FIBERLINES FOR BLEACHED EUCALYPTUS KRAFT PULPS - IMPACT ON BLEACHABILITY AND PULP PROPERTIES

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Abstract

A multitude of options is available when considering designing an "ultimate" fiberline for bleached eucalyptus kraft pulps.

With a flexible cooking plant there are excellent opportunities to optimise cooking and oxygen delignification for improved yield and bleachability and for tailor making pulps with special properties.

Hot acid treatment prior to bleaching or a hot first chlorine dioxide stage decreases brightness reversion and chlorine dioxide consumption. A drawback is increased effluent emissions, lower yield and impaired paper making properties. Milder conditions in the hot (D/A) stage decrease but do not eliminate these negative effects. The best choice is a first high consistency ozone stage that efficiently decrease chlorine dioxide consumption and effluent emissions, while retaining strength properties of the unbleached pulp.

Evidence is presented that the discoloration of eucalyptus pulp measured after thermal yellowing is not permanent. The initial brightness of the bleached pulp can almost fully be recovered by simply washing with water. This raises the question whether brightness reversion, measured after thermal yellowing of standard brightness sheets, is a real problem or a virtual one.

Introduction

A rapid growth in consumption of fine paper and tissue grade products has occurred over the last ten years, a trend that is expected to continue. A corresponding growth in pulp production is expected, indicated in figure 1. This has put an ever-increasing pressure on the development of technology for cooking and bleaching of hardwood kraft pulps. The focus of this development has been improved quality, especially in terms of higher brightness levels but also paper making properties, decreased effluent emissions and cost efficient pulp production.

An obstacle has been (and partly still is) the variability in hardwood raw material properties and the corresponding varying response to cooking and bleaching conditions (1, 2). Key factors contributing to the variability can be related to differences in wood morphological properties and chemical composition.

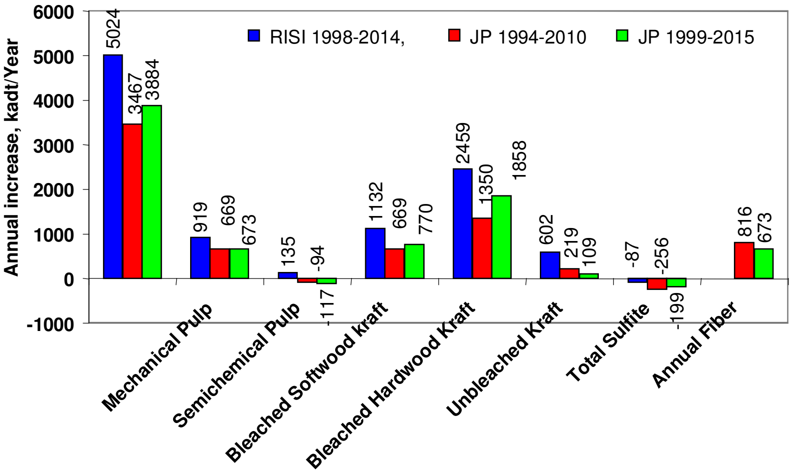

Figure 1. Forecasts for average annual increase of pulp production. Data extracted from Jaakko Pöyry and RISI reports

In recent years, hexenuronic acid (HexA) present in hardwood kraft pulp xylan has been identified as one important contributor to the variability observed. The formation of hexenuronic acid (HexA) from 4-O-methyl glucuronic acid, linked to the hardwood xylan backbone, in alkaline conditions was detected in the 1970's (3), but its presence in hardwood kraft pulps was not unveiled until the mid 1990's (4). HexA consumes potassium permanganate in the Kappa number analysis, thus giving a misleading measure of residual lignin. This observation and the fact that HexA and residual lignin react differently with commonly applied bleaching chemicals have shed further light on the complex chemistry of cooking and bleaching of hardwood kraft pulps (5,6,7).

I this paper I will discuss some of the current understanding of HexA formation/elimination in cooking and bleaching processes and the practical implications in terms of designing a fiberline for efficient removal of HexA groups in the production of bleached eucalyptus kraft pulp. A key concern is that the presence of HexA groups in bleached pulp will contribute to brightness reversion of the pulp and thus impairing its quality.

