From simple theory to industrial application – extended impregnation kraft cooking

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Abstract

The potential to increase the overall yield of bleached *Eucalyptus Urograndis* kraft pulps has been investigated by cooking to higher kappa number with the novel Extended Impregnation Cooking (EIC) technique. The extended impregnation results in considerable lower shive content and enable the kraft cook to be terminated at kappa number 27. The result shows that it is possible to extend the oxygen delignification of higher kappa number pulps. By extending the oxygen stage to kappa number 12 followed by bleaching to 90.5 % ISO brightness with a D*(OP)D sequence, a total yield gain of 2.5 % on wood can be obtained.

Key words: eucalyptus kraft pulp, ECF bleaching, xylan, lignin

Introduction

A higher utilization of the wood raw material in chemical pulp production will require a higher total selectivity of the kraft pulping process, which may also lead to improved physical properties. One of the possibilities is to end the kraft cook at higher lignin content, and then continue with more lignin-selective chemicals such as oxygen and different bleaching chemicals. One part of that yield gain can be retained after subsequent oxygen delignification and bleaching to final brightness resulting in an increased overall yield (McCubbin 1997; Moe, Ragauskas 1999: Rööst et al. 2000; Jiang et al. 2002; Lanna et al. 2002).

Terminating the kraft cook at a higher kappa number has a limit since the reject content increases with increasing kappa number. Incomplete impregnation of the cooking liquor into the wood chips have been shown to affect the reject content as well as the yield, bleachability and strength properties (Gullichsen et al. 1992; Gullichsen et al. 1995; Malkov et al. 2002; Costa et al. 2008)

In order to separate the fibers of the wood by chemical means at high lignin content, it is critical that hydroxide ion concentration across the chips is as even as possible. This is because of the large effect of the hydroxide ion concentration on the delignification rate. Furthermore the amount of slowly reacting lignin is increased by lower hydroxide ion concentration resulting in an earlier introduction of the residual phase delignification (Lindgren, Lindström 1997).

The newly developed technique is using the difference in temperature dependence between the neutralization reactions, which consumes hydroxide ions, and the diffusion of hydroxide ions during the impregnation stage of a kraft cook (Lindström 2009).

The technique uses longer impregnation time at lower temperature. This Extended Impregnation Cook (EIC) technique has the potential to result in less reject (shives) at higher kappa numbers. However, one consequence when cooking to higher kappa number is the higher residual lignin content in the unbleached pulp, which increase the demand of the subsequent oxygen delignification and bleaching chemicals. In order to maintain low bleaching chemical costs and low effluent load from the bleaching it is necessary to extend the delignification in the oxygen stage so that the kappa number of the pulp to be bleached still is relatively low. In the present work, the potential to increase the overall carbohydrate yield by cooking to higher kappa number utilizing the EIC technique will be investigated. Extended oxygen delignification and the effect on the bleaching consumption and effluent load will also be studied.

Experimental

Eucalyptus Urograndis wood chips were supplied by Fibria, Brasil. The EIC impregnation was performed with black liquor at 110 ºC for 90 minutes with a liquor-to-wood ratio of 7:1.
Effective alkali charge (EA) was 13.5 % and the sulfidity charge was 55 % in the impregnation. Liquor was then drained and fresh white liquor was charged to liquor-to-wood ratio of 4:1. The temperature was then increased to maximum cooking temperature, 135-144 °C. Total cooking time for all the EIC at maximum temperature was 4 h. During the 2 last hours the liquor-to-wood ratio was changed to 3.5:1. All the CK cooks were performed at 40 % sulfidity and 17 % EA. The liquor-to-wood ratio was 3.5:1. The temperature was rapidly increased to the cooking temperature, 158-161 ºC and the cooking time was set to 70 min. The O- and EOP-stages were performed in teflon-lined stainless steel autoclaves in a polyglycol bath. The D*- and D1 stages were performed in sealed plastic bags in a water bath. The conditions for the oxygen and bleaching stages are shown in Table 1. The D* was performed at 10 % pulp consistency for 120 min at 90 °C. The OP stage at 12 % pulp consistency for 60 min at 90 °C and pressurised with 0.2 MPa of oxygen. Finally, the D1 was performed at 12 % consistency for 120 min at 75°C. Three different charges of chlorine dioxide were added in the last D1- stage and the kraft pulps were compared at 90 % ISO brightness. The yield was determined gravimetrically after the oxygen stage except for the EIC27.5 pulps were the yield was estimated from the COD analysis of the filtrates. The yield after bleaching was estimated from the COD analysis of the filtrates collected from the bleaching. Kappa number (ISO 302:2004), limiting viscosity (ISO 5351:2004), ISO-brightness (ISO 2470:1999), brightness reversion 4 h at 105 °C on brightness sheets, COD (ISO 6060) and neutral carbohydrates analysed as alditol acetates in GC-FID.

