Ozone bleaching of South African Eucalyptus grandis *kraft pulps containing high levels of hexenuronic acids*

JEROME E. ANDREW, JONAS JOHAKIMU, AND NKANYISO E. NGEMA

ABSTRACT: Ozone use in conjunction with chlorine dioxide during pulp bleaching offers several advantages over conventional bleaching sequences that make use of chlorine dioxide only. Despite this, in South Africa, only one mill uses ozone. The current study was a preliminary investigation into the use of ozone in bleaching sequences for kraft pulps produced from South African *Eucalyptus grandis* wood chips, which typically contained high amounts of hexenuronic acids (HexA). The objective of the study was to compare the performance of ozone to other technologies used to remove HexA, such as acid hydrolysis (A) and hot chlorine dioxide (D_{HT}) stages. Bleaching sequences using chlorine dioxide (i.e., $OAD_0ED_1D_2$ and $OD_{HT}ED_1D_2$) were compared to bleaching sequences using ozone (i.e., OZD_0ED_1 and $OAZD_0ED_1$). The results showed that ozone preferentially reacted with HexA in the presence of lignin. When applied after oxygen delignification, ozone had the same HexA removal efficiencies as the A- and D_{HT}- stages at dosages in excess of 0.6%. When used in combination with the A-stage, the HexA removal efficiencies of ozone reached 96%. Consequently, up to 15% savings in the estimated bleaching chemical costs were achieved when the $OAZD_0$(EP)D sequence was used, compared to the standard reference sequence ($OAD_0ED_1D_2$). The residual HexA in the bleached pulp affected brightness reversion of the pulps, but this was only evident for the bleaching sequences that used chlorine dioxide, not for those that included ozone.

Application: This study provides preliminary results on the use of ozone for bleaching of high HexA-containing South African *E. grandis* kraft pulps.

Eucalypts are grown extensively throughout South Africa and have become important raw materials for the manufacture of tissue and printing and writing paper grades. In the production of bleached *Eucalyptus* kraft pulps, the bleaching process is usually carried out using chlorine dioxide as the primary oxidative bleaching chemical, and much effort has been focused on improving its efficiency during elemental chlorine free (ECF) bleaching [1]. For example, during kraft pulping, a significant amount of hexenuronic acids (HexA) are formed from the conversion of 4-*O*-methyl-glucuronic acid groups in the hot alkaline medium [2,3]. Although HexA are unreactive during oxygen delignification and peroxide bleaching stages, they have been shown to consume bleaching chemicals such as chlorine dioxide, ozone, and peracids because of their unsaturated structure [4]. This ultimately leads to higher bleaching chemical consumption, increased production costs, and increased effluent emissions [5]. Hexenuronic acid is also known to consume potassium permanganate in the kappa number test [6]. Because 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 measurement for the amounts of residual lignin in the pulp. The problem is more pronounced for hardwood pulps, which contain high amounts of HexA, in the range of 35-60 μmol/g [7,8]. *Eucalyptus* kraft pulps, in particular, have been reported to contain as much as 70-85 μmol/g of HexA [9]. Given that 10 μmol HexA can contribute to almost 1 kappa unit [6], the presence of HexA in *Eucalyptus* kraft pulps might account for up to 50%-60% of the kappa number. Several researchers have shown that significant savings in chlorine dioxide can be expected by removing HexA from the pulp before bleaching [4,10]. To remove HexA, most modern bleached *Eucalyptus* kraft pulp mills contain acid hydrolysis (A) or hot chlorine dioxide (D_{HT}) stages in some form in their bleaching sequences. Other options for the removal of HexA include the sequential use of ozone with alkali (Z/E) or ozone with chlorine dioxide (Z/D) [11].