Cooking conditions influence HexA formation

Daniel et. al. (8) have shown that HexA content of Eucalyptus globulus pulps is increased by lowering the cooking temperature (170 °C → 150 °C), decreasing the alkali charge (24% as Na_2O → 17%), decreasing the sulfidity (28% → 15%). Similar results, what regards the influence of temperature and alkali, have also been presented related to softwood kraft cooking by Gustavsson et. al. (9).

Table 1. HexA content of pulp is increased by modification to low temperature cooking

	Mill A: E. grandis		Mill B: E. globulus	
	Befor modification	After modification	Befor modification[1]	After modification[1]
HexA, mmol/kg	57	79	41	55
Kappa number	13.2	16.6	8.1	9.4
HexA contribution to Kappa[2]	6.0	8.3	4.3	5.8

1) measured after oxygen stage
2) 9.5 mmol HexA/kg is assumed to correspond to 1 kappa unit

These findings may also explain why we have experienced increasing HexA contents in mill eucalyptus kraft pulps in cases where digester plants have been modified to low-temperature cooking, exemplified in table 1.

Since above mentioned cooking parameters not only influence the HexA content and hence the bleachability and brightness stability of the pulp but also yield and papermaking properties it is a delicate problem to balance cooking and bleaching operations for optimum performance. Lammi et.al. (2) investigated a system comprising cooking (SuperBatch™), two stage oxygen delignification (OxyTrac™) and ECF bleaching of Eucalyptus urograndis and found that bleachability, yield and beatability were significantly improved as kappa number after cooking was increased from about 14 to 20.

Removal of HexA groups

Different procedures have been proposed to decrease HexA content of pulp in order to decrease ClO_2 consumption in ECF bleaching and the tendency of the pulp to yellow during ageing. Examples are bleaching in acidic conditions with for example Cl_2, ClO_2, CH_3COOOH or O_3 or by treating the pulp in a hot acid stage. Examples of such treatments are referred to below.

Table 2. Data from (10). Pulp bleaching by ADEDED sequence to 90 % ISO

A-stage conditions	Kappa number	HexA, mmol/kg	Act. Cl kg/ton	Brightness reversion, %ISO	Yield %
No A-stage	14.3	43.6	47.0	3.0	96.8
90 °C, 2 hours					
pH 2.5	11.2	35.1	41.5	2.6	95.1
pH 3.0	12.3	36.8	43.0	2.6	95.4
pH 3.5	12.1	39.1	43.5	2.8	95.7
pH 4.0	12.2	39.8	43.5	3.3	95.1
95 °C, 2 hours					
pH 3.0	-	-	39.0	3.2	94.6
pH 3.5	10.9	31	41.0	3.2	94.9

Hot acid stage (A): Furtado et. al. (10) investigated the effect of a hot acid stage prior to ECF bleaching (ADEDED and AODEDED or OADEDED) of Eucalyptus globulus pulp on yield, mechanical properties and bleach chemical consumption. The acid stage was performed at 90-95 ºC and pH 2.5-4 for 120 min. The hot acid stage in combination with the DEDED sequence resulted in a considerable yield loss, 1.1 – 2.2 % on pulp, corresponding to about 0.5 – 1% on wood. Surprisingly, no increase in yield loss was observed when the hot acid stage was combined with the ODEDED sequence. The A stage performed on the unbleached eucalyptus pulp had a fairly limited effect on the HexA content. Active chlorine consumption decreased but in some treatment cases brightness reversion even increased compared with the reference DEDED sequence, c.f. table 2.

Hot D stage (D_{HT}): Eiras and Colodette (11) investigated the effect of a hot D stage on the bleaching of an industrial oxygen delignified eucalyptus kraft pulp of kappa number 8.7 comparing D(EOP)D and D_{HT}(EOP)D sequences. The standard first D stage was performed at 60 C for 30 minutes whereas the D_{HT} stage was performed at 95 ºC for 180 minutes.

HexA content was decreased from 57.2 mmol/kg to 16.3 and 13.3 for the D(EOP)D and D_{HT}(EOP)D sequences respectively.

