Hexenuronic acid in South African grown eucalyptus hybrid clones

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ABSTRACT: Hexenuronic acid (HexA) is formed during kraft pulping by the conversion of 4-*O*-methyl-glucuronic acid groups in the strong alkali conditions. The amount of HexA formed is strongly influenced by the pulping conditions used. It can be removed from the pulp by including an acid hydrolysis stage in the bleaching sequence. Very little research has been carried out to examine HexA in pulps produced from South African grown tree species under local pulp and paper industry conditions. We investigated the influence of genotype and site quality of two commercially important South African grown *Eucalyptus* hybrid clones on the formation of HexA. We also studied the efficiency of acid hydrolysis in removing HexA, and the subsequent effects on kappa number and bleaching chemical consumption. The results show that pulps produced from *E. grandis x E. urophylla* (GU) clones contain significantly higher amounts of HexA compared to pulps produced from *E. grandis x E. camaldulensis* (GC) clones, grown on sites of similar quality. Both clones grown on sites of poor quality also showed significantly higher amounts of HexA compared to the same clones grown on good sites.

Application: This study correlates HexA to kappa number and illustrates the potential savings in chlorine dioxide. It also shows the influence of site and genotype on the amount of HexA formed during kraft pulping.

During kraft pulping, the reaction of 4-*O*-methyl-glucuronic acid groups in strong alkali conditions result in the formation of hexenuronic acid (HexA) [1-3]. HexA is unreactive in alkaline oxygen and peroxide bleaching stages [4]. However, due to their unsaturated nature, the acid groups react readily with chlorine dioxide, chlorine, ozone, and peracids [5]. This leads to higher bleaching chemical consumption, increased production costs, and increased effluent emissions [6]. HexA is also known to consume permanganate in the kappa number test [7]. Since kappa measurements are widely used in the control of pulping and bleaching processes, the presence of these unsaturated constituents affects the results of this analysis, giving higher measurements for the amounts of residual lignin in the pulp.

Despite the significant amount of research carried out, very little has been done to examine HexA in pulps produced from South African grown tree species, and its impact on local bleaching operations. Research has shown that the amounts of HexA formed in kraft pulps are strongly influenced by pulping conditions [8-16]. Thus, there is a need to quantify the amount of HexA formed during the pulping of South African grown tree species under the conditions used by the local pulp and paper industry.

It is well known that chemical properties of wood depend on species, site quality, and age of the tree [17-18]. It is therefore not surprising that the formation of HexA differs among tree species [11], with hardwood pulps exhibiting higher HexA groups than softwood ones [5]. South African pulp mills are faced with a wide variety of species, hybrids, and clones due to the practice of matching superior genotypes to site throughout the country. It can therefore be expected that the formation of HexA in pulps will vary considerably. The objective of this study was to quantify the variability of HexA in pulps produced from two commercially important South African grown eucalypt clones, and its effects on kappa number measurement and beaching chemical consumption.

EXPERIMENTAL

Material

Two *Eucalyptus* hybrid clones, *E. grandis x E. urophylla* (GU) and *E. grandis x E. camaldulensis* (GC) were sampled from two sites representing extreme differences in site quality. Site index gives an indication of site quality. A higher site index value corresponds to a favorable site for tree growth, and as a result, faster growing trees (**Table I**). Ten trees per site were felled and a 3 m bottom billet was taken from each tree. The billets were debarked and chipped into approximately 25 mm lengths using a 38 inch diameter, horizontal feed disc chipper (Precision Husky Corporation, Alabama, USA). The chips were screened to remove knots, bark, dirt,

Species	GU	GU	GC	GC
Site index	26.6	17.8	28.5	19.0
Site description	Good	Poor	Good	Poor
Age (years)	9	9	7	7
Mean DBH[a] (cm)	20.8	16.9	18.9	11.0
Mean total height (m)	30.0	20.4	27.4	19.4
Pulping time in min, at 170°C, to reach kappa 18-22	25	50	25	90

[a]Diameter at breast height of trees at time of sampling

I. Site description and influence on the pulping time, at maximum temperature, required to reach kappa 18-22.

rot, and any over- and under-sized material. They were then combined to produce a consolidated sample for each site before being allowed to air dry. The drying period was approximately three weeks, which proved to be sufficient for the chips to reach equilibrium moisture content with the atmosphere. The moisture content of the chips was determined by drying representative samples for each clone from each site in an oven set at 105 ± 3°C, to constant mass.