Ozone is a very efficient oxidant that reacts with most organic compounds. Its use in bleaching centers on reducing the operating and chemical costs and improving the environmental impact of the process [12]. Worldwide, about 30 mills use ozone [13,14], and in South Africa there has been some renewed interest in the technology [15]. The current study

Sulfidity	25%
Mass of o.d chips	800 g
Active alkali (as Na2O/o.d chips)	18%
Liquor-to-wood ratio	4.5:1
Pulping temperature	170°C
Time from ambient to maximum temperature	90 min
Time at maximum temperature	30 min
Target kappa number	20

I. Kraft pulping conditions.

was a preliminary investigation into the use of ozone for bleaching kraft pulps produced from *Eucalyptus grandis* wood chips. The objective of the study was to compare the HexA removal efficiency of ozone to other technologies, such as acid hydrolysis and hot chlorine dioxide stages, and its overall effect on bleaching of *Eucalyptus* pulps, which generally contain high amounts of HexA. For this purpose, bleaching sequences using chlorine dioxide (i.e., $OAD_0ED_1D_2$ or $OD_{HT}ED_1D_2$) were compared to bleaching sequences using ozone (i.e., OZD_0ED_1 or $OAZD_0ED_1$).

EXPERIMENTAL

Materials

E. grandis wood chips were collected from a kraft pulp mill in South Africa. The chips were screened in the laboratory using a vibratory screener to remove knots, bark, dirt, rot, and any over- and undersized material. Wood chips with a thickness of 3-8 mm were selected for pulping. Before pulping, the chips were air-dried for 2-3 weeks to reach equilibrium moisture content with the atmosphere. The moisture content of the chips was determined by drying representative samples in an oven set at 105°C to constant mass.

Pulping

Pulping was carried out in electrically heated rotating digesters using the kraft process. For each cook, 800 g of oven-dried (o.d) chips were pulped using the conditions summarized in **Table I**. After pulping, the cooked chips were washed with tap water, under high pressure, through a 10-mesh screen onto a 200-mesh screen to separate the fibers from the rejects. The screenings remaining on the 10-mesh screen were considered as rejects. The pulp remaining on the 200-mesh screen was placed into a cotton bag and dewatered by spin drying for 10 min.

Bleaching

Bleaching was carried out using $OAD_0ED_1D_2$ as the standard reference sequence. The acid hydrolysis (A) stage was included to remove HexA [4]. As an alternative to the A-stage, the A and D_0 stages were combined into a single stage and carried out at high temperature and at extended reaction times (i.e., hot chlorine dioxide [D_{HT}] stage) [16]. In some cases, hydrogen peroxide was used to reinforce the extraction stage or to replace the final D stage (i.e., $OAD_0[EP]D_1P$ and $OD_{HT}[EP]D_1P$). All stages were carried out in polyethylene bags immersed in a temperature-controlled water bath, except for oxygen delignification, which was carried out in the rotating digesters that were used for pulping. After each bleaching stage, before washing the pulp, an undiluted aliquot of the filtrate was taken for measurement of pH and residual bleaching chemicals.

When ozone was used, the bleaching sequences were OZD_0ED_1 or $OAZD_0ED_1$. In some cases, hydrogen peroxide was again used to reinforce the extraction stages. Ozone bleaching was carried out by first acidifying the pulp to pH 2-3 at 1% consistency. The acidified pulp was then dewatered by spin-drying and pressed to approximately 40% consistency. The pulp was fluffed, and 50-63 g of o.d.-equivalent pulp was

	O/O	A	D_{HT}	D0	E or EP	D_1	D_2	P	Z
Temp, °C	87/98	95	95	70	70	70	70	80	25
Time, min	30/60	180	180	120	60	120	120	180	*
ClO_2, %	-	-	KF 0.1; 0.15; 0.2; 0.3	KF 0.2; 0.3; 0.4	-	0.8	0.2	-	-
H_2O_2, %	-	-	-	-	0.3	-	-	0.6	-
NaOH, %	2.4	-	-	-	1.5	-	-	1	-
O_3, %	-	-	-	-		-	-	-	0.2; 0.4; 0.6
Mg, %	0.2	-	-	-	-	-	-	-	-
Const., %	10	10	10	10	10	10	10	10	40
End pH	10-11	2.5-3	2.5-3	2-3	10.5–11	3-4	4.5-5.5	11-11.5	3**

* Contact time of ozone with the pulp was varied according to the concentration of ozone gas produced and the dosage charged (see Table IV).

