56.71	9.94	53.75	9.59	49.53	5.93	39.03	6.40	33.87	4.91	31.013	4.79
GUA	66.52	9.94	63.68	9.59	60.29	5.93	51.53	6.40	33.67	4.91	30.792	4.79
GUW	54.41	7.89	59.51	7.70	46.24	5.06	42.50	6.47	35.03	5.03	33.616	4.95

Fitting the random coefficient regression model to the Viscosity data (96α pulp)

Model (4) presents equations that describe the way viscosity changes over the processing stages for each genotype. After trying the quadratic random coefficient model the quadratic

coefficients were found not to be significant hence a linear random coefficient model was fitted and slope parameters for some of the genotypes were found to be significant. Each genotype has its own set of intercept and linear coefficients and such coefficients are considered random according to Swamy (1970). In this section the parameters of models (4) without the quadratic term are estimated for each genotype. Bleaching conditions were found not to be a significant factor affecting viscosity (Tab. 3: F=0.65, df_1=2, df_2=17, p-value=0.5356) and neither were any interaction effects involving bleaching conditions therefore the parameters of the random coefficient model are significantly affected by genotype only, which implies that different genotypes have different model parameters.

Several covariance structures were tried and the unstructured (UN) and the first order antedependence (ANTE(1)) covariance structures were found to be of the best fit to the data with the same number of parameter estimates (Tab. 6: AIC=1598.4). The unstructured covariance structure was fitted to these data as this was also fitted to the Linear Mixed Model above.

The results for the random coefficient regression models for the various genotypes are presented in Tab. 4 below. The slope parameters of the models for the six genotypes indicated that *E.grandis* and *E.nitens* had the lowest and non-significant rates of change of viscosity over the processing stages (Tab. 4: Slope=-1.995 with p-value=0.2253 and Slope=-2.1222 with p-value=0.3159 respectively). In general the genotypes with the lowest viscosities before processing also had the lowest rate of change of viscosity over the processing stages (Tab. 4: Intercept for *E.grandis*=38.34463 and Intercept for *E.nitens*=43.9554).

Tab. 4: Parameter estimates for the random coefficient regression model (viscosity).

	Model parameter estimates, Standard deviations and p-values for t-tests					
	Intercept			**Slope**		
Genotype	**Parameter**	**(StdDev)**	**p-value**	**Parameter**	**(StdDev)**	**p-value**
E.dunnii	63.5289	2.9355	<0.0001*	-5.8961	0.9630	<0.0001*
E.grandis	38.4463	4.9086	<0.0001*	-1.9950	1.6115	0.2253
E.smithii	48.6429	4.4809	<0.0001*	-3.5687	1.4711	0.0215*
E.nitens	43.9554	6.3370	<0.0001*	-2.1222	2.0804	0.3159
GCG	58.1603	6.3370	<0.0001*	-5.6770	2.0804	0.0105*
GUA	70.8950	6.3370	<0.0001*	-7.9262	2.0804	0.0006*
GUW	58.1603	6.3370	<0.0001*	-5.1765	2.0804	0.0186*

*significant parameter at 5 % significance level

Tab. 5: Covariance structures for the linear mixed model (96α viscosity).

Covariance structure	**Number of parameters**	**-2 Res Log Likelihood**	**AIC**	**AICC**	**BIC**
Unstructured	21	736.2	778.2	789.8	812.1
ANTE(1)	11	759.6	781.6	784.5	799.3
AR(1)	2	844.3	848.3	848.4	851.5
ARMA(1,1)	3	844.2	850.2	850.4	855.0
CS	2	850.6	854.6	854.7	857.8
Toeplitz	6	843.8	855.8	856.7	865.5
SP(Pow)	2	844.3	848.3	848.4	851.5
SP(Gau)	2	845.7	849.7	849.9	853.0

Tab. 6: Covariance structures for the random coefficient regression model (96α viscosity).

Covariance structure	Number of parameters	-2 Res Log Likelihood	AIC	AICC	BIC
Unstructured	4	1590.4	1598.4	1598.8	1604.9
ANTE(1)	4	1590.4	1598.4	1598.6	1604.9
AR(1)	3	1613.5	1619.5	1619.6	1624.3
ARMA(1,1)	4	1613.5	1621.5	1621.7	1627.9
CS	3	1613.5	1619.5	1619.6	1624.3
Toeplitz	4	1613.5	1619.5	1619.6	1624.3
SP(Pow)	3	1613.7	1619.7	1619.8	1624.5
SP(Gau)	3	1613.7	1619.7	1619.8	1624.5

Tab. 7: Intercept and slope parameters estimated differences for the random coefficient regression model (96α viscosity).