Pulping

We pulped the chip samples in electrically heated rotating digesters, using the kraft process. The chip moisture contents were taken into account to maintain a constant liquor-to-wood ratio for all experiments. We varied the pulping times at maximum temperature to reach a kappa number between 18 and 22. Table I shows the pulping times at maximum temperature required to achieve the target kappa range for each clone from the different sites, and **Table II** summarizes the pulping conditions.

Bleaching

To determine the effect of HexA on the consumption of chlorine dioxide during bleaching, each pulp sample was divided into two sub-samples. One sub-sample was used as a control and bleached using an OOD_0ED_1 sequence to reach 90% ISO brightness. The second sub-sample was subjected to the same bleaching sequence, except for an acid hydrolysis stage (A), which was included between the oxygen delignification (OO) and chlorine dioxide (D_0) stages to remove HexA from the pulp. **Tables III-V** list the conditions for all stages. Oxygen delignification and acid hydrolysis was carried out in the rotating digesters that were used for pulping. The chlorine dioxide and alkaline extraction stages were carried out in polyethylene bags immersed in a temperature controlled water bath.

Several conditions for the acid hydrolysis stage were tested on the GU clone from the good quality site to evaluate the conditions under which maximum removal of HexA occurred without affecting pulp properties. These included three temperatures (95°C, 110°C, and 125°C) and three reaction times (60, 120, and 180 min) at a fixed pH of 3.5. The optimum conditions (data not shown) were found to be 95°C, reaction time 180 min, and pH 3.5. These conditions were applied to the remaining GU clone from the poor site and the GC clone from the poor and good sites to investigate the potential savings in bleaching chemicals for each of these clones to reach 90% ISO brightness.

Sulfidity (Na_2S)	25%
Mass of chips (oven dry)	800 g
Active alkali (as Na_2O)/oven dry chips	18%
Liquor-to-wood ratio	4.5:1
Pulping cycle	
Time from ambient to maximum temperature 170°C	90 min
Time at maximum temperature	see Table I
Target kappa number	18-22
Degassing temperatures	120°C and 140°C
Duration of blowdown to ambient pressure	20 min

II. Pulping conditions.

	1st Oxygen stage	2nd Oxygen stage
Temperature (°C)	87	98
Time (min)	30	60
Oxygen Pressure (kPa)	700	700
Consistency (%)	10	10
Kappa Factor (%)	0.125	0.125
$MgSO_4$ (%Mg)	0.1	0.1

III. Conditions for dual oxygen delignification stage.

Pulp consistency	8%
ClO_2 dosage (%)	Kappa factor x kappa number after A or O_2 stage
Reaction time	120 min
Temperature	70°C
Pressure	Ambient

IV. Conditions for chlorine dioxide stage.

Pulp consistency	8%
NaOH dosage	1.5% on oven-dried pulp
Reaction time	60 min
Temperature	70°C
Pressure	Ambient

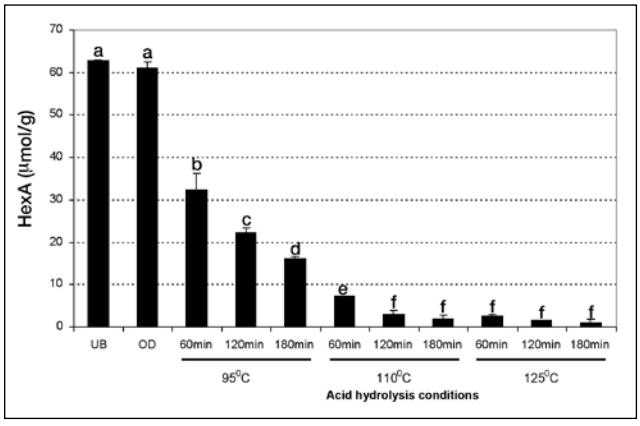
V. Conditions for alkaline extraction stage.