Table 1: One-stage oxygen delignification and bleaching, OD*(OP)D_1

Oxygen delignification	**CK17.9**	**EIC18.6**	**EIC27.5**	**EIC27.5**	**EIC27.5**[1]
Target kappa no	10-11	10-11	14-16	11-12	10-11
Pulp consistency, %	12	12	12	12	12
NaOH, kg/odt	17	17	20	34	35
Temperature, °C[2]	~95	~97	~98	~97	~105
Time, min	90	90	90	120	120
O_2 pressure, MPa	1	1	1	1	1
Bleaching					
H_2O_2, kg/odt	2	2	2	2	-
H_2SO_4 kg/odt	5	5	3	3	-
NaOH, kg/odt	9	9	11	9	-
ClO_2, kg act Cl/odt	19	20	37	25.5	-

[1] only oxygen delignification, [2] adjusted temperatures. In the bath approx. 5 ^oC higher

Results and Discussions

Seven kraft pulps of *Eucalyptus Urograndis* were lab cooked to different kappa numbers from 16.2 to 33.7 using the EIC technique. The EIC-impregnation was performed at longer time and lower temperature in order to enhance the diffusion of the cooking chemicals thus resulting in a more homogenous cooking of the wood chips and reduced shive content. In addition, as reference pulps, three conventional kraft pulps (CK) were lab cooked to kappa number 16.8 to 19.4. The chemical data of the investigated pulps is presented in Table 2.

Table 2: Chemical data of the EIC and CK kraft pulps

	Kappa no	Total yield % of wood	Screened Yield[1] % of wood	Lignin free Yield[2] % of wood	HexA[3] µmol/g	Viscosity[4] dm^3/kg	Hemi[5] contr.to Lignin free Yield % of wood	Cellulose[6] contr.to Lignin free Yield % of wood
	16.2	53.2	53.2	52.3	74	1440	9.3	43.0
	18.6	53.9	53.9	53.0	74	1500	9.3	43.7
Extended	20.7	54.0	53.9	52.8	70	1480	9.3	43.4
Imp.	22.9	54.8	54.7	53.4	70	1480*	9.5	44.0
Cook	24.7	54.7	54.6	53.1	69	1490*	9.3	43.8
(EIC)	27.5	57.3	57.1	55.3	70	1460*	10.3	45.0
	33.7	59.6	58.7	56.6	67	1500*	10.7	45.8
Conv.	16.8	52.0	51.4	50.6	60	1230	8.0	42.6
Cook	17.9	52.9	52.2	51.3	60	1260	8.2	43.1
(CK)	19.4	53.0	51.6	50.6	57	1320	8.2	42.4

[1] Sommerville screen with a slot size of 0.15 mm,[2] Lignin and shive free yield. Lignin content measured as Klason,[3] Gellerstedt and Li (1996), [4] Viscosity* was analysed after mild ClO_2 treatment at room temperature, [5] Hemicellulose = xylose + glucomannan(2 x mannose) + arabinose + galactose, [6] Cellulose = glucose – mannose

Interestingly, the carbohydrate yield (shown as the lignin free yield) for the EIC pulps increases when terminating the kraft cook at higher kappa number. This is not the case for the CK pulps which reach a point where the lignin free yield starts to decrease. Furthermore, the extended impregnation results in lower shive content in the EIC pulps compared to the CK pulps in the same kappa number interval. The shive content is maintained low for the EIC pulps up to kappa number 27.5 where it starts to rapidly increase, see figure 1.