They found that the D_{HT}(EOP)D sequence consumed 11% less ClO_2 and that brightness reversion was reduced. On the positive side was also a reduction in AOX content of the filtrate and lower OX content of the bleached pulp by 36% and 13% respectively.

On the negative side was a 1% lower yield in bleaching, corresponding to about half a percent on wood, and a 35% increase in dissolved organic material, measured as COD content of the filtrate. The pulp also required more beating energy to reach the same level of strength properties.

Ozone bleaching: Ozone bleaching was commercially introduced in the early 1990's, primarily to cope with increasing demands for pollution abatement in a cost efficient way (12, 13). Basically two technologies were adopted performed at medium (MC) and high (HC) pulp consistency respectively.

As the understanding of the effects of HexA content in kraft pulps on kappa number and brightness reversion grew in the late 1990's we found out that ozone was an excellent chemical in decreasing the HexA content of pulps and hence the brightness reversion of fully bleached pulps. This was shown by Bokström et.al, (14) and Wennerström (15) by comparing the sequences D(EOP)(DnD), (D/A)(EOP)(DnD) and (aZ(EO))(DnD), which is exemplified in figures 2 and 3. In this case the (D/A) stage is a variant of the D_{HT} stage referred to above, but carried out at milder conditions, 90 ºC and 60 min.

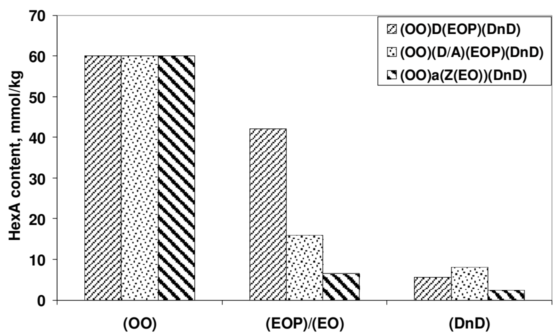

Figure 2. Hexenuronic acid content of the pulp after different bleaching stages for the sequence D(EOP)(DnD) with conventional D0 and hot (D/A) and a(Z(EO))(DnD). Final bleaching to a brightness of 90% ISO. (Eucalyptus pulp 1 in reference 15)

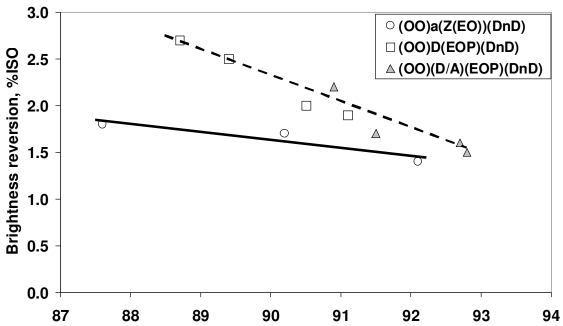

Figure 3. For this pulp the brightness reversion was equal for D0 and hot (D/A). Ozone bleached pulp showed the lowest brightness reversion. Reverted brightness was measured after 105°C for 4h. (Eucalyptus pulp 1 in reference 15)

Current fiberline alternatives for production of bleached Eucalyptus kraft pulps

The arguments for choosing a particular fiberline design vary from time to time. However, cost efficiency, quality of the product produced and environmental considerations are always key decision factors. Since targets for product quality and environmental emissions may vary from project to project this will eventually also influence the final design of the fiberline. In some cases flexibility, in terms of the fiberline being able to meet future stricter environmental demands or being able to produce a wider spectrum of pulp grades, is considered important.

It is no surprise then to see that the design of existing fiberlines can vary a lot, exemplified in table 3.