**Initial pH of pulp before ozonation.

II. Bleaching conditions.

	Kappa	HexA (μmol/g)	Brightness (%ISO)	Viscosity (mL/g)	Selectivity (mL/g/kappa unit)
Unbleached	19.2	82.6	32.0	1133	-
O_2 delignified	10.7	82.2	53.6	898	28
O – A	6.1	27.3	57.6	841	12
O – D_{HT} (KF 0.2)	3.8	26.5	64.5	808	13
O – D_{HT} (KF 0.3)	2.2	18.5	64.9	782	14

III. Properties of unbleached, oxygen delignified and acid hydrolyzed pulps, and pulps treated with hot chlorine dioxide (D_{HT} stage).

charged into a rotating round bottom glass flask, which served at the reactor vessel. Ozone was produced using a laboratory Indigo 2009 ozone generator (Wassertec Ozone Systems; Cape Town, South Africa). The ozone-containing gas was introduced to the bottom of the reactor through a glass tube and exited the reactor through another glass tube that was connected to two gas absorption bottles. The gas absorption bottles contained potassium iodide solution to trap any unreacted ozone gas. For support, the reactor vessel was immersed in a water bath while being held in an inclined position in the holding frame of a rotary evaporator. Measurement of the ozone concentration was carried out iodometrically at the start and at the end of the experiment. The average result of these measurements was taken as the amount of ozone generated during the course of the ozone bleaching stage. **Table II** summarizes the conditions for the individual bleaching stages.

Pulp properties

TAPPI Test Methods were used to measure pulp moisture contents (TAPPI T550 om-93 "Determination of equilibrium moisture in pulp, paper, and paperboard for chemical analysis"), kappa numbers uncorrected for HexA (TAPPI T236 cm-85 "Kappa number of pulp"), brightness reversion (TAPPI UM 200 "Brightness loss of bleached pulps") and HexA concentration (TAPPI T282 pm-07 "Hexeneuronic acid content of chemical pulp"). Micro-kappa numbers were measured on samples with kappa numbers less than 10, according to the French FDT 12-019 method. Intrinsic viscosity was measured using SCAN-CM 15:88 (1988) and pulp brightness was measured using a Technidyne Color-Touch ISO PC model that conformed to ISO 2469, 2470, and other standards.

RESULTS AND DISCUSSION

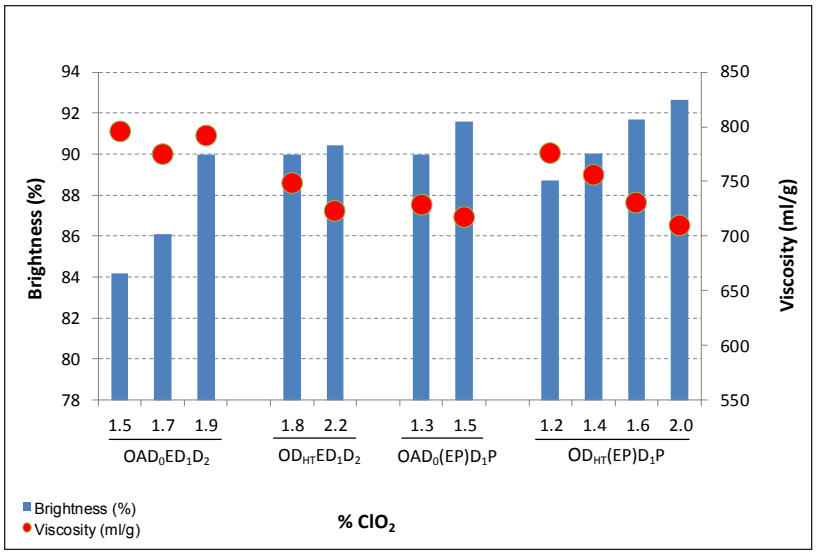
Chlorine dioxide-based bleaching sequences

Hardwood kraft pulps generally contain high amounts of HexA, ranging from 35 to 60 μmol/g [7,8]. However, *Eucalyptus* kraft pulps, in particular, have been reported to contain as much as 70-85 μmol/g [9]. To remove HexA from these pulps, the bleaching sequences generally contain an A or D_{HT} stage, which usually follows oxygen delignification.