Chemical analysis of wood and pulp

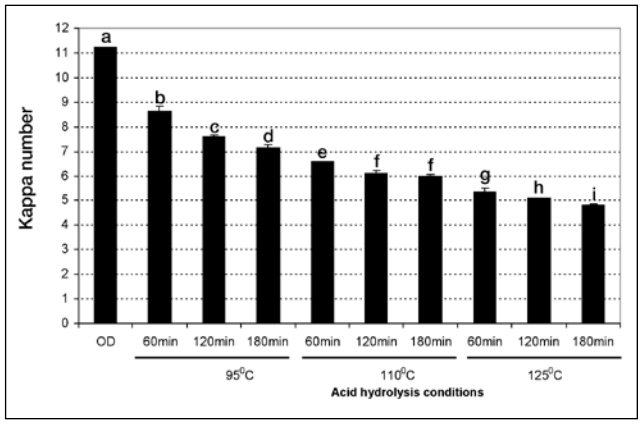
Hexenuronic acid content was measured at various points in the pulping and bleaching process, according to the method developed by Chai *et al.* at the Institute of Paper Science and Technology (IPST) in Atlanta, Georgia, USA [19]. Kappa number measurements were carried out according to TAPPI standard method T236 cm-85 (Kappa number of pulp). Xylose contents in wood were determined by acid hydrolysis of the sawdust (TAPPI T249 cm-85, Carbohydrate composition of extractive-free wood and wood pulp by gas-liquid chromatography), followed by analysis of the hydrolyzate using high performance anion exchange chromatography coupled with pulse ampherometric detection [20-21]. Lignin was determined by quantitatively filtering the hydrolyzed sample, obtained in the determination of xylose, under vacuum through a 0.45 μm filter paper. The material remaining on the filter paper was defined as the Klason lignin.

Statistical analysis

All experiments were carried out in triplicate and the mean results together with the standard deviations, denoted by the error bars, were reported. The differences in the acid



1. Effect of acid hydrolysis on HexA content of pulp of GU clone from good site (UB = unbleached pulp; OD = oxygen delignified pulp).



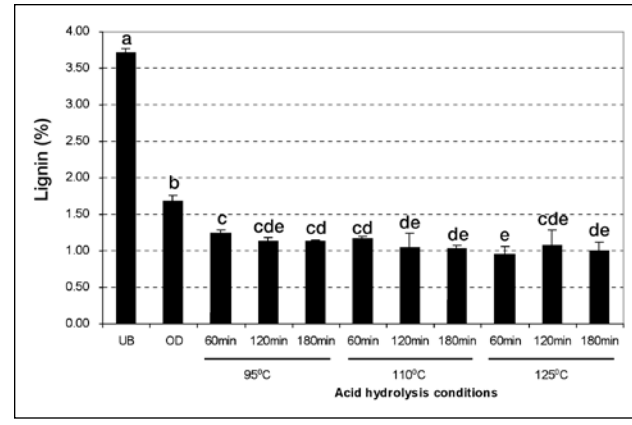
2. Effect of acid hydrolysis on kappa number of pulp of GU clone from good site (OD = oxygen delignified pulp).

hydrolysis conditions, between sites or between genotypes, were tested using analysis of variance (ANOVA) and Duncan's multiple range tests. The mean results displayed in the graphs were represented by letters with common letters indicating that there were no significant differences among the means at a 0.05% level of error.

RESULTS AND DISCUSSION

Effect of acid hydrolysis on hexenuronic acid content of pulp

The concentration of HexA in pulp decreased during acid hydrolysis as the temperature and reaction times of the A-stage increased (**Fig. 1**). Similar to findings by other researchers [5,8,22-24], the unbleached and oxygen bleached pulps showed no significant difference in HexA content due to its unreactivity during oxygen delignification. However, when acid hydrolysis was applied, the concentration of HexA dropped significantly with increasing reaction time and temperature. This decreasing trend continued until 110°C and 120 min where approximately 95% of HexA was removed. Beyond this point, increasing the temperature and/or reaction time had little effect on the residual concentration of HexA in the pulp.



3. Effect of acid hydrolysis on lignin content of pulp of GU clone from good site (UB = unbleached pulp; OD = oxygen delignified pulp).