	Intercept	Differences in intercepts and slopes viscosities (p-values in brackets)					
Genotype	Slope	*E.grandis*	*E.nitens*	*E.smithii*	GUW	GCG	*E.dunnii*
E.grandis	38.4463	-					
	-1.9950	-					
E.nitens	43.9554	5.5091 (0.4972)	-				
	-2.1222	0.1272 (0.9618)	-				
E.smithii	48.6429	10.1966 (0.1355)	4.6875 (0.5504)	-			
	-3.5687	1.5737 (0.4763)	-1.4465 (0.5745)	-			
GUW	58.1603	19.7140 (0.0199)*	14.2049 (0.1234)	9.5174 (0.2296)	-		
	-5.1765	3.1816 (0.2361)	3.0544 (0.3075)	1.6079 (0.5328)	-		
GCG	58.1764	19.7301 (0.0198)*	14.2209 (0.1230)	9.5334 (0.2289)	0.01606 (0.9986)	-	
	-5.6770	3.6821 (0.1720)	3.5548 (0.2364)	2.1083 (0.4145)	-0.5005 (0.8661)	-	
E.dunnii	63.5289	25.0826 (0.0001)*	19.5734 (0.0088)*	14.886 (0.0093)*	5.3686 (0.4480)	5.3525 (0.4494)	-
	-5.8961	-3.9011 (0.0464)+	-3.7739 (0.1102)	-2.3274 (0.1956)	-0.7195 (0.7558)	-0.2191 (0.9245)	-
GUA	70.8950	32.4487 (0.0003)*	26.9396 (0.0053)*	22.2521 (0.0075)*	12.7347 (0.1656)	12.7186 (0.1661)	7.3661 (0.2999)
	-7.9262	5.9312 (0.0317)+	5.8040 (0.0578)	4.3575 (0.0976)	-2.7496 (0.3575)	2.2492 (0.4506)	2.0301 (0.3829)

*Genotypes with significantly different intercept parameters

+ Genotypes with significantly different slope parameters

A diagrammatic presentation of the random coefficients regression model for the viscosity data for the 96α pulp is shown in Fig. 3. The genotypes with the steepest slopes also had the highest raw stage viscosities. In order of highest intercepts and hence in terms of the steepest slopes the genotypes can be ordered as indicated in Fig. 3 as:

1.GUA,2. *E.dunnii*, 3.GCG, 4.GUW, 5. *E.smithii*, 6. *E. nitens* and 7. *E.grandis*

The covariance and correlation between the slope and intercept parameter for all the models are given in the following matrices as

$$Cov(b_{0g}, b_{1g}) = \begin{bmatrix} 84.829 & -23.833 \\ -23.833 & 9.096 \end{bmatrix}.$$

with the correlation matrix,

$$Corr(b_{0g}, b_{1g}) = \begin{bmatrix} 1.000 & -0.858 \\ -0.858 & 1.000 \end{bmatrix}$$

The correlation between the intercept and the slope parameters is r =-0.858 which is a strong negative correlation. This shows the dependence of the rate of change of viscosity to initial

viscosity levels. This in turn implies that genotypes which start off with high viscosity levels have higher rates of change of viscosity.

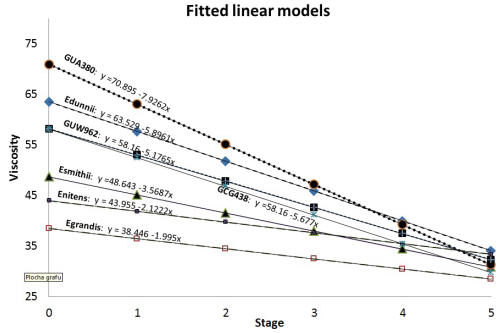

Fig. 3: Random coefficients regression models for the seven genotypes.

Results in Tab. 7 show that the low slope parameter of *E.grandis* is significantly different from the slope parameters of *E.dunnii* (Tab. 7: difference in slope= -3.9011, p-value=0.0464) and GUA (Tab. 7: difference in slope= -5.312, p-value=0.0317). The other genotypes do not have significantly different slope parameters but this is mainly due to the fact that the parameter estimates have high standard deviations (Tab. 4: ranging from 0.9630 to 2.0804).