Table III shows the properties of the unbleached, oxygen delignified, and acid hydrolyzed pulps, together with the pulps that were treated with hot chlorine dioxide at two kappa factors (KF). The kappa number of the unbleached pulp was reduced by 45% during oxygen delignification, from 19.2 to 10.7, and the intrinsic viscosity decreased by 20%, from 1133 mL/g to 898 mL/g. The drop in viscosity per kappa number drop was around 28 mL/g/kappa unit, which was in the acceptable selectivity range for oxygen delignification [7] and consistent with industrial oxygen delignified kraft pulps from South African mills [1].

A high concentration of HexA was found in the unbleached pulp (~82 μmol/g). As expected, there was not much difference in HexA concentration in the unbleached and the oxygen delignified pulps because HexA is not reactive during oxygen delignification [4,17]. When the A-stage followed oxygen delignification, the kappa number of the oxygen delignified pulp was further reduced, from 10.7 to 6.1, and the HexA concentration was reduced from 82 to 27 μmol/g. HexA has previously been shown to consume potassium permanganate in the kappa number test [4,18], and so the decrease in kappa number was largely attributed to this drop in HexA concentration. By correlating the decrease in kappa number with the decrease in HexA concentration, it was found that 10 μmol HexA contributed to 0.83 kappa units, which was consistent with previous findings by other researchers [6]. Although the A stage was effective in removing HexA, it did not brighten the pulp to a large extent. The increase in brightness after the A-stage was 4 points, or 7.5% higher than the oxygen delignified pulps.

Installation of the A-stage as a standalone stage might require significant capital investment [19,20]. An alternative to the A-stage is the D_{HT} stage, in which the conventional D_0 stage is operated at high temperature for 2-3 hours at pH 3. The D_{HT} stage is based on the principle that chlorine dioxide reacts preferentially with lignin more than with HexA and is consumed instantaneously by lignin [16]. By extending the reaction time, the pulp is then exposed to the prevailing high temperature and acidic medium, which destroys HexA groups. The results in Table III demonstrate this dual delignification-HexA hydrolysis effect of the D_{HT} stage. The D_{HT} stage carried out at KF 0.2 showed similar levels of HexA as the pulps subjected to acid hydrolysis, but had a much lower kappa number. When the chlorine dioxide dosage was increased in the D_{HT} stage (KF 0.3), the HexA concentration



1. Evolution of brightness and viscosity for fully bleached pulps using various bleaching sequences.

decreased further, from 26.5 μmol/g to 18.5 μmol/g. With an excess addition of chlorine dioxide (at KF 0.3), it was reasonable to expect that during acid hydrolysis of HexA there were simultaneous reactions of chlorine dioxide with HexA [20,21], which were initially present in high concentrations in the oxygen delignified pulp. The drop in viscosity was slightly more severe for the pulps treated in the D_{HT} stages, between 4%-7% lower for KF 0.2 and KF 0.3, compared to the pulps that were acid hydrolyzed. The increase in brightness for the DHT-treated pulps was about 11 points, or 20% higher than the oxygen delignified pulps, thus emphasizing the dual action of the DHT stage.