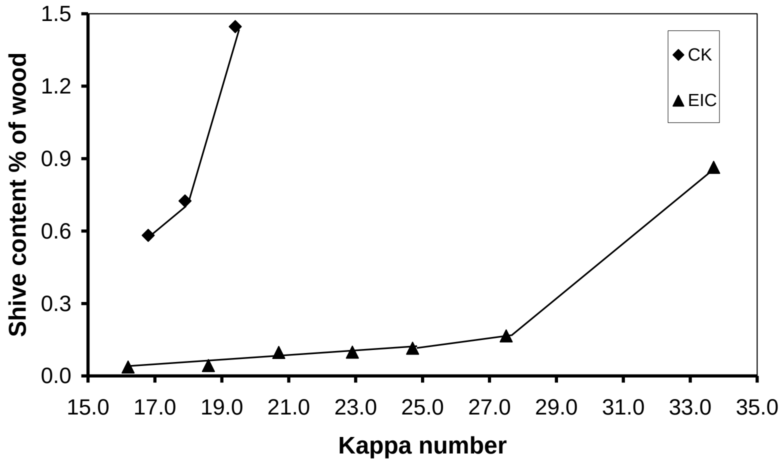

Figure 1: Shive content vs kappa number for EIC and CK pulps

The long impregnation time in combination with the low cooking temperature shift the defibration point towards higher kappa number. The defibration point for the EIC pulps seems to appear around kappa number 28 to 34, compared to 17 to 19 for the CK pulps. In view of the fact that the shive content starts to increase rapidly above the defibration point, an EIC pulp cooked to 27-28 is preferable chosen in order to achieve higher carbohydrate yield without too high shive content. The EIC technique enables a carbohydrate yield gain of 1.7 % when changing from the CK to the EIC technique at standard kappa number 18-19, but even higher yield gain of 4.0 % when terminating the EIC cook at kappa number 27.5.

The important question is how much of the gained yield after the cook is preserved after the bleaching. The unbleached higher kappa number pulp EIC27.5 and the standard kappa number pulps EIC18.6 and CK17.9 were oxygen delignified. The target kappa number after oxygen delignification for EIC18.6 and CK17.9 were 10-11. For the EIC27.5 three target kappa numbers were chosen. One milder oxygen delignification to kappa number 14-16, one harsh to kappa number 11-12 and one even harsher to kappa number 10-11. The pulps except the latter were then bleached to 90.5 % brightness using a D*(OP)D_1 bleaching sequence. The results from the oxygen delignification and bleaching are shown in Table 3a and Table 3b. It is possible to extend the oxygen delignification of higher kappa number pulps. However, extending the EIC27.5 to kappa number 10-11 decreases the viscosity excessively. In Figure 2, the brightness is shown versus chlorine dioxide consumption (as active chlorine). Since the kraft pulps were oxygen delignified to different kappa number, the chlorine dioxide consumption is also compared when calculated as a multiple of active chlorine. See Figure 3. The EIC27.5, EIC18.6 and CK17.9 oxygen delignified to kappa numbers 9.9 to 11.8 are easy to bleach and reach brightness 90.5% ISO with a chlorine dioxide consumption corresponding to around 1.9 x kappa kg active Cl/odt. The EIC27.5 oxygen delignified to kappa number 14 requires about 2.6x kappa kg active Cl/odt to reach the same brightness. Thus it seems to be better to extend the oxygen delignification for the higher kappa number pulp in order to reduce the charged amount of chlorine dioxide. The carbohydrate loss in the oxygen stage is higher for the EIC pulps than the CK pulp shown as greater viscosity loss. Despite the higher yield loss in the oxygen stage, the overall yield after bleaching for the EIC pulps are higher than the CK pulp. Cooking with the EIC instead of the CK technique to kappa number 18-19 and then bleach to 90.5 % ISO brightness result in a 1 % higher overall yield. On the other hand, terminating the kraft EIC cook at higher kappa number 27.5 and then extending the oxygen delignification to kappa number 11.8, a 2.6 % overall yield gain can be obtained.

Table 3: Oxygen delignification and bleaching with D*(OP)D to 90.5 % ISO

Table 3a. Results from oxygen delignification of EIC and CK pulps.

O	**CK17.9**	**EIC18.6**	**EIC27.5**	**EIC27.5**	**EIC27.5**
Kappa number	9.9	10.7	14.0	11.8	10.3
Limiting viscosity number, dm^3/kg	1010	1140	1200	960	900
COD, kg/odt	25	37	59	73	-
Yield, % of pulp	98.5[1]	97.8[1]	96.5[1]	95.7[1]	-

1 Estimated yield determined from COD value, 17 kg COD corresponds to 1% yield loss.

Table 3b. Yield and COD content of bleached EIC and CK pulps to an ISO brightness of 90.5 %

OD*(OP)D	**CK17.9**	**EIC18.6**	**EIC27.5**	**EIC27.5**
Kappa number after O	9.9	10.7	14	11.8
Total gravimetric yield, %	95.6	94.5	91.7	91.9
COD, kg/odt	26	28	44	36
Total overall yield, %	49.9	50.9	52.4	52.5

However, the effluent load measured as COD is higher for the EIC than the CK pulps. One probable explanation is the higher dissolution of carbohydrates in the oxygen stage and bleaching. The final pulp viscosity at 90.5% ISO vary from 880 to 990 dm^3/kg for the bleached pulps.