Effect of acid hydrolysis on kappa number of pulp

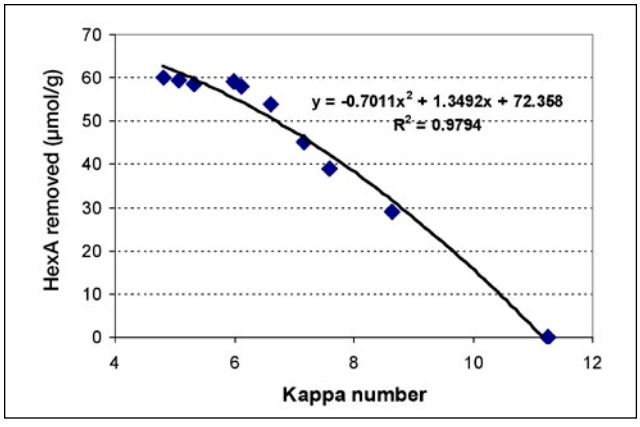
An increase in the temperature and reaction time during acid hydrolysis significantly reduced the kappa number of the oxygen delignified pulps for all tested conditions (**Fig. 2**). For the longest time (180 min) and at the highest temperature (125°C), the kappa number was reduced by 6.5 units, from 11.3 (no hydrolysis treatment) to 4.8. The reason for this decrease is due largely to the removal of HexA, which is known to consume potassium permanganate in the kappa number test [7,25].

Effect of acid hydrolysis on lignin content of pulp

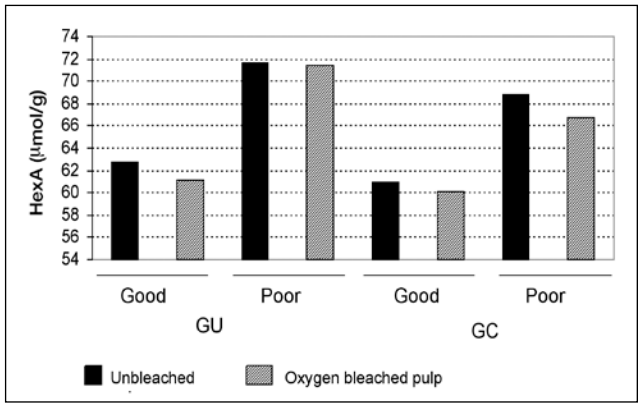
Analysis of the lignin content of the pulp showed that lignin was removed during acid hydrolysis (**Fig. 3**). At 95°C, 60 min, lignin removal was approximately 0.4%. Beyond this point, the lignin content appeared to remain fairly constant during acid hydrolysis, even with further increase in temperature and reaction time. This is important because it showed that the decrease in kappa number during acid hydrolysis was due largely to the decrease in the concentration of HexA and not to the loss of lignin.

Treatment	Residual KN	KN Reduction	Residual HexA (µmol/g)	HexA Reduction	$HexA_{red}/KN_{red}$
O_2 delignified pulp	11.25	—	61.17	—	—
95°C, 60 min	8.64	2.61	32.27	28.90	11.1
95°C, 120 min	7.60	3.65	22.25	38.92	10.7
95°C, 180 min	7.16	4.09	16.13	45.04	11.0
110°C, 60 min6.60	4.65	7.25	53.95	11.6	
110°C, 120 min	6.12	5.13	3.15	58.02	11.3
110°C, 180 min	5.99	5.26	1.87	59.30	11.3
125°C, 60 min	5.33	5.92	2.48	58.69	9.9
125°C, 120 min	5.08	6.17	1.75	59.42	9.6
125°C, 180 min	4.82	6.43	1.02	60.15	9.4