Full bleaching sequences for *Eucalyptus* pulps are typically $OAD_0ED_1D_2$ or $OD_{HT}ED_1D_2$. In most instances, the extraction stage is reinforced with oxygen and/or peroxide, and the D_2 stage is often replaced with a final peroxide stage (i.e., $OAD_0[EOP]D_1P$ or $OD_{HT}[EOP]D_1P$) [12, 22]. **Figure 1** shows the evolution of brightness and accompanying pulp viscosities as a function of the total amount of chlorine dioxide consumed for the aforementioned sequences. For practical reasons, the extraction stages were reinforced with peroxide only. The results show that bleaching using the standard reference sequence, $OAD_0ED_1D_2$, required 1.9% chlorine dioxide to reach a target brightness of 90%. The consumption of chlorine dioxide was reduced slightly to 1.8% to reach the same level of brightness when the A and D_0 stages were replaced with the D_{HT} stage in the $OD_{HT}ED_1D_2$ sequence, resulting in a 5% savings in chlorine dioxide. When peroxide was incorporated into the bleaching sequences, chlorine dioxide consumption for the $OAD_0(EP)D_1P$ was 32% lower than the standard reference sequence needed to reach 90% brightness. For the $OD_{HT}(EP)D_1P$ sequence, the savings in chlorine dioxide was 26%, compared to the standard reference sequence. The viscosities of the various bleached pulps differed slightly, not more than 10%, and on average, the viscosities of the standard reference bleaching sequences were between 6%-8% higher compared to the other sequences.

Ozone-based bleaching sequences

Typical bleaching sequences for hardwood and softwood pulps that incorporate the use of ozone are $ZD_0(EP)D_1$, $Z(EOP)D_0P$, or ZD_0ED_1 [22]. The role of ozone in these bleaching sequences is often to replace chlorine dioxide as a delignifying agent. Generally, oxygen delignification precedes ozone delignification. This is to minimize the amount of ozone used, and as a result, minimize its effect on fiber quality. To remove HexA, the A-stage is still preferred and normally precedes the ozone stage, again to minimize the amount of ozone used because of its reactivity with HexA [4,7,17]. The A-Z combination is possible because ozone stages are increasingly carried out at higher temperatures, up to 75°C in some instances [23].

Table IV lists some typical data from ozonation of oxygen delignified and acid hydrolyzed pulps at three dosage levels of ozone. The data show that ozone reactivity was 90%-95%. An increase in ozone dosage led to a decrease in its reactivity when ozonation followed the A-stage. This was probably be-

Treatment	O_3 Concentration (mg/min)	Mass of O.D. Pulp	O_3 Charge (%)	O_3 Reaction Time (s)	O_3 Consumption (as % on pulp)	O_3 Reactivity (%)
O-Z	95.2	50	0.2	63	0.19	93.9
O-Z	95.2	50	0.4	126	0.38	93.9
O-Z	95.2	50	0.6	189	0.57	94.6
O-A-Z	91.7	63	0.2	82	0.19	94.5
O-A-Z	91.7	63	0.4	165	0.37	92.7
O-A-Z	91.7	63	0.6	247	0.54	89.7

IV. Typical results from ozonation of pulps for the three dosage levels of ozone.

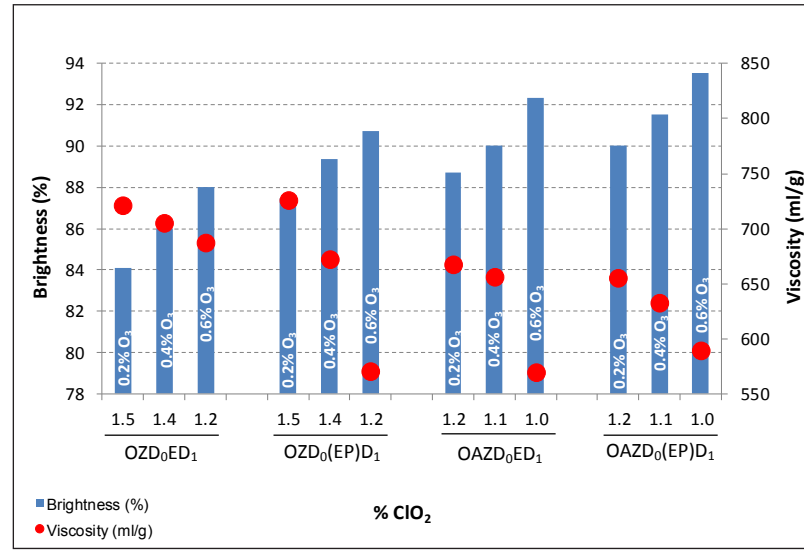
Treatment	Kappa	Viscosity (mL/g)	Selectivity (mL/g/kappa unit)	HexA (µmol/g)	Kappa (HexA contribution)*	Kappa (lignin contribution)
O_2 delignified	10.7	898	-	82.4	6.8	3.9
O-Z (0.2%)	6.1	801	21.0	46.4	3.9	2.2
O-Z (0.4%)	5.1	755	25.5	33.3	2.9	2.2
O-Z (0.6%)	3.9	688	30.4	22.3	1.9	2.0
O-A	6.1	841	12.4	27.3	2.3	3.8
O-A-Z (0.2%)	3.3	730	22.7	9.4	0.8	2.5
O-A-Z (0.4%)	2.7	676	27.8	5.0	0.4	2.3
O-A-Z (0.6%)	2.2	614	33.4	3.2	0.3	1.9
* The contribution of HexA to kappa was calculated using the relationship shown earlier where 10 µmol = 0.83 kappa unit.						