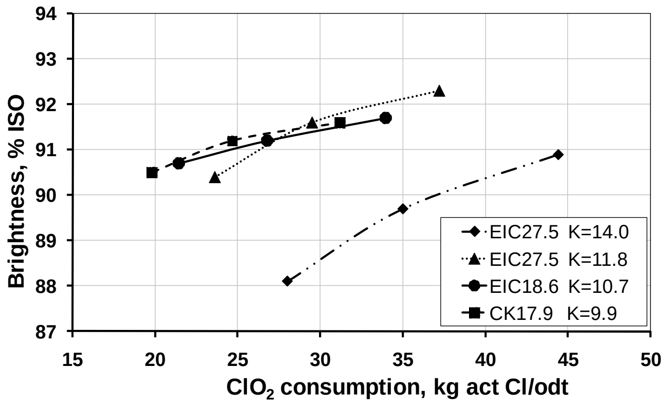

Figure 2: Sequence D*(EOP)D_1, brightness versus chlorine dioxide consumption

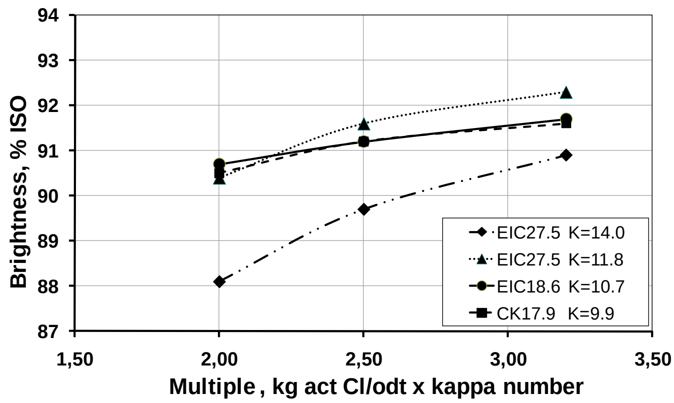

Figure 3: Sequence D*(OP)D_1, brightness versus chlorine dioxide multiple

Process considerations

A mill producing 500 000 air dry (ad) t/year of fully bleached Eucalypt pulp using conventional kraft cooking change to an EIC kraft cooking concept with cooking kappa number of 27. This change would give an increase in production of around 13 % assuming limited recovery boiler and recirculated liquor from the oxygen delignification to the recovery system. The economic benefit of such production increase is about 20 MUSD/year taking into account the increased cost for bleaching chemicals. The calculation is based on a price for bleached Eucalypt kraft pulp of 600 USD/adt, a wood cost of 100 USD/adt, a production cost of 300 USD/adt, NaOH (oxidized white liquor) 0.1 USD/kg, ClO_2 2.9 USD/kg, H_2SO_4 0.08 USD/kg, NaOH (bleaching) 0.25 USD/kg, H_2O_2 0.8 USD/kg, $MgSO_4$ 0.25 USD/kg.

Conclusions

In order to separate the fibers of the wood by chemical means at high lignin content, it is critical that hydroxide ion concentration across the chips is as even as possible. The newly developed technique is using the difference in temperature dependence between the neutralization reactions, which consumes hydroxide ions, and diffusion during the impregnation stage of the kraft cook. The EIC technique results in considerable lower shive content and enable the cook to be terminated at kappa number 27.5. Further on, by extending the oxygen delignification to kappa number 11.8 and subsequent D*(OP)D-bleaching to 90.5 % ISO brightness, a total yield gain of 2.6 % on wood can be obtained with equivalent chlorine dioxide consumption as standard conventional kraft pulp. However, the carbohydrate loss in the oxygen delignification and bleaching is greater for higher kappa number pulps, the latter resulting in a higher effluent load. This can be avoided by cooking with the EIC technique to kappa number 18-19. However, this will reduce the overall yield gain to 1.0 %.

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