Table 3. Four different fiberline alternatives for production of bleached Eucalyptus kraft pulps

Mill	Wood specie	Cooking	Oxygen	Bleaching	Brightness %ISO	Production, adt/d	Start-up
Advance Agro, Thailand	camaldulensis	SB[1]	O	D(EOP)D	90	650-700 (design 560)	1996
StoraEnso Celbi, Portugal	globulus	CC[2]	O	Q(PO)DD	90	abt 900	1999
VCP Jacarei, Brasil	grandis	CC[2]	O	a(Ze)DP[3]	90	2400	2002
Arauco Valdivia, Chile	globulus/nitens (and Pinus radiata)	SB[1]	(OO)	D(EO)DD	91	2200	2003

1) SuperBatch™
2) Compact Cooking
3) "a" denotes an acidification stage at low temperature before the (Ze) stage

The Advance Agro fiberline in Thailand, schematically outlined in figure 4, started up in 1996. It was initially designed for a production of 560 adt/d of bleached Eucalyptus camaldulensis kraft pulp at 87 %ISO, but is today running at more than 100 adt/d above design capacity, producing 90 %ISO pulp. This fiberline comprises SuperBatch™ cooking, oxygen delignification and a three-stage ECF bleach plant. It targets kappa 14 and 8 after cooking and oxygen delignification respectively. Advance Agro built the world's first fiberline utilising only TwinRoll™ presses as brown stock and bleach plant washers. In this project a low effluent volume was important and this was facilitated by the introduction of TwinRoll presses in the bleach plant.

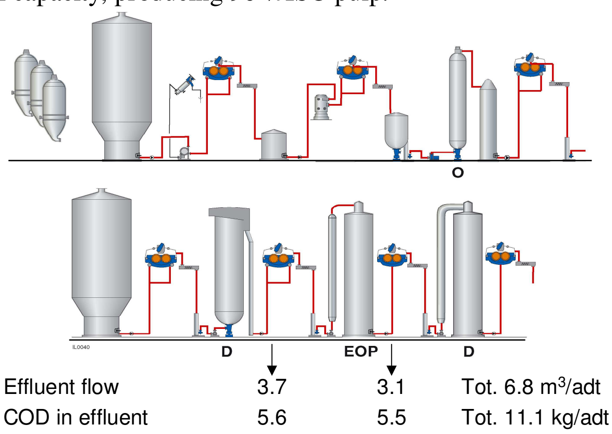

Figure 4. Advance Agro fiberline

Increased cost efficiency has pushed for increased single line capacities, which is underlined by the VCP Jacarei and Arauco Valdivia installations, exceeding 2000 adt/d.

The VCP Jacarei fiberline, outlined in figure 5, takes advantage of a high consistency ozone bleaching stage, ZeTrac™, in order to decrease the harmful effects of HexA and to facilitate a light ECF bleaching sequence.

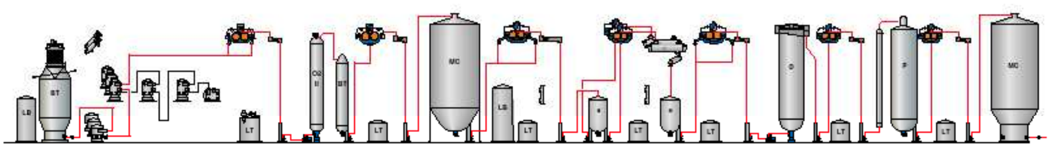

Figure 5. VCP Jacarei 2100 tpd hardwood fiberline with an Oa(Ze)DP bleach sequence.

There is a growing interest in high consistency ozone bleaching as a cost efficient way to further decrease effluent emissions and to facilitate light ECF and TCF bleaching sequences. Today eight mills are using the ZeTrac technology, c.f. table 4. Ruzomberok in Slovakia has made the most recent decision to go with ozone bleaching in order to meet the environmental demands that are put on the mill.

Table 4. ZeTrac™ references

Mill	Country	Pulp	Capacity, adt	Bleaching	Brightness, %ISO
IP Franklin	USA	Swd	1000	OaZ(EO)D	83 (%GE)
SCA Östrand	Sweden	Swd	1250	(OO)Q(OP)a(Zq)(PO)	88
SENA, Wisconsin Rapids	USA	Hwd	650	OaZ(EO)DD	88.5 (%GE)
ZPR Rosenthal	Germany	Swd	900	(OO)Q(OP)D(Z(POP))	90
Burgo Ardennes	Belgium	Hwd	1100	(OO)D(Z(EO))(DD)	89
Oji Nichinan	Japan	Hwd	750	OaZEPD	85
VCP Jacarei	Brasil	Hwd	2100	Oa(Ze)DP	90
Ruzomberok[1]	Slovakia	Swd/Hwd	900/1300	(OO)a(Z(EO))(Dn)D	88

1) Start up 2004

Impact on bleachability and pulp properties

Starting with SuperBatch cooking and two stage oxygen delignification a series of bleaching tests was carried out to compare three different pre-bleaching alternatives: D-, (D/A)- and a(Ze)-. These were followed by (Dn)D or (DnD) final bleaching stages.