V. Kappa numbers, viscosities and HexA contents of oxygen delignified and acid hydrolyzed pulps treated with ozone at three dosage levels.

cause of the lower kappa numbers of these pulps (i.e., lower concentration of HexA) compared to the oxygen delignified pulps. **Table V** shows the viscosities, kappa numbers, and HexA contents of pulps treated at the three ozone dosages after oxygen delignification or acid hydrolysis.

The results in Table V show that the kappa number decreased from 10.7 to 6.1 when the oxygen delignified pulp was treated with 0.2% ozone. At the same time, it appeared that the ozone also reacted with HexA, as its concentration decreased by more than 40%, from 82 µmol/g to 46 µmol/g. Using the correlation shown earlier in this study where 10 µmol HexA was found to contribute to 0.83 kappa units, the residual HexA present in the 0.2% ozonated pulp contributed 3.9 units to the kappa number of that pulp. By difference, the remaining 2.2 units were assumed to be attributed to lignin (although it is known that other unidentifiable groups beside HexA and lignin may contribute to the kappa number [18]). By increasing the ozone dosage to 0.4% and 0.6%, it was found that the drop in kappa number was attributed more to the removal of HexA than to the removal of lignin. This implied that the ozone reacted preferentially with HexA and not much in the delignification reactions. This was consistent with findings of other researchers who have shown that ozone can react up to 2.5 times faster with HexA than with lignin [20].

When ozone was applied to the pulp that was acid hydrolyzed before ozonation, a similar trend was observed. The kappa number was reduced from 6.1 to 3.3 when an ozone dosage of 0.2% was used. At the same time, the HexA removal was 66%, a decrease in concentration from 27 µmol/g to 9 µmol/g. When the ozone dosage was increased further, the reaction ozone with HexA was again evident, accompanied



2. Evolution of brightness and viscosity for fully bleached pulps using various bleaching sequences incorporating the use of ozone.

with a slight degree of delignification, probably because of the low HexA concentration. As expected, viscosity decreased as the ozone dosage increased. Ozone selectively was marginally higher when ozonation followed oxygen delignification compared to when ozone was applied after the acid hydrolysis stage. This might be explained by the higher HexA concentration in the oxygen delignified pulp, compared to the acid hydrolyzed pulp.

Figure 2 shows the full bleaching brightness and viscosity results of the pulps listed in Table V using D_0ED_1 and $D_0(EP)D_1$ sequences. Pulp brightness increased with increasing ozone dosages, even though the amount of chlorine dioxide used was progressively decreased. It was found that it was more beneficial to apply ozone after the A-stage than after oxygen delignification. For example, a brightness of 88% was achieved using 1.2% chlorine dioxide and 0.6% ozone when

Treatment	Residual HexA (μmol/g)	Removal Efficiency (%)
O_2	82.2	-
O – A (95°C, 180min, pH 3)	27.3	67
O – D_{HT} (KF 0.2)	26.5	68
O – D_{HT} (KF 0.3)	18.5	77
O – Z (0.2%)	46.4	44
O – Z (0.4%)	33.3	59
O – Z (0.6%)	22.3	73
O – A – Z (0.2%)	9.4	89
O – A – Z (0.4%)	5.0	94
O – A – Z (0.6%)	3.2	96