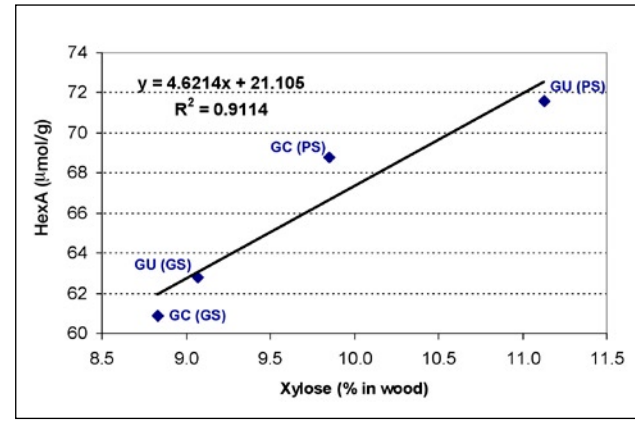
VI. Contribution of hexenuronic acid (HexA) to kappa number (KN). The reduction in kappa number and hexenuronic acid after acid hydrolysis is calculated from the oxygen delignified pulp.



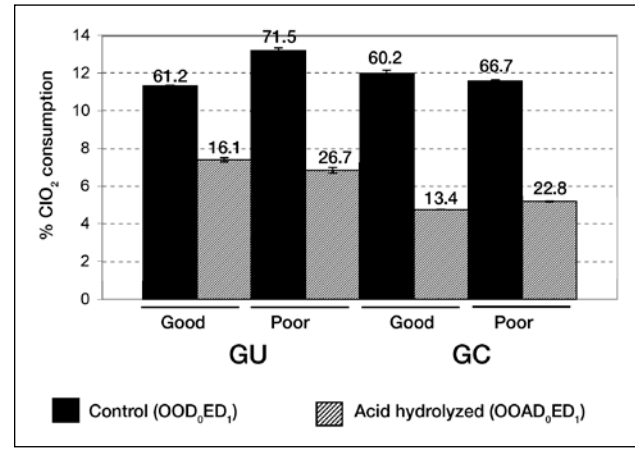
4. Correlation between reduction in hexenuronic acid (HexA) concentration and kappa number after acid hydrolysis.



5. Hexenuronic acid (HexA) content in unbleached and oxygen bleached pulp of GU and GC clones from good and poor sites.



6. Correlation between xylose content in wood and hexenuronic acid in unbleached pulps of GU and GC clones. (GS = good site and PS = poor site).



7. Consumption of chlorine dioxide, expressed as percent total active chlorine, required for control pulps (without acid hydrolysis) and pulps acid hydrolyzed before bleaching, to reach 90% ISO brightness. The quantities included indicate the concentration of HexA, in µmol/g, before bleaching.

Correlating kappa number to hexenuronic acid content

The kappa number reduction after acid hydrolysis was correlated to the HexA reduction after acid hydrolysis (**Table VI**). The contribution of HexA to kappa number ranged between 9.4 and 11.6 μmol HexA per kappa number unit, depending on the acid hydrolysis conditions. This finding was consistent with other studies that showed that approximately 10 μmol HexA contributed to 1 kappa unit [4,6-7,13,19].

A graphical representation of the results from Table VI shows the significant correlation between the drop in kappa number and the removal of HexA during acid hydrolysis (**Fig. 4**).

Effects of site and genotype on HexA content

Figure 5 shows the HexA concentration of the unbleached and oxygen delignified pulps of the GU and GC clones from the good and poor site qualities. Both clones from the poor site showed significantly higher HexA contents compared to their corresponding clones from the good sites. An analysis of the wood xylose content showed that the clones grown on the poor site had significantly higher xylose contents (**Fig. 6**). The higher xylose content suggests a higher methyl-glucuronic acid content [26], which results in the formation of higher amounts of HexA groups during pulping. Among clones grown on sites of similar quality, the unbleached pulps of the GU clones showed significantly higher HexA contents compared to the GC clones from corresponding sites. Here again, the higher xylose content in the GU clones compared to the GC clones could explain this observation.

Effect of HexA on bleaching chemical consumption

Figure 7 shows the amounts of chlorine dioxide, expressed as percent total active chlorine, required for each clone to reach 90% ISO brightness. The controls were subjected to a four-stage bleaching sequence (OO-D_0ED_1). The acid hydrolyzed pulps were subjected to a five-stage bleaching sequence (OO-AD_0ED_1) to remove HexA. The conditions for acid hydrolysis were a temperature of 95°C, reaction time of 180 min, and pH of 3.5. In all cases, the reduction in the level of HexA after acid hydrolysis led to a significant reduction in the consumption of chlorine dioxide. Savings in chlorine dioxide of 35% and 48% were obtained for the pulps of the GU clones from the good and poor sites, respectively. For the GC clones, chlorine dioxide consumptions dropped by more than half,

with the good and poor sites showing savings up to 61% and 55%, respectively.