The most important bleaching results at a reverted brightness of 90 %ISO are summarised in table 5.

Table 5. Bleach chemical consumption and costs at 90 %ISO reverted brightness. The pulp was produced in the laboratory from Eucalyptus grandis chips in pilot cooking and oxygen delignification equipment.

Sequence Kappa no.	D(EOP)(Dn)D 10.9		(D/A)(EOP)(Dn)D 10.9		A(Ze)(Dn)D 10.9		A(Ze)(DnD) 10.7	
Reverted brightness[1], %ISO	90		90		90		90	
Brightness before reversion, %ISO	92.3		92.1		92		92	
	kg/bdt	USD/bdt	kg/bdt	USD/bdt	kg/bdt	USD/bdt	kg/bdt	USD/bdt
H_2SO_4	6	0.48	6	0.48	12	0.96	12	0.96
Ox. Wh.liq.as NaOH					12	0.72	12	0.72
NaOH	16.5	4.13	16.5	4.13	5	1.25	5	1.25
H_2O_2	3	2.73	3	2.73	0	0	0	0
O_2	3	0.21	3	0.21	0	0	0	0
O_3	0	0	0	0	6	7.08	6	7.08
ClO_2, act. Cl	35.5	13.5	28.5	10.8	13.5	5.13	15.5	5.89
Total cost, USD/bdt		21.1		18.4		15.1		15.9

1) 4 h at 105 °C and dry atmosphere

All sequences produced high brightness pulps. Brightness reversion was slightly higher for the D- and (D/A)- pre-bleached pulps.

A significant bleach chemical cost reduction was achieved with the (D/A)- pre-bleaching stage compared with D-. An even larger reduction was obtained with the a(Ze)-sequences. The large reduction in chlorine dioxide consumption – more than 20 kg/bdt – and the use of oxidised white liquor in the (Ze) stage instead of fresh caustic are the main factors for this cost reduction.

Total dissolved organic material expressed as COD content of spent bleach liquors was the same for the D(EOP)(Dn)D and a(Ze)(DnD) sequences, 20.7 kg/bdt. For the (D/A)(EOP)(Dn)D sequence the amount was 23.3 kg/bdt, an increase of more than 10%. There is obviously still an impact on yield by the (D/A) stage in spite of the milder conditions applied in the (D/A) stage in this work – 85 ºC for 120 min – compared with the reporting of Colodette (11), 95 ºC for 180 min.

In the a(Ze)(DnD) sequence 16.6 kg COD/bdt was dissolved in the (Ze) stage. In a mill situation the alkaline effluent from this stage will partly be recycled to brown stock washing, thus decreasing COD emissions from the bleach plant as well as fresh water consumption. For the other sequences this is not easily done since also the alkaline (EOP) filtrate will contain chlorides that promote corrosion in the chemical recovery plant.

In a separate study, also using eucalyptus pulps, it was found that a reduction in chlorine dioxide consumption had a very significant effect on the amount of organic halogens (OX) present in the pulps after bleaching, which is shown in table 6.

Table 6. Reduction of organic halogenes (OX) in pulp by oxygen delignification and ozone bleaching.The pulp was produced from a mixture of E. globulus and E. nitens.