VI. HexA removal efficiencies of the A, D_{HT}, and O_3 stages.

Bleaching Sequence Type	Average Residual HexA (μmol/g)	Average Brightness Loss (%)
$OAD_0(EP)D_1P$	6.2	3.5
$OAD_0ED_1D_2$	4.9	2.1
$OD_{HT}ED_1D_2$	3.7	1.9
$OD_{HT}(EP)D_1P$	2.2	1.6
OZD_0ED_1	8.8	1.9
$OZD_0(EP)D_1$	5.0	2.1
$OAZD_0ED_1$	1.4	2.0
$OAZD_0(EP)D_1$	0.8	2.4

VII. Average brightness loss values for various bleaching sequences.

the OZD_0ED_1 bleaching sequence was used. The same level of brightness required only 1.2% chlorine dioxide and 0.2% ozone when using the $OAZD_0ED_1$ sequence. This might be because of the low levels of HexA in the pulps that were acid hydrolyzed before ozonation. The use of peroxide to reinforce the extraction stages clearly led to improved brightness levels for both bleaching sequences. As expected, pulp viscosity decreased with increasing ozone charge. The decrease appeared to be more pronounced when the A-stage was used in the bleaching sequence and when peroxide was used during extraction.

Brightness reversion

Brightness and brightness reversion are important properties that need to meet well-defined specifications for bleached *Eucalyptus* kraft pulps [11,24,25]. In the case of brightness reversion, residual HexA in the bleached pulp has been cited as one of the leading causes of reversion [4,26-29]. Technologies such as the A-stage and D_{HT} stages have been developed and implemented in industry to remove HexA. **Table VI** compares the HexA removal efficiencies of ozone to these technologies before full bleaching. The A-stage and D_{HT} stage (KF 0.2) showed similar removal efficiencies for HexA, around 68%. The removal efficiency was increased to 77% when the KF in the D_{HT} stage was increased to 0.3. When ozonation followed oxygen delignification, similar levels of HexA removal as the A- and D_{HT}-stages were achieved only when the ozone dosage exceeded 0.6%. The A-Z combination gave the best HexA removal efficiencies, where close to 90% HexA was removed using a 0.2% ozone dosage. This increased to 96% removal when the ozone was increased to 0.6%.

After full bleaching, brightness reversion increased as the residual HexA concentration in the bleached pulps increased (**Table VII**). These findings were similar to those of other researchers [4,26-29]. However, this trend was observed only for the sequences that used chlorine dioxide as the main

Bleaching Sequence	% ClO_2	% H_2O_2	% O_3	* Cost of Bleaching Chemical (US$)
$OAZD_0(EP)D_1$	1.2	0.15	0.2	16.2
$OAZD_0ED_1$	1.1	0	0.4	16.4
$OD_{HT}ED_1D_2$	1.8	0	0	18.0
**** $OAD_0ED_1D_2$**	**1.9**	**0**	**0**	**19.0**
$OAD_0(EP)D_1P$	1.3	0.75	0	20.5
$OD_{HT}(EP)D_1P$	1.4	0.75	0	21.5
$OZD_0(EP)D_1$	1.2	0.15	0.6	21.6

* Based on US$ 1.00/kg chlorine dioxide and hydrogen peroxide and US$ 1.35/kg ozone [23,32].
** Standard reference bleaching sequence.

VIII. Comparison of oxidative bleaching chemical consumption and cost to reach 90% ISO brightness. The cost of other chemicals used in bleaching such as caustic and sulfuric acid was not considered as these were kept constant.

bleaching chemical. The use of ozone during bleaching has been reported to reduce brightness reversion [27], however, this was not clearly evident from the results of this study. A possible explanation for this could be that the formation of carbonyl groups from carbohydrate oxidation during ozonation [30], which are sensitive to brightness reversion [31], might have offset any improvement in brightness stability achieved through the removal of HexA by ozone. On average, the brightness loss of pulps bleached using ozone was similar to those bleached using chlorine dioxide as the main bleaching chemical.