CONCLUSIONS

The random coefficient model sought to look at the family of parameters of the linear models that were fitted to the seven genotypes to describe the behaviour of viscosity under the six processing stages of dissolving pulp. The random coefficient model explored the variations in the parameter estimates across the seven genotypes and compared them as well as comparing how model parameters of the same genotype relate to each other.

An important result coming from fitting this model to viscosity data is that the higher the raw stage viscosity the higher the rate of change in the viscosity over the processing stages. This result means that the system makes more efficient use of the bleaching chemicals in dealing with viscosity for pulps that start off with high raw stage viscosities. This implies that genotypes which start off with similar viscosity levels respond in a similar manner to the chemical pulping process as far as viscosity is concerned. Such genotypes can be mixed during processing.

It might be worthwhile to measure off viscosity at the raw stage of the pulp before deciding on the amounts and concentrations of chemicals to be used for a specific consignment of raw pulp in order to attain higher levels of efficiency. The correlation between the viscosity of raw pulp (intercept) and the rate of change of viscosity over the processing stages (slope) is -0.858 which indicates a strong negative relationship between raw pulp viscosity and its rate of change over the processing stages. This means that the system is more efficient when processing genotypes that start off with high viscosity levels which might point to the fact that genotypes with low viscosities at the raw pulp stage require lesser chemical concentrations as excess chemicals are not utilised to the extent they are utilised by genotypes with higher raw stage viscosities.

The genotypes were also ranked in terms of their response rate to the processing stages with GUA having the highest rate of decline of viscosity and *E.grandis* having the lowest rate of decline

of viscosity.

The limitations of the study were mainly the consideration of processing stages as time points as there was no controlled time lapse between stages. The stages are therefore points of measurements which are not on an interval scale.

There is wide scope for future study in this area and this includes, but not limited to considering as many of the variables that determine pulp quality as possible using multivariate techniques. These variables include cellulose content (various celluloses including α and γ-celluloses), lignin content and other chemical pulp properties.

REFERENCES

1. Biermann, C.J., 1996: Handbook of pulping and papermaking. Academic Press. An Imprint of Elsevier, 2nd ed. San Diego, 783 pp.
2. Bollen, K.A., Curran, P.J., 2006: Latent curve models: A structural equation perspective. Wiley series in probability and mathematical statistics. Wiley, New York, 285 pp.
3. Burnhan, K.P., Anderson, D.R., 2004: Multimodel inference: Understanding AIC and BIC in model selection. Sociological methods and research 33(2): 261-304.
4. Casey, J.P., 1980: Pulp and paper, chemisty and chemical technology. 3rd Ed. Vol 4. John Wiley & Sons. Toronto.
5. Jahan, M.S., Ahsan, L., Noori, A., Quaiyyum, M.A., 2008: Process for the production of dissolving pulp from *Trema orientalis* (Nalita) by prehydrolysis kraft and soda-ethylenediamine (EDA) process. BioResources 3(3): 816-828.
6. Littell, R.C., Milliken, G.A., Stroup, W.W., Wolfinger, R.D., Schabenberger, O., 2006: SAS for mixed models. Second edition. SAS Institute Inc. North Carolina, 834 pp.
7. Liu, C., Cao, D., Chen, P., Zagar, T., 2007: RANDOM and REPEATED statements - How to use tem to model the covariance structure in proc mixed. Eli Lilly & Company. Indianapolis.
8. Patrick, K., 2011: The dissolving pulp gold rush in high gear. Paper 360º.[Online] 1st September 2011. P.8. Available from: http:www.tappi.org. (Accessed 12 April, 2013).
9. Sundstrom, D.W., Klel, H.E., Daubenspeck, T.H., 1983: Use of byproduct lignin as externders in asphalt. Ind. Eng. Chem. Prod. Res. Dev. 22: 496-500.
10. Swamy, P.A.V.B., 1970: Efficient inference in a random coefficient regression model. Biometrica 38(2): 311-323.
11. Tasman, J.E., Berzins, V., 1957: The permanganate consumption of pulp materials. Tappi Journal 40(9): 695-704.
12. Viscosity of pulp. Tappi T230 om-94, 1994, Tappi Press, Atlanta.

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