Sequence	Kappa before first D-stage	Total act Cl kg act. Cl/odt	Brightness %ISO	OX g/odt
D(EOP)DnD	14.6	40	91.0	290
(OO)D(EOP)DD	9.3	28	92.2	190
(OO)a(Z(EO))DD	1.5	7	91.6	60

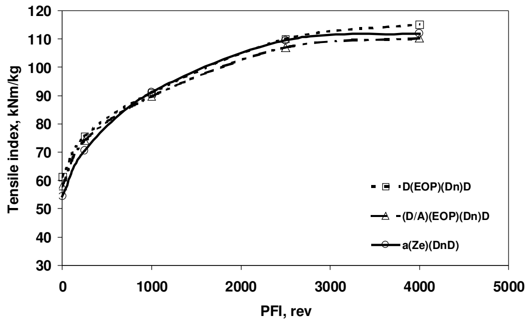

Figure 6. Tensile index vs. PFI rev for bleached eucalyptus pulps

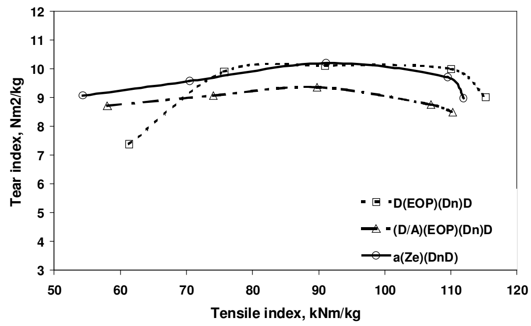

Figure 7. Tear index vs. tensile index for bleached eucalyptus pulps

With one exception, testing of hand sheet pulp properties after PFI beating of pulps referred to in table 5, shown in figures 6. 7 and 8, did not show any significant differences when comparing D-, (D/A)- and a(Ze)- pre-bleached alternatives. The (D/A)- pre-bleached pulp displayed about 10% lower tear index.

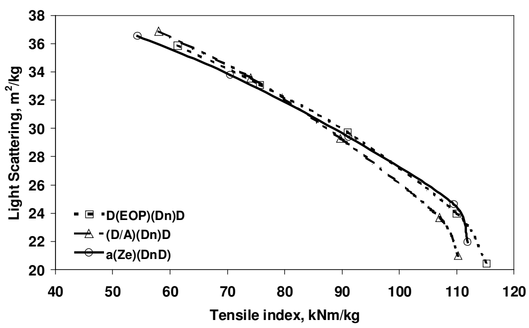

Figure 8. Light scattering vs. tensile index for bleached eucalyptus pulps

Brightness reversion – is it a real or virtual problem?

For market kraft pulp heat induced brightness reversion is considered a problem, especially for hardwood pulps. The chemical reactions that are responsible for the discoloration of pulp start already when drying the pulp and continue during storage and shipping to the paper mill. As already discussed the content of HexA in the pulp after bleaching plays a major role for the discoloration reactions causing the brightness reversion.

Brightness reversion is commonly measured on standard brightness sheets before and after a heat treatment. However, there is today no generally accepted standard procedure, ISO or corresponding. Especially, there is a multitude of heat treatment procedures, where temperature, treatment time and moisture conditions are different.

Recent findings of Granström et. al., presented in a licentiate thesis (16), may question whether brightness reversion is a real problem or a virtual one. Granström found that discoloured compounds formed during thermal ageing of bleached birch kraft pulps partly could be washed out from the pulp.

To follow up on this we conducted a series of tests on brightness sheets made from eucalyptus kraft pulps, which had been bleached with different sequences and already subjected to a brightness reversion procedure. After washing the pulp brightness was measured again.

The results from this simple test, shown in figure 9, confirmed that the findings by Granström concerning birch kraft pulps also hold true for eucalyptus pulps. The initial brightness measured before brightness reversion was regained after washing the pulp that had been subjected to brightness reversion procedure.

The question "Brightness reversion – is it a real or virtual problem?" seems to be relevant. The practical implications of these observations need to be further investigated.