Comparison of bleaching sequences

Table VIII provides a comparison of the oxidative bleaching chemical consumption and the estimated costs of the various sequences to reach a brightness level of 90%. By including ozonation in the bleaching sequence, the estimated bleaching chemical cost was reduced by up to 15%, compared to the standard reference sequence ($OAD_0ED_1D_2$). This was the case only when ozonation followed the acid hydrolysis stage ($OAZD_0[EP]D_1$ and $OAZD_0ED_1$). When ozonation followed oxygen delignification, a high concentration of ozone was required to achieve 90% brightness. This was the result of the high HexA concentration in the oxygen delignified pulps, which consumed ozone. The use of the D_{HT} stage led to marginal savings in bleaching chemical costs compared to the A-stage. Although the use of peroxide led to significant savings in chlorine dioxide, these savings where not sufficient to offset the cost of the peroxide.

CONCLUSIONS

Ozone reacted preferentially with HexA in the presence of lignin. When applied after oxygen delignification, HexA removal efficiencies similar to those of the A- and D_{HT}- stages were obtained with ozone dosages in excess of 0.6%. When used in combination with the A-stage, the HexA removal efficiencies reached 96%. Consequently, up to 15% savings in the estimated bleaching chemical costs were achieved with the $OAZD_0(EP)D$ sequence compared to the $OAD_0ED_1D_2$ standard reference sequence. The residual HexA in the bleached pulp affected brightness reversion of the pulps, but this was only evident for the bleaching sequences that used chlorine dioxide, and not for those that incorporated the use of ozone. This was possibly because of a higher carbonyl

ABOUT THE AUTHORS

Eucalypts are an important source of hardwoods for South African pulp and paper mills. The high level of hexenuronic acids (HexA) present in kraft pulps produced from them is an important factor to consider during bleaching. Ozone is not widely used in the country as a bleaching chemical and its potential to reduce the operating and chemical costs prompted the study.

Findings in this study were consistent with the findings of other researchers. For example:

- South African *Eucalyptus* kraft pulps contain significant amounts of HexA at levels that are similar to that reported by other researchers.
- HexA contribute significantly to the kappa number of the pulp, accounting for 50%-60% of the kappa.
- Removal of HexA can lead to significant savings in bleaching chemicals, thus reducing production costs and environmental footprint.

Past work by our Research Centre investigated the use of A-stage and D_{HT} stage to remove HexA. This work is an extension of the past work to test the applicability of ozone to remove HexA and possibly reduce operating and chemical costs further for *Eucalyptus* kraft pulps. In contrast to other researcher's findings, we were not able to realize any improvement in brightness stability when using ozone.

The most interesting finding was the combined use of A-Z that gave the best outcome. However, it would be important to understand the performance of ozone at higher temperatures closer to that used during the A-stage, as the ozone stage operated at 25°C is not practical for industrial application. The A-Z combination might be of interest to mills to further reduce their operating costs and environmental footprint.

Our Research Centre has several projects in progress that are related to biorefinery applications (i.e., producing bioenergy and new biomaterials), in addition to pulp and paper. For traditional pulp and paper making, it is important to understand, for example, the impact of the hemicelluloses extraction processes on pulp and paper properties during the subsequent pulping and bleaching stages. As a result, we will also be investigating the bleachability of prehydrolyzed kraft pulps for our local resources in the context of a biorefinery.

Andrew

Johakimu

Ngema

Andrew is researcher, Johakimu is senior research applications and development engineer, and Ngema is engineer-in-training, Forestry and Forest Products Research Centre, Council for Scientific and Industrial Research (CSIR), Congella, South Africa. Email Andrew at jandrew@csir.co.za.

content resulting from ozone oxidation of the carbohydrate fraction of the pulp, which might have offset any improvement in brightness stability achieved through the removal of HexA by ozone. **TJ**

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