CONCLUSIONS

Kraft pulps produced from South African grown *Eucalyptus* hybrid clones contain significant amounts of HexA. In addition, it was found that both species and site quality influenced the amount of HexA formed during kraft pulping. Pulps produced from GU clones were found to contain significantly higher amounts of HexA compared to GC clones from similar sites. For both clones, pulps produced from trees grown on poor sites showed significantly higher HexA concentration compared to pulps produced from trees grown on good sites.

The presence of HexA was shown to contribute to the kappa number, which can lead to inflated measurements for residual lignin in pulps. In industry, this has serious implications for the control of pulping and bleaching processes. These processes usually make use of online kappa number sensors to monitor the process, which in most instances, are calibrated against the conventional TAPPI standard method that is used to measure kappa number. In correlating the kappa number reduction to HexA reduction after acid hydrolysis, we found that 9.4–11.6μmol HexA contributed to 1 kappa unit. In this study, analysis of the HexA content in the unbleached pulps of the GU and GC clones showed HexA concentrations of 60-70 μmol/g. If an average contribution of 10.7 μmol HexA to 1 kappa unit is considered, this means that pulps produced at kappa 20, measured using the conventional TAPPI standard method, equates to a true kappa number of 13-14, after correction for HexA.

The amounts of chlorine dioxide required to bleach pulps to 90% ISO brightness were also found to be negatively affected by the presence of HexA. By including an acid hydrolysis stage (95°C, 180 min, pH 3.5) in the bleaching sequence, chlorine dioxide savings ranging between 35% and 61% were achieved, depending on the site quality and species.

This study showed that the removal of HexA by acid hydrolysis has a significant effect on bleaching efficiency, and thus offers a distinct advantage for the production of bleached chemical pulps. However, the use of acid hydrolysis in pulp mills will only be considered if the chemical and strength properties of pulp are not compromised. Investigations into this are presently underway.

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INSIGHTS FROM THE AUTHORS

Research has shown that HexA is an important factor to consider when producing bleached chemical pulp. The South African pulp and paper industry was keen to find out the implications associated with HexA, and its removal, on pulp produced from our local resources. Before this work, no one had really investigated HexA in a South African context. We were not even sure of the levels found in our pulps. This work was seen as a first step in increasing our understanding on the topic. Many of the findings in this study were consistent with the findings of other researchers.

There is no standard method available for the measurement of HexA in pulps. In South Africa none of the pulp mills measured HexA. One of the objectives of the study was to identify from literature a suitable method for measurement of HexA. The method had to be quick, uncomplicated, and accurate to be used in industry. In this study, we were able to identify a method that meets this requirement. The accuracy of the method was verified by inter-laboratory comparisons between us and two other research institutes – one using the same method (Institute of Paper Science and Technology) and another using a different method (Royal Institute of Technology). The results from the comparison correlated very well. The inter-laboratory study was used to provide evidence of the reproducibility and comparability of the method developed by IPST researchers, who then submitted their method to the TAPPI standards department as a proposed new provisional method (TAPPI T New WI 3015, Hexeneuronic acid content of chemical pulp).

The most surprising finding was the amount of ClO_2 that could be saved by removing HexA from the pulp. Besides the obvious savings in operating costs, other benefits are the potentially lowered impact on the environment when producing bleached pulp. Due to the presence of HexA in kraft pulps, kappa numbers were previously measured incorrectly. This means that pulp quality and yield can now be improved and optimized by varying delignification during pulping, and pulps with higher kappa numbers can be produced.

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Potential benefits to mills include pulping to higher kappa numbers, varying the level of delignification during the oxygen stage, and optimizing ClO_2 consumption, thereby lowering operating costs and environmental impact.

The next step will be to study the impact of the A-stage on the pulp strength properties. Acid hydrolysis used to remove HexA would be meaningless if strength properties are compromised.

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Editor's Note

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