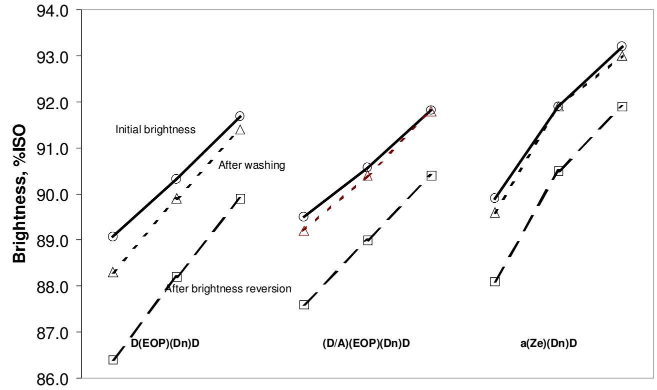

Figure 9. Brightness is almost fully regained after washing ot the pulp that has been subjected to thermal yellowing (4h at 105 ºC)

Concluding remarks

Many aspects can be relevant when trying to design the "ultimate" fiberline for bleached eucalyptus kraft pulps. There is the balance between investment costs and operating costs to be considered. Also pulp quality and environmental emissions are key factors.

The cooking plant sets its fingerprint on the pulp to be further processed in the line. A batch cooking plant, like SuperBatch, gives the best flexibility in terms of adjusting cooking conditions to handle different raw materials in admixture or separately. So far, this advantage has come with a higher investment cost in comparison with current continuous cooking technologies.

We have learnt that formation of HexA in cooking can be influenced by the cooking conditions. Modern continuous cooking concepts, utilising lower temperatures in cooking, increase HexA content in the pulp.

We have also learnt that the presence of HexA in hardwood kraft pulps limits the delignification degree in a subsequent oxygen delignification system. There are, however, opportunities to optimise cooking and oxygen delignification for improved yield and bleachability or for tailor making of pulps with special properties.

High consistency ozone bleaching has shown to be the most cost efficient way to decrease HexA content of pulp. An ozone stage in comparison with hot acid treatment, A, or hot (D/A) also gives a higher yield and lower effluent emissions. In addition to giving a lower pulp yield hot acid treatment or a hot (D/A) also negatively influence the paper making properties of the pulp.

Figure 10 outlines one fiberline alternative that is close to the "ultimate" fiberline for bleached eucalyptus kraft pulp to 90% ISO. It comprises SuperBatch™ cooking OxyTrac™ oxygen delignification and light ECF bleaching with ZeTrac™ high consistency ozone bleaching. A final peroxide stage may be added if brightness levels exceeding 90% ISO are required.

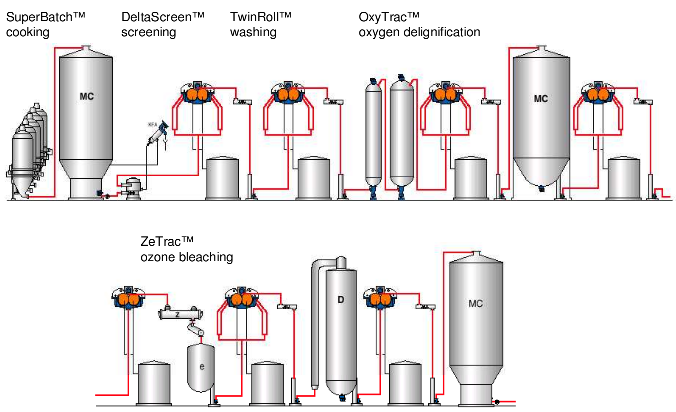

Figure 10

Experimental

Table 7. General bleaching conditions

	A(Ze)	D	(D/A)	(EOP)	(Dn)	(DnD)	D
Consistency, %	5/42	10	10	12	12/8	12/12/12	12
Temperature, °C	20/35/55	55	85	80	65-80	65-85	70-85
Time, min	20/~3/10	60	120	60	120/5	120/5/120	120
PO_2, MPa				0.2			

Analysis methods:

Kappa number	SCAN C 1:00
Brightness	ISO 2470:1999
Hexenuronic acid	According to the VVT method (JPPS Vol 25, no 9:p 306 (1999))
COD	SS-EN 028142
PFI	SCAN C 24:96
Physical properties	SCAN C 28:76
Lab sheet forming	EN ISO 5269:1:2000
Light scattering	ISO 9416:1998

Acknowledgement

This paper is based on the skilful work of my colleagues at Metso Paper's Fiber Technology Center in Sundsvall, Sweden.

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